

Multifunctional Composite Si and C-based particles

Cross-reference to related applications

This application claims the benefit of U.S. Provisional Application No. 63/616,188 titled
5 "Multifunctional Composite Si-particles" filed December 29, 2023, U.S. Provisional Application
No. 63/571,951 titled "Multifunctional Composite Si-particles" filed on March 29, 2024, U.S.
Provisional Application No. 63/571,965 titled "Polymer Brush Coated Silicon-Carbon
Composite Materials" filed on March 29, 2024, and U.S. Provisional Application No.
63/571,715 titled "Enhanced Performance of Current Collectors through Polymer Brush
10 Coating" filed on March 29, 2024, all of which are incorporated by reference in their entirety
herein.

Field

The present disclosure provides methods for forming polymer brushes on a Si and C-based
15 particles, thus, enabling easy large-scale production of polymer brushes covalently bound to
Si and C-based particles. In particular, the methods allow for easy control of the graft-density
due to the formation of multifunctional composite Si and C-based particles. The disclosure
also provides a multifunctional composite Si and C-based particle as well as a multifunctional
composite Si and C-based particle upon which polymer brushes are formed. The disclosure
20 also provides systems for forming the polymer brush coated particles, and devices including
the polymer brush coated particles, which devices may also include polymer brush coated
electrodes.

Background

25 Silicon particles are used in a variety of applications including electronics, solar cells,
semiconductors, and as anode materials in electrochemical cells.

The properties of materials change as their size approaches the nanoscale. For example,
silicon nanoparticles are typically considerably more reactive compared to a bulk version
30 thereof. This increase in reactivity can arise due to the increase in surface area relative to the
bulk volume as particle size decreases. In addition, smaller particles typically have more
internal strain, which can lead to further surface reactivity enhancement.

In particular, while bulk silicon will typically only form a thin layer of oxide at its surface upon
35 interaction with oxygen and water, oxide layer thickness and non-uniformity will increase
significantly as particle sizes go below 100 nm, while nanometer-sized Si-particles may
deteriorate entirely in the presence of oxygen. This is particularly true for bare and H-
terminated Si-particles which have highly reactive Si-Si bonds. Therefore, Si-particle surfaces

are often passivated with organic molecules (e.g., alkyl chains) to render the Si-particles more resistant to oxidation.

Furthermore, the increased reactivity of Si-particles, compared with bulk silicon in the form of silicon wafers, for example, means that the Si-particles are typically not compatible with typical polar and hydrophilic solvents, which have high affinity to water and oxygen dissolution, or carry -OH groups themselves (for example, acetone, isopropanol, etc.). However, the addition of passivating organic moieties may alter the compatibility with various solvents.

Silicon finds particular use as an anode storage material in lithium ion cells due to its very high lithium uptake compared to carbon-based storage materials. However, a challenge that arises is the change in volume that occurs when lithium alloys with silicon, which can lead to significant performance loss through extensive cycling. Additionally, formation of the surface-electrode interface (SEI) can lead to significant gas formation during initial cycling. There is therefore an ongoing need to provide silicon materials that can be used as anode materials that address these challenges.

There remains a need for methods of functionalising Si-particles to provide particles suited for use in a variety of applications. It would be particularly useful to provide Si-particles that have defined solubility and surface properties.

Likewise, there is interest in improving graphite particles, carbon-coated silicon particles and Si/C composite particles. While the electrochemical reaction of graphite is intercalation (on charge) and de-intercalation (on discharging), as opposed to the corresponding charge/discharge cycling of silicon being the lithiation and the de-lithiation reactions, the consequences of such cycling is analogous – volume expansion (on charging) and contraction (on discharge) – though the extent of the changes would be much smaller than those associated with the silicon, roughly about 5 to 10% rather than the upto 400% volume expansion for silicon. As such, one of the failure mechanisms for the capacity loss would be caused by the anode components – silicon, graphite, carbon-coated and/or Si/C composite particles – losing the electrical connectivity to the overall electrochemical circuit of an energy storage device, i.e., the particle losing its electrical connection through physical displacement from the circuit by repeated volume expansion and contraction cycles.

To address these challenges, significant strides have been made in employing nanoscale modifications and incorporating diverse materials to enhance the performance of Si and Si-based anodes in LIBs. Various methods, including nanostructure modifications and material

incorporation, have been explored to mitigate issues such as volume expansion and SEI formation. Specifically, the integration of specific materials into Si anodes has shown promise in mitigating volume expansion, enhancing contact area with electrodes and electrolytes, improving lithiation/delithiation rates, and ultimately augmenting battery performance.

5 However, existing strategies for enhancing Si anode performance typically involve complex nanoscale modifications, material combinations, and electrolyte adjustments. These approaches often suffer from limitations in scalability and reproducibility, hindering their feasibility for large-scale manufacturing. Moreover, the incorporation of additional materials or additives to improve anode performance can increase production costs and introduce

10 compatibility issues with existing battery manufacturing processes. In comparison, SiO_x materials have demonstrated some advantages for anode applications due to the less severe volume change effects. However, SiO_x materials still cannot fully overcome the common problems of Si-based anodes.

15 Consequently, Si/C composites have drawn wide attention in silicon anode development, where the carbon materials serve as a protective and supportive framework for silicon. The choice of carbon in a mixture with silicon is due to its low-cost fabrication, structural/compositional flexibility, and large-scale manufacturability. Common types of carbon components in Si/C include silicon covered by carbon coating (or carbon shell) and

20 silicon embedded in the carbon matrix.

The most straightforward approach to produce Si/C composites is to produce silicon particles covered with carbon materials. For example, Wang et al. reported a core-shell style Si/C anode material (J. Power Sources, 2011, 196, 10, 4811-4815). The silicon component was

25 composed of amorphous Si clusters and ordered SiO₂ domains, and the carbon layer was prepared with epoxy resin precursor with thermal treatment. This material delivered a reversible specific capacity of about 800 mAh/g. Similarly, yolk-shell structures have been utilized in Si/C composite design to allow internal void space to accommodate silicon volume change. Liu et al. reported a yolk-shell Si/C anode material that was pomegranate-like, where

30 the primary silicon nanoparticles were encapsulated by a conductive carbon shell with sufficient internal free space for volume expansion and the secondary composite particles were encapsulated by a thicker carbon layer to reduce direct electrolyte contact. (Nat. Nanotechnol, 2014, 9, 187-192) Due to the protection of the carbon structures, superior cyclability of 97% capacity retention after 1000 cycles was achieved. In addition to void space

35 between yolk and shell, porous structures could also be produced inside silicon itself (namely porous silicon materials). For instance, Liu et al. developed pitch pyrolytic carbon-coated nanoporous Si/graphite (NP-SiC/Gr) composites where nanoporous silicon was prepared by chemical dealloying of Al-Si alloy and subsequent coating with pitch (Energy Fuels, 2023, 37,

6, 4624-4631). Upon blending with graphite material, NP-Si@C/Gr delivered a reversible capacity of NP-SiC/Gr is 764.2 mAh/g.

5 A different approach to produce Si/C composites is to embed silicon particles in a carbonaceous matrix as the hosting framework. For example, Xu et al. reported SiOx particles embedded between the interior and surface of graphite by exfoliating and restoring the structure of artificial graphite. (Adv. Funct. Mater. 2018, 28, 1705235) The resultant SiOx anodes delivered high reversible capacities of 645 mAh/g with about 90% capacity retention after 500 cycles. In another example, Kwon et al. developed a Si/C structure with silicon
10 nanocrystals embedded in micro carbon balls. (Nano Lett., 2020, 20, 1, 625-635) Such Si/C composite was produced with microemulsion method and low-cost corn starch as a biomass precursor and delivered a capacity of 1,800 mAh/g with 80% retention over 500 cycles.

However, the coatings or matrix of carbon materials cannot completely resolve the intrinsic
15 volume change issue of Si materials. The repeated expansion and shrinking of Si-based anode materials would inevitably cause electrode composite failure in long-term battery operation. It is necessary to further develop another level of structurally controlling components outside carbon coating for Si materials. Moreover, it should be noted that mass production of Si-based anode materials would have to rely on low-cost Si sources (e.g. silicon kerf, metallurgical Si,
20 or Ferrosilicon), cheap processing, and affordable carbon sources. Such manufacturing factors would limit the application of sophisticated Si/C material design. A critical need for innovative approaches that can deliver robust, cost-effective, and scalable Si-based LIBs capable of meeting the stringent requirements of commercial applications is still needed.

25 As demand for high-performance lithium-ion batteries (LIBs) continues to rise, particularly in the electric vehicle (EV) market, ongoing research endeavors are focused on material innovation to enhance performance, reduce overall battery weight, and lower manufacturing costs. In this context, current collectors (CCs) play a crucial role, as the weight of aluminum (Al) and copper (Cu) significantly impacts the price, weight, and energy density of LIB
30 systems. Among various strategies to advance LIB technology, significant attention has been directed towards the development of lithium metal batteries (LMBs) as a promising avenue for next-generation energy storage systems. Lithium metal has a high theoretical capacity of 3860 mAh/g, a lightweight nature (0.534 g/cm³), and the lowest electrochemical potential (-3.04 V vs. standard hydrogen electrode). With lithium metal serving as the anode, LMBs offer
35 distinct advantages over traditional LIBs, including higher theoretical energy densities and the potential for lighter weight designs. However, the commercial viability of LMBs is hindered by inherent challenges, such as dendrite formation and electrolyte instability. To address these obstacles, extensive research initiatives have been undertaken, including modifications

to separators, optimization of electrolyte compositions, incorporation of electrolyte additives, exploration of solid or gel electrolytes, application of protective layers onto lithium metal anodes, and development of artificial solid electrolyte interphase (SEI) layers. Additionally, efforts have been directed toward enhancing electrochemical stability through modifications to current collectors (CCs). These advancements underscore the multifaceted approach toward advancing battery technology and meeting the evolving demands of diverse industries.

Summary

In an aspect of the present disclosure, a composite particle is provided, the composite particle comprising: a silicon core decorated with at least a first moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymerization initiating group, and a second moiety comprising a second anchoring component covalently bonded to the silicon core, and a functional group. The composite particle may have an average diameter ($D_{[4,3]50}$) from about 10 nm to about 500 nm, as measured by dynamic light scattering. The first and second anchoring components may be selected from $-C^+(R^{A1})(R^{A2})CH(R^{A3})-$, $-C^+HCH-$, or $-C^+MeCH-$, wherein C^+ represents the carbon covalently bonded to a silicon of the Si-particle, and R^{A1} , R^{A2} , R^{A3} are each independently selected from H or Me. The polymerization initiating group may comprise a radical stabilising group (Rad) and a leaving group (LG). The polymerization initiating group may be: Rad-LG, wherein Rad is covalently bonded to the remainder of the first moiety and selected from $-(C_6(R^{Rad2})_4)-C^*(R^{Rad1})_2$, $-(C_{10}(R^{Rad2})_6)C^*(R^{Rad1})_2-$, $-C^*(R^{Rad3})_2$, $-OC(O)C^*(R^{Rad1})_2$, or $-NR^{Rad1}C(O)C^*(R^{Rad1})_2$, wherein C^* represents the carbon attached to LG, each R^{Rad1} independently denotes H or methyl, each R^{Rad2} independently denotes H or R^{Rad3} , R^{Rad3} denotes methyl, and LG is selected from Cl, Br or I. The functional group may denote H, $-C_6H_5$, $-C_6F_5$, $-C(O)O-R^{FG3}$, or CN, wherein R^{FG3} denotes CH_3 or *tert*-butyl. The relative surface stoichiometry of first moiety may be at least 0.5%. The silicon core may comprise crystalline silicon.

In an aspect of the present disclosure, a method of forming a composite particle is provided, the method comprising: providing silicon particles, a first moiety precursor comprising a first anchorable component and a first functional group (such as a polymerization initiating group), and a second moiety precursor comprising a second anchorable component and a functional group, and decorating the silicon particles by reacting the first anchorable component of the first moiety precursor to form a first anchoring component of a first moiety and reacting the second anchorable component of the second moiety precursor to form a second anchoring component of a second moiety, wherein the first anchoring component and the second anchoring component are covalently bonded to the silicon particle. The composite particle may be an aggregate of particles, said aggregate having an outermost surface and a plurality of internal surfaces, and comprising external composite particles and optionally internal

particles, wherein the optional internal particles comprise a silicon core, the external composite particles comprise a silicon core, and an external surface region, the external surface region comprising an area decorated with the first and second moieties covalently bonded to the silicon core of the external composite particles through the first and second
5 anchoring component, wherein said decorated area of the external surface region of the external composite particles forms the outermost surface of the aggregate, and wherein none of the surface of the optional internal particles forms part of the outermost surface of the aggregate.

10 In an aspect of the present disclosure, a method of forming a composite particle is provided, the method comprising the steps of providing silicon particles, a first moiety precursor comprising a first anchorable component and a polymerization initiating group, and a second moiety precursor comprising a second anchorable component and a functional group,
15 decorating the silicon particle by reacting the first anchorable component of the first moiety precursor to form a first anchoring component of a first moiety and reacting the second anchorable component of the second moiety precursor to form a second anchoring component of a second moiety, wherein the first anchoring component and the second anchoring component are covalently bonded to the silicon particle. In the method, the silicon particles may be exposed to HF so as to form Si-H moieties on at least a part of the surface, prior to
20 reaction with the first and second moiety precursors. The method may be such, wherein the first and the second moiety precursors are immobilised on the surface of a Si-particle in the same step. The ratio of first moiety precursors to second moiety precursors used to decorate the Si-particle may be from 1:9 to 9:1. The silicon core may have an average diameter ($D_{[4,3]}$) from about 10 nm to about 500 nm, as measured using dynamic light scattering.
25 The first moiety precursor may comprise 4-vinyl benzyl chloride, and the second moiety precursor may comprise *tert*-butyl acrylate, styrene, pentafluorostyrene, or acrylonitrile.

In an aspect of the present disclosure, a polymer brush composite particle is provided, the polymer brush composite particle comprising a silicon core decorated with at least a first
30 moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymeric moiety, and a second moiety comprising a second anchoring component and one or more functional groups. The polymeric moiety may have a linear polymeric chain with an average length of from about 2 repeat units to about 1000 repeat units.

35 In an aspect of the present disclosure, a method of forming a polymer brush composite particle is provided, said method comprising providing a composite particle comprising a silicon core decorated with at least a first moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymerization initiating group, and a second

moiety comprising a second anchoring component covalently bonded to the silicon core, and a functional group, forming a polymerization reaction composition comprising one or more polymerization catalysts and one or more monomers, and exposing the composite particle to the polymerization reaction composition. The polymer brushes may be synthesised by SIP (Surface-Initiated Polymerization). In the method, the polymerization reaction composition may be formed from a polymerization composition comprising at least one dormant transition metal catalyst, an activation agent comprising an oxygen scavenger, and one or more monomers, wherein the one or more monomers may be provided as a part of the polymerization composition, a part of the activation agent, or as a discrete composition.

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The methodologies described herein provide decorated silicon particles that have controllable solubility/dispersibility. For instance, the decorated particles can have a combination of hydrophilic and hydrophobic layers, allowing solubility tuning. Moreover, the particles have a passivated silicon surface that shows good stability under conditions that would cause reaction such as oxidation of an untreated silicon particle.

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The present disclosure provides methods for forming polymer brushes on a Si and C-based particles, thus, enabling easy large-scale production of polymer brushes covalently bound to Si and C-based particles. In particular, the methods allow for easy control of the graft-density due to the formation of multifunctional composite Si and C-based particles. The disclosure also provides a multifunctional composite Si and C-based particle as well as a multifunctional composite Si and C-based particle upon which polymer brushes are formed.

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The present disclosure pertains to scalable techniques for manufacturing polymer brushes on current collectors tailored for electrochemical cells, including alkali-metal-based or anode-free systems. These techniques enable the creation of multifunctional current collectors with various polymer brush configurations. Moreover, this disclosure introduces methods for producing multifunctional current collectors that capitalize on the enhanced lithiophilicity imparted by the polymer brushes, thereby in some embodiments promoting uniform lithium deposition and optimizing performance in alkali-metal-based or anode-free configurations. An embodiment of this disclosure introduces electrochemical cells, and more specifically, polymer brush-based primers for the electrodes of such cells.

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The present disclosure provides structures for devices, including lithium batteries, which combine the polymer brushes on Si and C-based particles with polymer brushes on current collectors.

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Description of the drawings

Embodiments of the present disclosure are shown in the accompanying drawings. The drawings are in no way intended to be limiting on the scope of the disclosure.

- 5 Figure 1A shows a schematic cross section of a decorated Si-particle.
- Figure 1B is a conceptual depiction of the immobilisation of first and second moieties on the surface of a Si-particle to form a decorated particle (arrow 1) and subsequent polymer brush formation on said decorated particle (arrow 2).
- Figure 2 shows FTIR spectra for five reactions carried out with different relative ratios of
10 tert-butyl acrylate (tBA) and 4-vinylbenzyl chloride (4-VBC). The numbering of each of the spectra corresponds to the reaction number seen in *Table 1*.
- Figure 3 shows relative surface stoichiometry of 4-VBC in co-grafting experiments with 4-VBC and tBA, as a function of the fraction of 4-VBC in solution.
- Figure 4 shows thermogravimetric analysis (TGA) for poly(tert-butyl methacrylate) (PtBA)
15 and poly(methacrylic acid) (PMAA) polymer brushes (PBs) grown from a Si-particle decorated with a solution of tBA/4-VBC in a ratio of 90:10. Dashed line shows the decorated Si-particle prior to PB formation. Light grey full line shows the particle with poly(methacrylic acid) polymer brushes. Dark grey full line shows the particle with poly(tert-butyl methacrylate) polymer brushes.
- 20 Figure 5 shows FTIR transmission spectra for Si nanomaterials with a Base Layer of tBA/4-VBC in a 90:10 ratio, with PtBA polymer brushes (curve number 1) and PMAA (curve number 2) polymer brushes, respectively.
- Figure 6A shows FTIR spectra for five reactions carried out with different relative ratios of
25 pentafluorostyrene and 4-vinylbenzyl chloride (4-VBC). The numbering of each of the spectra corresponds to the reaction number seen in *Table 6*.
- Figure 6B shows a detail of the spectra from Figure 6A.
- Figure 7 shows raw data for the 30:70 ratio of PFS and 4-VBC co-grafting experiment fitted with three components in the top diagram and relative residuals from the fitting of the data in the bottom diagram.
- 30 Figure 8 shows relative surface stoichiometry of 4-VBC as a function of the fraction of 4-VBC in solution.
- Figure 9 shows thermogravimetric data indicating formation of polymer brushes on the mixed layer of PFS/4-VBC.
- Figure 10 shows KBr FTIR spectra for the process of going from a Si-particle decorated with
35 a 10:90 4-VBC/PFS reaction mixture composition (curve number 1), to forming poly(tert-butyl methacrylate) polymer brushes (curve number 2), and finally removing the tert-butyl group to reveal polymer brushes of poly(methacrylic acid) (curve number 3).

- Figure 11 shows FTIR spectra obtained from co-grafting acrylonitrile and 4-vinylbenzyl chloride. The numbering of each of the spectra corresponds to the reaction number seen in *Table 10*.
- Figure 12 shows relative surface stoichiometry of 4-VBC when co-grafting with acrylonitrile as a function of the fraction of 4-VBC in solution.
- Figure 13 shows FTIR spectra obtained by varying the concentration of 4-VBC during the hydrosilylation reaction. The numbering of each of the spectra corresponds to the reaction number seen in *Table 14*.
- Figure 14 shows normalized peak areas pertaining to 4-VBC as a function of solution concentration of 4-VBC.
- Figure 15A shows FTIR spectra of Si nanomaterial modified with tert-butyl acrylate (1), and Si nanomaterial modified with acrylic acid (2), obtained by de-tert-butylation of the tert-butyl acrylate modified Si nanomaterial.
- Figure 15B shows a detail of the spectra from Figure 15A.
- Figure 16 shows particle size distributions for the various process steps, from 1 to 4: 1) Native Si nanomaterial prior to any treatment & etching. 2) Si nanomaterial after ultrasonication, HF etch, and grafting with 4-VBC. 3) Si nanomaterial after poly(tert-butyl methacrylate) polymer brush formation from the surface of the Si nanomaterial, and finally 4) Si nanomaterial after de-tert-butylation to form poly(methacrylic acid) polymer brushes tethered from the surface of the Si nanomaterial.
- Figure 17 shows a FTIR spectrum of Si nanomaterial modified with poly(methacrylic acid) polymer brushes formed on a particle decorated with 4-VBC.
- Figure 18A shows FTIR spectra of the untreated Si Nanomaterial (3), the HF-etched Si nanomaterial (2), and the same material after the diazonium initiated hydrosilylation reaction with 100% tert-butyl acrylate to decorate a Si-particle (1).
- Figure 18B shows a detail of spectra (1) and (2) from Figure 18A.
- Figure 19 shows ATR FTIR spectra of an Si nanomaterial with a poly(methacrylic acid) polymer brush (top spectrum) and the same material after titration with LiOH to a final pH value of 7 (bottom spectrum).
- Figure 20 shows titration data for Si nanomaterial modified with a poly(methacrylic acid) polymer brush being titrated with lithium hydroxide in an aqueous solution of 0.1 M LiNO₃.
- Figure 21 shows a TEM micrograph of an aggregation of silicon nanoparticles.
- Figure 22 shows a schematic cross-sectional representation of an electrochemical cell, for example a secondary lithium-ion cell, comprising an anode according to the present disclosure.

- Figure 23 shows IR spectra for graphite-I (Spectrum 1), graphite-PtBMA (Spectrum 2), graphite-PMAA (Spectrum 3), and graphite-PMAA-Li (Spectrum 4).
- Figure 24 shows a schematic cross section of a polymer brush decorated on the graphitic carbon surface of Si/C composite material. Following the preparation of Si/C composite materials, a conformal carbon coating can be applied to the surface before polymer brush decoration. Silicon nanoparticles (31) are embedded within carbon matrix (32), and the outer layer (33) consists of a graphitic carbon coating, designed to enhance conductivity and stability. Finally, polymer brushes (34) on the outer surface improve adhesion.
- Figure 25 shows a diagram illustrating a polymer brush decorating the porous silicon. Following the graphitic carbon coating step, a polymer brush can be applied to both the inner and outer surfaces of the porous silicon. A porous silicon particle (41) with open pores (42) is coated with a carbon layer, and the carbon layer is decorated with polymer brushes (44 & 45).
- Figure 26 shows a process flow diagram for mechano-chemical synthesis of Si/C composite.
- Figure 27 shows a process flow diagram for MG-Si-based synthesis of Si/C composite.
- Figure 28 shows a process flow diagram for silica-based synthesis of Si/C composite.
- Figure 29 shows a process flow diagram for silicon nanoparticle-based synthesis of Si/C composite.
- Figures 30A&B show an electrode including electrically conductive support, and a polymer brush layer according to one embodiment described herein. Layer 1 is termed the anchoring layer, adjacent to the surface of the electrically conductive support layer 2. A polymer brush layer (layer 3) can be initiated from this anchoring layer. Layer 4, referred to as the electroactive layer, can comprise either cathode or anode active material. In anode-free battery configurations, lithium ions migrate from the electrolyte solution to form a metallic lithium layer on the surface of polymer brush decorated electrically conductive support during the battery cycling process.
- Figure 31 shows a polymer brush layer including first and/or second moieties 23 attached to electrically conductive support (layer 22) according to one or more implementations described herein. The polymer brush 24 is grown from the initiator moieties 23.
- Figure 32 depicts a process flow diagram outlining the steps involved in implementing a method for creating an electrode structure as described herein.

Detailed description

Methods of forming a composite particle and a composite particle upon which polymer brushes are covalently bound are disclosed herein. Said composite particles are also comprised as described by the present disclosure.

5

Si-particles

The present disclosure relates to composite particles comprising a silicon core. The silicon core of the disclosure may be a silicon nanoparticle (Si-nanoparticle). The Si-nanoparticle may have an average diameter (D50) from about 10 nm to about 500 nm, for example from about 25 nm to about 300 nm, such as from about 50 nm to about 200 nm, such as from about 75 to about 150 nm. For certain applications, the average diameter (D50) may be about 50 nm, about 75 nm, about 100 nm, about 125 nm, about 150 nm, about 175 nm or about 200 nm.

15 By "diameter" as used herein is meant the $D_{[4,3]}$ volume weighted mean diameter as measured using dynamic light scattering, for instance using a Microtrac Nanotrac Flex. Using this methodology, the diameter for non-spherical particles may be reported as the diameter of a sphere of the same volume. The "average diameter" as used herein is therefore the median (D50) value of this metric, sometimes referred to as the $D_{[4,3]}50$ average diameter.

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The silicon core may have any morphology. For example, the silicon core may be spherical.

The silicon core may suitably have an aspect ratio of from 1:1 to 3:1, such as from 1:1 to 2:1, or even from 1:1 to 3:2.

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By "aspect ratio" is meant the ratio of the longest dimension of the particle to the shortest dimension of the particle.

30 The silicon core may be crystalline. For example, the silicon core may be monocrystalline or polycrystalline.

Composite particle

35 The composite particle may comprise a silicon core which is decorated with at least two moieties, see Figure 1A. Each of the two moieties may be covalently bonded to the silicon core through anchoring components.

In the context of this disclosure, decoration of a particle/core is meant that organic molecules are covalently attached to said particle/core.

The composite particle comprising a silicon core may be decorated with at least a first moiety comprising a first anchoring component covalently bonded to the silicon core, and first functional group (such as a polymerization initiating group), and a second moiety comprising
5 a second anchoring component covalently bonded to the silicon core, and a second functional group.

The composite particle may alternatively be described as a silicon core surrounded by a base layer, said base layer comprising first and second moieties which are covalently bonded to
10 the silicon core.

To form the particle of the disclosure, silicon particles are reacted with components for forming the first and the second moieties. The components for forming the first and the second moieties may also be referred to as first moiety precursors and second moiety precursors
15 respectively. The reaction between the Si-particles and the first and second moiety precursors leads to said precursors being immobilised on the surface of the Si-particle. The immobilisation reaction is depicted in Figure 1B (arrow 1).

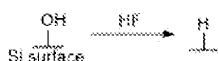
Anchorable component and anchoring group

20 Both the first and the second moiety precursors comprise an anchorable component (A'). The anchorable component may be the same or different for the different moiety precursors.

By reacting the anchorable component of each of the first and second moiety precursors with the surface of the Si-particle, a covalent bond forms between said anchorable component and
25 said Si-particle resulting in the formation of an anchoring component (A), i.e., a component of the moiety which is covalently bonded to the silicon core. Hence, the first and the second moieties may be covalently bound to the surface of the Si-particle through anchoring components. Thus, a first and second moiety precursor and the corresponding first and second moiety differ in that the anchorable component (A') of the precursor has reacted to form an
30 anchoring component (A). The process of anchoring the first and second moieties onto the surface may be referred to as immobilization. Hydrosilylation is an example of an immobilization technique and involves addition of an Si-H across an unsaturated bond.

The surface of Si-particles may typically comprise -OH groups and bridge -O- groups, due to
35 the natural oxidation of silicon by atmospheric oxygen. In order to allow immobilization of the anchorable group on the surface of the silicon particle via Si-C link, it may be necessary to convert the oxidised Si-surface to provide a Si-surface that is H-terminated.

Thus, the Si-particle may be treated to form Si-H groups on at least part of the surface of the silicon particle. Pre-treatment to form Si-H groups may comprise exposure hydrogen fluoride (HF). The pre-treatment removes Si-O bonds to form Si-H bonds (i.e. an H-terminated Si-surface). For example, the pre-treatment removes the silicon surface layer containing Si-O groups leading to hydrogen passivation of the surface as seen below:



The pre-treatment ensures that the surface of the Si-particles is at least partly H-terminated. By at least partly is meant that at least 50% of the Si atoms at the surface have Si-H bonds, for example at least 75%, such as at least 85%, for example at least 90%, such as at least 95%.

A general reaction scheme for the reaction between an H-terminated Si-surface and a moiety precursor may be depicted as:



As is evident from this scheme, the moiety precursor may be depicted as:



wherein A' may be an anchorable component, Z may be a linking group, and FG may be a functional group.

The corresponding moiety may be depicted as:



wherein A may be an anchoring component, Z may be a linking group, and FG may be a functional group.

The anchorable component may typically contain an unsaturated group capable of undergoing a hydrosilylation reaction with the H-terminated Si-surface. Thus, the anchoring group may covalently bind to the silicon surface via a Si-C bond.

Hydrosilylation reaction with the H-terminated Si-surface requires cleavage of Si-H bonds to form surface Si radicals. Homolytic cleavage of Si-H bonds will occur at temperatures above

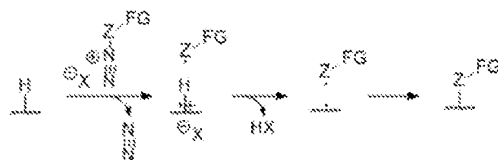
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120°C, and the reaction can be run at $T > 150^\circ\text{C}$, for example. Some compounds with anchorable groups that are compatible with such elevated temperatures (for example, boiling point or decomposition point of the compound is $> 150^\circ\text{C}$) will react with the H-terminated Si-surface under heat treatment. This may be depicted as per the reaction scheme below:

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Diazonium salts provide a suitable option for direct reaction with the H-terminated silicon surface at much lower temperatures down to room temperature of $\sim 20^\circ\text{C}$, as depicted below:

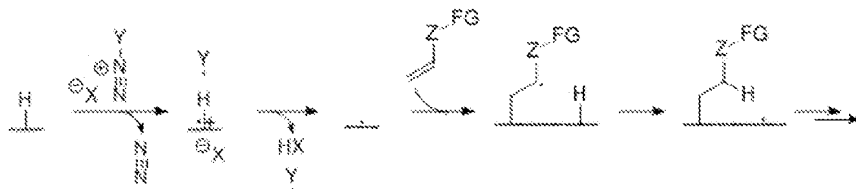


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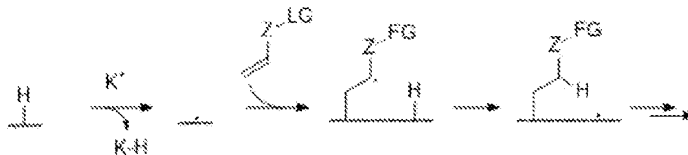
For diazonium activation reactions, the counter ion (X^-) may be an organic or inorganic anion such as chloride (Cl^-), bromide (Br^-), tetrafluoroborate ($[\text{BF}_4]^-$), or tosylate ($p\text{-H}_3\text{CC}_6\text{H}_4\text{SO}_3^-$).

However, diazonium salts are more typically used as a co-reactant to activate the H-terminated Si-surface of Si-nanoparticles, forming a radical that may react with a suitable anchorable group. Other suitable co-reactants are selected from iodonium salts (having a suitable counterion X^- as per those listed for the diazonium salts above), or radical initiators such as AIBN (azobisisobutyronitrile).

20 Hydrosilylation via diazonium-initiated radical generation may be depicted below:



Hydrosilylation initiated by a generic radical forming species, K activated with heat treatment at $T < 120^\circ\text{C}$ is depicted below:



wherein K may be a radical forming species such as azobisisobutyronitrile (AIBN).

5

Thus, surface decoration by first and second moieties may suitably occur via hydrosilylation, particularly hydrosilylation via diazonium-initiated radical generation.

When a hydrosilylation reaction is used for immobilization, the anchorable component (A') typically comprises an unsaturated carbon moiety, while the anchoring component (A) may be a saturated version thereof. For example, the anchorable component may comprise an alkene group which through the immobilisation reaction is converted into an anchoring component comprising an alkane group. Alternatively, the anchorable component may comprise alkyne group which through the immobilisation reaction is converted into an anchoring component comprising alkene group. Exemplary pairs of anchorable component/anchoring component may be selected from ethenyl/ethylene, 1-methylethenyl/1-methylethylenyl, 2-methylethenyl/2-methylethylenyl, 1,1-dimethylethenyl/1,1-dimethylethylenyl, 1,2-dimethylethenyl/1,2-dimethylethylenyl, 1,1,2-trimethylethenyl/1,1,2-trimethylethylenyl, or ethynyl/ethenyl.

20

The anchorable component/anchoring component may suitably be selected from ethenyl/ethylenyl.

Thus, A' may be selected from $R^{A1}(R^{A2})C=C(R^{A3})-$, $HCC-$, or $MeCC-$, wherein R^{A1} , R^{A2} , R^{A3} may each independently be selected from H or methyl (Me). A' may suitably be selected from $R^{A1}(R^{A2})C=C(R^{A3})-$.

25

Likewise, A may be selected from $-C^+(R^{A1})(R^{A2})CH(R^{A3})-$, $-C^+HCH-$, or $-C^+MeCH-$, wherein C^+ represents the carbon covalently bonded to a silicon of the Si-particle, and R^{A1} , R^{A2} , R^{A3} are each independently selected from H or Me. A may be selected from $-C^+(R^{A1})(R^{A2})CH(R^{A3})-$. R^{A1} and R^{A2} may denote H, and R^{A3} may denote H or Me.

30

Above, exemplary reaction schemes between Si-surfaces and moiety precursors are shown. The same reactions may apply for both moiety precursors.

35

By "first and second moiety (precursor)" is meant "a first moiety, a second moiety, a first moiety precursor or a second moiety precursor". Similarly, "first moiety (precursor)" means "first moiety or first moiety precursor", while "second moiety (precursor)" means "second moiety or second moiety precursor".

5

A'/A and/or Z may be the same for both the first and second moiety (precursor). That is, the first anchorable component/anchoring component may or may not be the same as the second anchorable component/anchoring component. Similarly, the first linking group may or may not be the same as the second linking group.

10

A' may comprise a diazonium salt, an alkene group such as ethenyl or propenyl, or an alkyne group such as ethynyl or methyl ethynyl.

In such embodiments, this would mean that A may comprise a bond, an alkylene group such as ethylene or propylene, or an alkenyl group such as ethenyl or propenyl.

15

Linking group

Z is a linking group. Generally speaking, Z may be a wide variety of chemistries. However, there are some considerations that need to be taken into account. Firstly, the silicon surface usually comprises Si-H groups. Therefore, the linking group may be chosen so as to not comprise any groups that oxidise the silicon surface. For instance, the linking group may not comprise any nucleophilic OH or NH groups, such as alcohols or primary or secondary amines. Secondly, as shown by the reaction schemes above, the typical mode of attachment to the silicon surface is via a free radical reaction, for instance via addition across an unsaturated carbon-carbon bond. This type of radical addition will create a free radical, usually at the carbon that connects to the linker group. In view of this, the linker group should be compatible with free radical reactions, and be able to stabilise a free radical on an atom to which it is connected.

20

25

A linker group may be compatible with free radical reactions if it does not contain any groups that would compete with the anchorable group in the reaction pathways specified above. For instance, multiple ethylenyl groups in the linker group may compete with the anchorable group leading to a less controlled surface decoration.

30

It is of course known that most functional groups will react with free radicals. However, suitable design of the linker group can mitigate side reactions.

35

The linker group should be compatible with the reactions used for propagation of the polymer brush after anchoring to the Si-particle.

These design criteria still leave a wide range of options for Z.

5

For instance, Z may be a bond. Alternatively, Z may comprise a functional group selected from arylene, alkylene, ester, ether, or amide.

10 Z may additionally be optionally substituted with groups such as halogen. However, if using such substituents, the relative reactivity of the halogen in free radical reactions should be considered to ensure that the halogen is less reactive than the anchorable group and any polymerizable group that may be present.

15 Fluorine may be used, though any one of chlorine, bromine and iodine may be used providing it is attached to a moiety that would yield a free radical that is inherently less stable than any free radical formed by the anchorable or any polymerizable group. For instance, an aryl halide may be suitable in the linker group, whereas an alkyl chloride adjacent to an unsaturated group will form a stabilised radical which may lead to side reactions that compete with the immobilization of the anchoring group and possibly any subsequent polymerization reactions.

20 For instance, Z may be selected from a bond, Z^1 , Z^2 , $-(CH_2CH_2O)_{1-20}-(CH_2)_{1-2}-$, $Z^3-C(O)O-Z^3$, $Z^3-C(O)NH-Z^3$, $Z^3-C(O)NMe-Z^3$, or Z^3-O-Z^3 , wherein Z^1 denotes C_1-C_{10} -alkylene optionally substituted with F, Z^2 denotes phenylene or naphthylene, optionally substituted with F or Cl, and Z^3 denotes Z^1 or Z^2 .

25 In some cases, Z may be selected from a bond, Z^1 , Z^2 , or $-(CH_2CH_2O)_{1-20}-(CH_2)_{1-2}-$, wherein Z^1 denotes C_1-C_{10} -alkylene optionally substituted with F, and Z^2 denotes phenylene or naphthylene, optionally substituted with F or Cl.

30 In some cases, Z may be selected from a bond, Z^1 , or Z^2 , wherein Z^1 denotes C_1-C_{10} -alkylene optionally substituted with F, and Z^2 denotes phenylene or naphthylene, optionally substituted with F.

In some cases, Z may be selected from a bond or Z^2 , wherein Z^2 denotes phenylene, optionally substituted with F.

35

In some cases, Z may denote a bond.

Functional groups

While A'/A and/or Z may be the same for both the first and second moiety (precursors), the groups may typically be terminated with different functional groups. The first moiety may be terminated with one or more first functional groups, while the second moiety may be terminated with one or more second functional groups.

The design criteria of the functional group generally follow the same principles as the linking group, i.e. that the functional group may be compatible with the reaction that leads to the anchorable group being immobilized on the surface when forming the anchoring group.

The functional group is typically at the surface of the decorated Si-particle, which means that it may have more significant influence on the surface properties of the particle.

The first moiety may contain a first functional group, which may be a polymerization initiating group.

By "a polymerization initiating group" is meant a group comprising a radical stabilising group, and a leaving group.

The first functional group may be a polymerization initiating group comprising a radical stabilising group and a leaving group.

A radical stabilising group may be a group that stabilises a radical. Typically, a radical may be stabilised through hyperconjugation or resonance.

The radical stabilising group may comprise a carbon atom which may be directly bound to the leaving group. Removal of said leaving group typically leads to the formation of a radical. Therefore, the carbon atom which may be directly bound to the leaving group will be the carbon on which the radical will be formed.

Said carbon may be highly substituted to ensure sufficient radical stabilisation. For example, said carbon may be a tertiary carbon. One of the substituents on the carbon is the linking group which is bound to the anchorable/anchoring component. The remaining substituent(s) may be alkyl, for example methyl, ethyl, propyl, or butyl. Alternatively, one or more of the substituents may comprise a lone pair which increases radical stabilisation. For example, the substituents may include functional groups such as ether, ester, and amide. Alternatively, one or more of the substituents may comprise an unsaturated moiety such as phenylene or naphthalene, which stabilise a radical through resonance.

Alternatively, said carbon may be a secondary carbon, that is a carbon which is bound to the leaving group and a substituent selected from a substituent having a lone pair or a substituent which is unsaturated. Said substituent is further bound to the linking group, which is bound to the anchorable/anchoring component.

A neighbouring lone pair increases radical stability. Exemplary substituents with lone pairs include functional groups such as ether, ester, and amide.

Said secondary carbon may be adjacent to an unsaturated moiety such as a phenylene or naphthalene group to allow for radical stabilisation through resonance. Upon radical formation, this would result in the formation of a benzylic radical. Said phenylene or naphthalene group may also be bound to the linking group.

A leaving group is an atom or group of atoms that detaches from a substrate during a reaction, particularly a polymerization reaction to form a brush polymer as described herein. Any leaving group known to the person skilled in the art may be suitable. Typical leaving groups include halides and pseudohalides.

Thus, the functional group in the first moiety may be represented as: Rad-LG, wherein Rad may be a radical stabilising moiety covalently bonded to the remainder of the first moiety (for instance covalently bonded to Z), and LG is a leaving group.

In some cases, Rad may be selected from $-(C_6(R^{Rad2})_4)C^*(R^{Rad1})_2$, $-(C_{10}(R^{Rad2})_6)C^*(R^{Rad1})_2$, $-C^*(R^{Rad3})_2$, $-OC(O)C^*(R^{Rad1})_2$, $-NR^{Rad1}C(O)C^*(R^{Rad1})_2$, or $-OC^*(R^{Rad1})_2$, wherein C^* represents the carbon covalently bonded to LG, each R^{Rad1} independently denotes H or C_1 - C_4 -alkyl, each R^{Rad2} independently denotes H, F, Cl, R^{Rad3} , NO_2 , $-O-R^{Rad3}$, $-C(O)O-R^{Rad3}$, or $C(O)N(R^{Rad1})_2$, and each R^{Rad3} independently denotes C_1 - C_4 -alkyl.

In some cases, Rad may be selected from $-(C_6(R^{Rad2})_4)C^*(R^{Rad1})_2$, $-(C_{10}(R^{Rad2})_6)C^*(R^{Rad1})_2$, $C^*(R^{Rad3})_2$, $-OC(O)C^*(R^{Rad1})_2$, or $-NR^{Rad1}C(O)C^*(R^{Rad1})_2$.

In some cases, Rad may be selected from $-(C_6(R^{Rad2})_4)C^*(R^{Rad1})_2$, $-OC(O)C^*(R^{Rad1})_2$, or $-NR^{Rad1}C(O)C^*(R^{Rad1})_2$.

In some cases, Rad may be selected from $-(C_6(R^{Rad2})_4)C^*(R^{Rad1})_2$.

In some cases, each R^{Rad1} independently may denote H or methyl.

In some cases, R^{Rad1} may denote H.

In some cases, each R^{Rad2} may independently denote H, F, Cl, R^{Rad3} , or $-O-R^{\text{Rad3}}$.

5

In some cases, each R^{Rad2} may independently denote H, R^{Rad3} , or $-O-R^{\text{Rad3}}$.

In some cases, each R^{Rad2} may independently denote H, or R^{Rad3} .

10 In some cases, R^{Rad2} may denote H.

In some cases, R^{Rad3} may denote methyl.

15 The above specified groups of Rad, R^{Rad1} , R^{Rad2} , and R^{Rad3} may be combined in any combination.

For instance, Rad may suitably be selected from $-(C_6(R^{\text{Rad2}})_4)C^*(R^{\text{Rad1}})_2$, $-(C_{10}(R^{\text{Rad2}})_6)C^*(R^{\text{Rad1}})_2$, $-C^*(R^{\text{Rad3}})_2$, $-OC(O)C^*(R^{\text{Rad1}})_2$, or $-NR^{\text{Rad1}}C(O)C^*(R^{\text{Rad1}})_2$, wherein C^* represents the carbon attached to LG, each R^{Rad1} independently denotes H or methyl, each R^{Rad2} independently denotes H or R^{Rad3} , and R^{Rad3} denotes methyl.

25 In some cases, Rad may be selected from $-(C_6(R^{\text{Rad2}})_4)C^*(R^{\text{Rad1}})_2$, $-(C_{10}(R^{\text{Rad2}})_6)C^*(R^{\text{Rad1}})_2$, $-C^*(R^{\text{Rad3}})_2$, $-OC(O)C^*(R^{\text{Rad1}})_2$, or $-NR^{\text{Rad1}}C(O)C^*(R^{\text{Rad1}})_2$, wherein C^* represents the carbon attached to LG, each R^{Rad1} independently denotes H or methyl, each R^{Rad2} independently denotes H, F, Cl, R^{Rad3} , NO_2 , $-O-R^{\text{Rad3}}$, $-C(O)O-R^{\text{Rad3}}$, or $C(O)N(R^{\text{Rad1}})_2$, and R^{Rad3} denotes methyl.

30 In some cases, Rad may be selected from $-(C_6H_4)C^*(R^{\text{Rad1}})_2$, $-(C_{10}H_6)C^*(R^{\text{Rad1}})_2$, $C^*(R^{\text{Rad3}})_2$, wherein C^* represents the carbon attached to LG, R^{Rad1} denotes H or methyl, and R^{Rad3} denotes methyl.

In some cases, Rad may be selected from $-(C_6H_4)C^*H_2$ or $-(C_{10}H_6)C^*(H)_2$.

35 In some cases, Rad may denote $-(C_6H_4)C^*H_2$.

Exemplary leaving groups (LG) may be selected from chloride, bromide, iodide, tosylate (toluenesulfonate), triflate (trifluoromethanesulfonate), or mesylate (methanesulfonate).

The first moiety (precursor) may comprise a leaving group (LG) selected from chloride, bromide or iodide. These leaving groups may be combined with any of the Rad groups denoted above.

- 5 The first moiety may comprise one or more sites for polymerization. For example, the first moiety may comprise two polymerization initiating groups. Exemplary first moiety precursors include 4-vinylbenzyl chloride.

10 The second moiety (precursor) may comprise one or more functional groups (FG). The functional groups may be chosen so as to not suitable to initiate polymerization by acting as leaving groups under the conditions suitable to remove the leaving group(s) of the first moiety. The presence of one or more functional groups within the second moiety (precursor) allows for fine tuning of the properties of the composite Si-particle. The second moiety may alter a variety of different properties. For example, the second moiety may impart
15 hydrophobic, hydrophilic, ionic, H-bonding, acidic, and/or basic properties.

The second moiety (precursor) may comprise one or more functional groups. For example, suitable functional groups may be selected from H, alkyl, aryl, carboxylic acid ester, carboxylic acid amide, nitrile, fluoride, or ether.

20

In some cases, the second moiety (precursor) may comprise one or more functional groups selected from H, alkyl, aryl, carboxylic acid ester, nitrile, fluorine, or ether.

25 The second moiety (precursor) may comprise only one functional group. Alternatively, two or more functional groups may be present within the second moiety (precursor).

Carboxylic acid esters are compatible with the anchorable/anchoring moiety and may be hydrolyzed once the anchoring moiety has been immobilized to yield a carboxylic acid, this acidifying the surface layer.

30

Thus, the functional group in the second moiety may be represented as: FG denotes $-R^{FG1}$, $-C_6(R^{FG2})_5$, $-C_{10}(R^{FG2})_7$, $-C(O)O-R^{FG3}$, $-C(O)N(R^{FG1})_2$, $-OC(O)-R^{FG1}$, $-N(R^{FG1})-C(O)-R^{FG1}$, CN, $-(CH_2)_{1-4}-O-CH_2-R^{FG1}$, $-(CH_2CH_2O)_{1-20}-(CH_2)_{0-1}CH_3$, or F, wherein each R^{FG1} independently denotes H or C_{1-4} -alkyl, each R^{FG2} independently denotes H, F, Cl, R^{FG3} , NO_2 , $-O-R^{FG3}$, $-C(O)O-R^{FG3}$, or $C(O)N(R^{FG1})_2$, and R^{FG3} denotes C_{1-4} -alkyl.
35

In some cases, FG may denote R^{FG1} , $-C_6(R^{FG2})_5$, $-C_{10}(R^{FG2})_7$, $-C(O)O-R^{FG3}$, $-OC(O)-R^{FG1}$, CN, $-(CH_2)_{1-4}-O-CH_2-R^{FG1}$, $-(CH_2CH_2O)_{1-20}-(CH_2)_{0-1}CH_3$, or F.

In some cases, FG may denote R^{FG1} , $-C_6(R^{FG2})_5$, $-C(O)O-R^{FG3}$, CN, $-(CH_2CH_2O)_{1-20}-(CH_2)_{0-1}CH_3$, or F.

- 5 In some cases, FG may denote R^{FG1} , $-C_6(R^{FG2})_5$, $-C(O)O-R^{FG3}$, CN, or $-(CH_2CH_2O)_{1-20}-(CH_2)_{0-1}CH_3$.

In some cases, FG may denote H, $-C_6(R^{FG2})_5$, $-C(O)O-R^{FG3}$, or CN.

- 10 In some cases, FG may denote H, $-C_6H_5$, $-C_6F_5$, $-C(O)O-R^{FG3}$, or CN.

In some cases, FG may denote H, $-C_6H_5$, $-C_6F_5$, $-C(O)O-R^{FG3}$, or CN, wherein R^{FG3} denotes CH_3 or *tert*-butyl.

- 15 In some cases, FG may denote H, $-C_6F_5$, $-C(O)O-R^{FG3}$, or CN, wherein R^{FG3} denotes *tert*-butyl.

In some cases, each R^{FG1} may independently denote H or methyl.

In some cases, R^{FG1} may denote H.

20

In some cases, each R^{FG2} may independently denote H, F, Cl, R^{FG3} , or $-O-R^{FG3}$.

In some cases, each R^{FG2} may independently denote H, F, R^{FG3} , or $-O-R^{FG3}$.

- 25 In some cases, each R^{FG2} may independently denote H, F, or CH_3 .

In some cases, R^{FG2} may denote H or F.

These above embodiments of FG, R^{FG1} , R^{FG2} , and R^{FG3} may be combined in any combination.

30

Exemplary second moiety precursors may be selected from *tert*-butyl acrylate, styrene, pentafluorostyrene, or acrylonitrile. For example, the second moiety precursors may be selected from *tert*-butyl acrylate, styrene, or pentafluorostyrene.

- 35 For several grafting methods, the rate of immobilization of the moiety precursors may be accelerated by usage of an initiator species which is consumed at the onset of the reaction or by employing a catalytic species such as a transition metal complex or the diazonium salt as

depicted above. In such cases, modifying the nature and loading of initiator and/or catalyst may result in further control in the grafting step of the base layer.

Composite particle

5 The composite particle (that is the silicon particle which is decorated with the first and second moieties) may have a slightly larger diameter than the undecorated silicon particle. The difference in size may typically not be measurable, since the decoration of a particle with a relatively large moiety which for instance contains a C₁₀-alkylene chain as a linking group may only increase the particle diameter by a few nanometres, while a width of the initial particles
10 size distribution (PSD) is on the order of tens of nm and up to 100 nm and the typical non-spherical particle morphology contributes to such a wide PSD as well. Overall, this decoration may have minor impact on the D50 value for particles and will be difficult to measure in a reliable way using methods such as dynamic light scattering.

15 In an embodiment of the disclosure, the composite particle has an average diameter (D50) from about 10 nm to about 500 nm, for example from about 25 nm to about 300 nm, such as from about 50 nm to about 200 nm, such as from about 75 to about 150 nm. The average diameter (D50) may in particular be about 50 nm, about 75 nm, about 100 nm, about 125 nm, about 150 nm, about 175 nm or about 200 nm.

20 To form the composite particle, first and second moieties are immobilized onto the surface of Si-particles to form a decorated particle.

Thus, in an aspect of the disclosure, a method of forming a composite particle is provided,
25 the method comprising: providing silicon particles, a first moiety precursor comprising a first anchorable component and a first functional group (such as a polymerization initiating group), and a second moiety precursor comprising a second anchorable component and a second functional group; decorating the silicon particle by reacting the first anchorable component of the first moiety precursor to form a first anchoring component of a first moiety and reacting
30 the second anchorable component of the second moiety precursor to form a second anchoring component of a second moiety, wherein the first anchoring component and the second anchoring component are covalently bonded to the silicon particle.

In some cases, the silicon particles comprise Si-H groups on the surface of the particle. The
35 providing of silicon particles (i.e. step a.i.) may comprise exposing the silicon particle to HF so as to form Si-H moieties on at least part of the surface of the silicon particle.

Typically, the first and second moiety precursors may be provided as one or more mixtures with one or more solvents.

Solvents may be chosen so as to be compatible with the reaction to convert the anchorable component to the anchoring component. Additionally, the solvent may have low reactivity towards the silicon surface. Solvents include, but is not limited to, ethers, cyclic ethers, aromatic solvents and the like, such as those selected from acetonitrile, tetrahydrofuran, ethyl acetate, methyl *tert*-butyl ether, xylene, toluene, dioxane, or hexane. In some cases, the solvent is selected from tetrahydrofuran, xylene, toluene, or dioxane. In addition, anhydrous and deoxygenated solvents may be applied to prevent Si surface oxidation by residual moisture and oxygen.

The reaction leading to the decoration of the silicon particle (i.e. the reaction of the first and/or second anchorable component to form the first and/or second anchoring component) may be diazonium immobilization reaction or a hydrosilylation. Hydrosilylation may in some cases be suitable.

The first and the second moiety precursors may typically be immobilized on the surface of a Si-particle in the same step. This may also be referred to as co-immobilization.

When immobilizing the first and second moiety precursors simultaneously, they may be allowed to react until complete coverage of the surface of the Si-particle. This implies that the reaction between the moiety precursors and the surface of the Si-particle has stalled and there is no space for additional moieties to be attached. This does not necessarily mean that all hydrides on the Si-surface (Si-H moieties for example) are exchanged with first or second moieties. More likely, it means that steric hindrance of the bound moieties prevents access to the remaining hydrides on the surface. The remaining hydrides on the surface may subsequently be oxidized resulting in the formation of Si-OH moieties on the surface. Surprisingly the decoration layer of immobilized species passivates the silicon surface meaning that Si-H bonds can be retained under a range of conditions that would otherwise oxidise the surface.

Complete reaction between the surface of the Si-particle and the first and second moiety precursors, given that coverage of the surface may act to protect the surface, may be the suited choice. For example, it is known that oxygen and moisture cause deterioration of Si-particles (in particular, bare and H-terminated silicon). The deterioration caused by oxygen and moisture may be diminished upon decoration of the particle with first and second moieties.

The total number of immobilized moieties on the Si-particles may vary depending on various factors such as the reaction time, the temperature, and the concentration of species which undergo grafting to the substrate. Further, it depends on the steric structure of the species being immobilised onto the surface. Compared to the immobilization of small moieties, immobilization of bulky, sterically hindering moieties may result in a lower maximum total number of immobilised moieties than can be obtained for a smaller moiety.

A schematic of the composite silicon particle containing a surface decoration of immobilised first and second moieties is shown in Figure 1A. The relative ratio of first and second moieties can be used to control the surface properties of the particle. For instance, the decoration of a particle with multiple moieties allows for control of the surface properties of the particle, such as control of its solubility, dispersability, adhesion, hydrophobicity, hydrophilicity, acid/base properties such as pI, as well as its reactivity. and electronic and ionic conductivity. Additionally, the relative amount of first moiety having a polymerizable group may impact the nature of the polymer brush formed on the decorated particle.

Since the surface reactivity of the composite particle may be controlled by the ratio of the first and second moiety, the disclosure provides a methodology for decorating Si-particles to obtain specific properties. In particular, by decorating the particle with at least two different moieties (namely first and second moieties), control of the grafting-density during formation of polymer brushes may be obtained. By varying the ratio between the first and the second moieties, a higher or a lower number of initiation sites for the subsequent polymer brush formation may be obtained. This in turn may affect the formation of the polymer brushes.

For example, the ratio of first moiety precursors to second moiety precursors used to decorate the Si-particle may be from 2:98 to 98:2, such as from 5:95 to 95:5, for example from 1:9 to 9:1, such as from 1:6 to 6:1, for example from 1:3 to 3:1, such as from 1:2 to 2:1, for example from 2:3 to 3:2.

In some cases, the ratio of first moiety precursors to second moiety precursors used to decorate the Si-particle may be from 1:9 to 1:1, such as from 1:6 to 2:3, for example from 1:4 to 2:3, such as from 1:3 to 1:2.

In some cases, the ratio of first moiety precursors to second moiety precursors used to decorate the Si-particle may be from 1:1 to 9:1, such as from 3:2 to 6:1, for example from 4:1 to 3:2, such as from 3:1 to 2:1.

The reactivity of the first moiety precursors and the second moiety precursors towards the Si-particle surface may be different. Therefore, a mixture comprising a first moiety precursors to second moiety precursors ratio of 1:1 might not lead to a composite particle whereupon first moieties and second moieties are bound in a ratio of 1:1.

5

Without wishing to be bound by theory, it is believed that the difference in reactivity may be caused by different steric properties and/or different electronic properties of the moiety precursors. For example, a relatively larger moiety precursor may show less reactivity compared to a relatively smaller one. Similarly, it is generally known that alkynes display higher reactivity than the corresponding alkene in hydrosilylation reactions.

10

To determine the ratio between the first and second moieties which constitute the decoration of the composite particle, the relative density of each component may be obtained. The relative density is used to describe the amount of a certain moiety immobilised on a Si-particle, relative to the maximal obtainable amount of said moiety immobilised on a Si-particle. The maximal obtainable amount corresponds to the amount of immobilised moiety upon reacting an excess of a single type of moiety with the surface of a Si-particle.

15

The amount of a moiety on a Si-particle may be determined using Fourier transform infrared spectroscopy (FTIR). As different functional groups provide different peaks in an infrared spectrum (IR spectrum), these peaks may be used to determine relative amounts of a moiety upon integration.

20

After determining the relative density, the relative surface stoichiometry may be calculated. The relative surface stoichiometry is the ratio of the relative grafting density for one of the grafted species ($Relative\ density_{Species\ 1}$) to the sum of all the relative grafting densities ($Relative\ density_{All\ species}$):

25

$$Relative\ surface\ stoichiometry_{Species\ 1} = \frac{Relative\ density_{Species\ 1}}{Relative\ density_{All\ species}}$$

30

The relative surface stoichiometry of first moiety on the silicon particle is at least 0.5%, such as at least 1%, for example 5%, such as at least 10%, for example at least 15%, such as at least 20%, for example at least 25%, such as at least 30%, for example at least 40%, such as at least 50%, for example at least 60%, such as at least 75%, for example at least 85%, such as at least 90%.

35

The relative surface stoichiometry of second moiety on the silicon particle is at least 5%, such as at least 10%, for example at least 15%, such as at least 20%, for example at least 25%, such as at least 30%, for example at least 40%, such as at least 50%, for example at least 60%, such as at least 75%, for example at least 85%, such as at least 90%.

5

The relative surface stoichiometry may be fitted to the reaction mixture composition, and thus determine the relative rate constants of the reaction to the surface. This can be accomplished using an equation based on the work of Faucheux *et al.* (see "*Langmuir* 2006, 22, 1, 153–162") describing the grafting of two species with different rate constants to a surface with reactive sites which are consumed upon grafting of molecules:

10

$$\frac{n_2}{n_1 + n_2} = \frac{\frac{k_2}{k_1} \cdot c_2}{1 + \left[\left(\frac{k_2}{k_1} \right) - 1 \right] \cdot c_2}$$

wherein n_1 and n_2 denominates the *relative grafting density* of species 1 and 2, and thus $\frac{n_2}{n_1 + n_2}$

15

is the *relative surface stoichiometry* of species 2, k_1 and k_2 are the rate constants for reaction of species 1 and 2 to the surface, c_2 is the fraction of reactive species 2 in the reaction mixture.

Typically, only one type of first moiety precursor and one type of second moiety precursor are immobilized onto the surface resulting in a composite particle decorated with only one type of first moiety and one type of second moiety.

20

However, for various reasons, it may be beneficial to use more than one first moiety and/or more than one second moiety when decorating the Si-particle.

25

The first moiety may also be referred to as a polymerization initiating species. This implies that polymeric chains may be grafted from the first moieties. For example, the first moiety may be an SI-ATRP (surface-initiated atom transfer radical polymerization) initiator, SI-NMP (surface-initiated nitroxide-mediated polymerization) initiator, SI-PIMP (surface-initiated photoiniferter-mediated polymerization) initiator, SI-A(R)GET surface-initiated photoiniferter-mediated polymerization) initiator, SET-LRP (single-electron transfer living radical polymerization) initiator or SARA ATRP (supplemental activator and reducing agent atom transfer radical polymerization) initiator. The introduction of more than one type of polymerization initiating species opens the possibility of doing two different polymerization. For example, first an ATRP-like polymerization from the ATRP-initiators, and subsequently growing a different polymeric structure under RAFT-conditions from the RAFT initiator.

30

In some cases, the Si-particle may be decorated with more than one type of first moiety.

Similarly, the decoration of a Si-particle with more than one second moiety may provide opportunities for improving different properties of the surface of the Si-particle, such as pI,
5 hydrophobicity, hydrophilicity, dispersibility, adhesion, as well as electronic and ionic conductivity.

In some cases, the Si-particle may be decorated with more than one type of second moiety.

10 Polymer brush composite particle

After having formed the composite particle, which comprises a Si-core decorated with first and second moieties and wherein the first moieties have polymerization initiating groups, polymer brushes may be formed from said first moieties. See arrow 2 in Figure 1B.

15 The polymer brushes may also be referred to as surface polymers.

"Surface polymers" describes a polymeric structure having polymer chains that are chemically bonded to a surface at one end through a covalent bond.

20 Two methods, known by persons skilled in the art, can be used to achieve such polymeric structure, namely the "grafting to" approach and the "grafting from" approach. In the "grafting to" approach, polymers are pre-prepared in solution and then deposited onto the surface in question, since the pre-prepared polymers are designed in such a way that one of the chain-ends has some affinity for the surface of interest. Upon contact with the surface of
25 interest, the polymers will self-assemble on said surface forming surface bound polymers. In the "grafting from" approach, small molecules capable of acting as polymerization initiators are covalently bound to the surface of interest in a pre-polymerization step. Subsequently polymerization is initiated via the polymerization initiators. Accordingly, surface polymers are grafted from the surface.

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"Grafting to" is a method of attaching a polymer chain to a surface. The polymer chains are covalently attached to the surface at one chain-end. The method comprises pre-forming polymers in solution, said polymers having a reactive chain-end group. In solution, these polymers are not yet surface attached. The reactive end group can react with a suitable
35 reactive group on the surface in question. Typically, the reactive group is deposited or in another way pre-formed on the surface. The pre-formed polymer is brought into solution, where the conformation of the individual polymer chains is subject to solvent interactions and energetics. Generally, the chains will adopt some version of the coiled configuration to

maximize entropy. This conformation is retained when the reactive chain-ends react with the reactive groups on the surface. The area occupied by grafting this polymer coil to the surface is generally much larger than the area occupied by the reactive surface group, and, thus, neighbouring reactive surface groups are blocked for reaction by the polymer coil. A much
5 higher polymer grafting density could theoretically be obtained if a chain was grafted to the surface in a stretched, linear conformation. Such a conformation is, however, not readily achievable for polymers in solution given the entropically favoured coiled conformation which the chains will adopt in solution. The straight and linear polymer conformation is highly unfavoured by entropy and is thus not generally observed for polymers in solution. However,
10 a surface polymer decoration comprising polymer chains with a more linear conformation, attached to the surface with a much higher density can be obtained using the "grafting from" methodology described below.

While the "grafting to" approach allows for simple preparation procedures, in that one can prepare the polymers using conventional polymerization methods and store those polymers
15 before initiating the self-assembly procedure, the "grafting to"-approach lacks the ability to form high density surface bound polymeric structures. The main problem being the self-assembly process being halted by the steric repulsion between the pre-made polymer chains as they self-assemble on the surface.

The "grafting from"-approach allows for the formation of highly dense surface bound polymer
20 structures, as the small molecules can form a much more densely packed layer on the surface (compared to large polymer molecules). As such, the surface bound polymer structure formed by a "grafting from" approach results in a much higher density. Additionally, as the "grafting from" approach allows for highly dense surface bound polymer structures, a brush-like structure can be achieved, thus, the name "polymer brush". In these structures, the polymers
25 are stretched and forced to stand up-right as a result of the steric repulsion between the neighboring polymers creating a unique structure recognized by people skilled in the art as a "polymer brush" structure. On surfaces, the structures are tethered/attached, usually covalently, at one end to a surface, typically to a solid or semisolid surface, thereby differing from polymers formed in solution and deposited onto a surface subsequently.

30 In the "grafting from" approach the surface polymer growth (surface polymer chain propagation, extension of the chain by monomer units) is initiated from initiator-functionalized surfaces, in particular using a controlled/"living" polymerization technique, such as radical polymerization.

Different polymerization techniques have facilitated the specific design and synthesis of
35 surface polymers with strict molecular control and desired properties. In particular, the

surface polymers can be viewed as nanoscale "building blocks" with a wide range of uses, varying from redox activity to biocompatibility and surface alteration, and due to the flexibility of the surface polymers, highly tailored thin films of surface polymers can be created with respect to chemical composition, thickness, grafting density and architecture.

5

When forming surface polymers, the surface comprising polymerization initiation groups is brought into contact with suitable monomers, catalysts, ligands and optionally a solvent, or suitable monomers, catalysts, ligands, an oxygen scavenger and optionally a solvent, whereby the surface polymer can form using certain reaction conditions. The polymerization
10 initiators and the monomers are chosen so as to suit the purposes and properties of the resulting surface polymers. Surface polymers may also be formed as layers of surface polymers by repeating the polymeric architecture, e.g., using another starting monomer (co block polymers).

- 15 Several methods for forming surface polymers are known, among them SI-ATRP (surface-initiated atom transfer radical polymerization), SI-RAFT (surface-initiated reversible-addition fragmentation chain transfer), SI-NMP (surface-initiated nitroxide-mediated polymerization), SI-PIMP (surface-initiated photoiniferter-mediated polymerization), and SI-A(R)GET (surface-initiated activators (regenerated) by electron transfer) ATRP. A review is
20 given in Chem. Rev. 2009, 109, 5437–5527. Other approaches include SET-LRP (single-electron transfer living radical polymerization), SARA ATRP (supplemental activator and reducing agent atom transfer radical polymerization), and (ARGET) ATRP ((Activators ReGenerated by Electron Transfer) agent atom transfer radical polymerization). In order for the polymerizing chains to progress, a monomer, a catalyst, a ligand and a solvent is needed.
25 In (ARGET) ATRP and SET-LRP polymerizations, some reactions activate the catalyst, thereby, promoting polymerization, and at the same time, other reactions deactivate the catalyst to impede polymerization. SARA-ATRP and SET-LRP is described, e.g., in <https://www.cmu.edu/maty/atrp-how/procedures-for-initiation-of-ATRP/SARA-ATRP-or-SET-LRP.html>. From WO 2019/196999 A1, which is incorporated by reference in its entirety,
30 as if fully set forth herein, an alternative oxygen-tolerant method for forming surface polymers is disclosed. The catalytic system used is halogen free as a complex is formed between a transition metal and a ligand. A major advantage of the catalytic system disclosed is that the complex formed between the transition metal and the ligand is inactive (i.e., not available for initiating polymerization of the monomer) and stable (oxygen-insensitive), but
35 the system can be activated "on demand" by an oxygen scavenger, reducing the transition metal of the transition metal ligand complex, thus, initiating polymerization and propagation of the surface polymers. These methods may all be used to propagate polymer brushes from initiator sites on the silicon particles, forming decorated silicon particles as disclosed herein.

For propagating polymer brushes, a polymerization reaction composition may comprise a monomer, a catalyst, a ligand, a catalyst activator, and optionally a solvent. In some cases, the monomer may act as the solvent.

5

Examples of suited catalyst activators include, but is not limited to, sodium ascorbate, ascorbic acid, hydrazine, hydrazine hydrate, sodium hypophosphite, glucose, tin 2-ethylhexanoate, sodium phenoxide, sodium dithionite, a mixture of iron powder and sodium chloride, hydrogen carbonate, citric acid, and pyrogallol acid, as well as mixtures thereof. The activator for the catalyst (e.g., oxygen scavenger) may be used in excess compared to the transition metal. Excess may, e.g., be 1-250 times.

Examples of suited catalysts may be based on a transition metal (as defined in the Periodic Table of Elements). Suitable examples of transition metals comprise compounds derived from copper (Cu), iron (Fe), and ruthenium (Ru). In some cases, the catalyst may be based on transition metals derived from Cu and/or Fe species. Specific examples of such catalysts include Cu₂O, CuO, CuCl, CuCl₂, CuBr, CuBr₂, FeO, Fe₂O₃, Fe₂O₄, FeCl₂ and FeCl₃, as well as combinations thereof. In an embodiment the catalyst is based on Cu. The catalyst concentration in the polymerization reaction composition may be in the range 0.001–1 mM.

The concentration of Cu in the polymerization reaction composition may be in the range 0.02–0.32 mM, for example 0.02 mM, 0.04 mM, 0.08 mM, 0.16 mM, or 0.32 mM.

In accordance with the methods disclosed herein, catalyst activator may be added several times during surface polymer formation to control polymer brush formation with progressing time.

At least one ligand may be comprised in the polymerization reaction composition. The ligand may be a nitrogen-containing compound. Non-limiting examples of such nitrogen-containing compounds are bi-, tri-, or tetradentate amine ligands (containing two, three or four amine substituents) which are aliphatic and/or aromatic in nature. In particular, such ligands include *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me₆TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), and 2,2'-bipyridyl (BiPy) and combinations thereof. The amount of ligand in the polymerization reaction composition is defined as a ratio to the concentration of catalyst in the polymerization reaction composition. The ratio of ligand to catalyst in the polymerization reaction composition is in the range 0.001:1 – 1000:1. The ratio of ligand to catalyst in the polymerization reaction composition may be in the range 0.005:1 – 100:1, for example 0.13:1, 0.5:1, 1.0:1, 2.0:1,

3.5:1, 7.5:1 or 12:1. In general, excess amount ligand as compared to amount catalyst may be used.

The monomers for surface polymer formation may be any such desired for the final product.

- 5 Non-limiting examples of appropriate monomer types include anionic, cationic, zwitterionic, protic and aprotic monomers, and include acrylates; methacrylates; halogen-substituted alkenes; acrylamides; methacrylamides; and styrenes, as well as mixtures thereof.

- 10 The generic monomer structure comprises a polymerizable part (an alkenyl group), which in certain embodiments is connected to a functional group responsible for the specific functionality (e.g., adhesion, permeability, electric and ionic conductivities) of the certain monomer through a certain linker chemistry.

- 15 For acrylate monomers, non-limiting examples of functional moieties include but are not limited to: alkyl groups, sulfonates, fluorosulfonates, carboxyls, metal carboxylate, ethers, poly(ether) groups, bis(sulfonyl)amides, fluorinated sulfonates, perfluoroalkyl carboxylate, borate, fluorinated borate, borate ester derivatives, tetraphenylborate, bis(trifluoromethane)-sulfonimide, triflimides and derivatives thereof, halogenated alkyl chains, and mono-, di-, and tri-alkoxy silanes.

- 20 The polymerizable part and the functional part of monomer can, in certain embodiments, be connected by linker moiety. Non-limiting examples of appropriate linker chemistries include but are not limited to: alkyl chains, esters, ethers, poly(ethers), amines, amides, aryls, and any combination(s) thereof.

- 25 Non-limiting examples of appropriate acrylate monomers containing alkyl linkers include but are not limited to: C₁-C₁₆-alkyl, such as methyl acrylate, ethyl acrylate, *tert*-butyl acrylate, and lauryl acrylate.

- 30 Non-limiting examples of monomers using ether and poly(ether) linker chemistry include but are not limited to: poly(ethylene glycol) methyl ether acrylate, and poly(ethylene glycol) acrylate.

- 35 Non-limiting examples of monomers without linker chemistry include but are not limited to: acrylic acid; and lithium acrylate; and sodium acrylate.

For methacrylate monomers, non-limiting examples of appropriate functional moieties include but are not limited to: carboxylic acids, metal carboxylates, esters, alkyl alcohols, oxiranes,

linear and branched alkyl groups, sulfonates, fluorosulfonates, bis(sulfonyl)amides, fluorinated sulfonates, perfluoroalkyl carboxylate, borate, fluorinated borate, borate ester derivatives, tetraphenylborate, bis(trifluoromethane)sulfonimide, triflimides, and derivatives thereof, halogenated alkyl chains, and mono, di, and tri-alkoxy silanes.

5

Non-limiting examples of linker chemistries include but are not limited to: alkyl chains (such as C₁-C₁₆-alkyl), esters, ethers, poly(ethers), amines, amides, aryls, and any combination(s) thereof.

10 Non-limiting examples of methacrylate monomers include but are not limited to: methacrylic acid, lithium methacrylate, sodium methacrylate, methyl methacrylate (MMA), potassium 3-sulfpropyl methacrylate, 2-hydroxyethylmethacrylate (HEMA), glycidyl methacrylate (GMA), ethyl methacrylate, *n*-butyl methacrylate, *tert*-butyl methacrylate, and lauryl methacrylate.

15 Non-limiting examples of appropriate halogen-substituted alkene monomers include but are not limited to: vinyl chloride, vinylidene difluoride, tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene.

Non-limiting examples of appropriate acrylamide monomers include but are not limited to:
20 acrylamide, *N*-iso-propylacrylamide, *N*-*tert*-butylacrylamide, and *N*-hydroxyethyl acrylamide.

Non-limiting examples of appropriate methacrylamide monomers include but are not limited to: *N*-iso-propylmethacrylamide, methacrylamide, *N*-*tert*-butylmethacrylate, and *N*-hydroxyethyl methacrylamide.

25

Non-limiting examples of appropriate styrene monomers include but are not limited to styrene; 4-methylstyrene, 2,3,4,5,6-pentafluorostyrene, *p*-divinylbenzene, 4-chlorostyrene, sodium 4-vinylbenzenesulfonate, lithium 4-vinylbenzenesulfonate, and 4-vinylphenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate.

30

Monomer(s) may be chosen to provide compatibility/adhesion/elasticity, as appropriate for a specific application. Monomer(s) can also be selected to enhance or diminish electrical and/or ionic conductivity, and/or permeability. Monomers may be chosen to improve interface stability of a surface in question.

35

Polymer brush thickness may be from 1–1,000 nm. The thickness of the polymer brush may depend on the specific intended application and may be from 1–500, 1–250 nm, 5–100 nm, 120–250 nm, 10–80 nm, or 10–30 nm. It is typically not possible to accurately measure the

thickness of the dried polymer layer. Instead, the surface polymer thickness can be estimated from DLS measurements of the suspended particles. As the solvent can penetrate into and swell the surface polymer, the results obtained can be dependent on the solvent used. Moreover, the dispersibility/solubility of the particles will be dependent on the solvent, meaning that direct comparisons between particles having differently treated surfaces may not be possible. For the sake of understanding, the particles decorated with a polymer brush may have a $D_{[4,3]}$ value of from about 50 nm to about 1.5 μm , such as from about 150 nm to about 1.2 μm , such as from about 200 nm to about 750 nm.

- 10 The polymer brush layer may be applied or formed by repeating certain of the above steps to build up block co-polymers. The same or different monomers can be applied relative to the monomers used to form previous layers. Forming additional layers of surface polymer can be repeated multiple times to obtain a more complex or thicker surface polymer. Surface polymers can also be formed using two or more different monomers grown from one type or different types of initiators thereby forming random or mixed surface polymers, respectively. Hence, two or more functional groups (e.g., halogen atoms, hydroxyl groups, or amine groups) may be incorporated, resulting in a polymer brush with a unique set of combined properties, each of which is inherent from individual monomers.
- 15
- 20 The polymer brush may be formed from the surface-immobilized initiators upon contact with a polymerization reaction composition comprising ligand, catalyst, monomer, catalyst activator and solvent.

- The concentration of polymerization initiator species (first moieties) has significant impact on polymer chain growth. Higher concentration of such species may lead to close proximity of growing macro radicals. This may result in recombination, preventing further polymer chain growth. Polymer chain loops forming as a result of the recombination may be beneficial for mechanical properties of the particles. Lower concentration of polymer initiator species may allow for unconfined polymer chain growth and enable extended polymer chain formation. Such higher molecular weight polymer chains may increase the degree of entanglement leading to improved cohesion between individual particles.
- 25
- 30

- Certain densities of polymer initiator species between higher and lower regimes, growing polymer chains may extend out perpendicularly to the surface, forming dense polymer layers with decreased permeability of various species through the polymer shell. As such, the density of the first moiety bound to the composite particle can allow control over the formation of polymer brushes, and the overall properties of the polymer brush composite particle.
- 35

The disclosure herein further relates to a polymer brush composite particle.

The polymer brush composite particle may comprise a silicon core decorated with at least a first moiety comprising a first anchoring component covalently bonded to the silicon core, and
5 a polymeric moiety, and a second moiety comprising a second anchoring component covalently bonded to the silicon core, and one or more functional groups.

The linear polymeric chain of the formed polymer brush may have an average length of from about 2 repeat units to about 1000 repeat units, such as from about 5 repeat units to about
10 750 repeat units, for example from about 10 repeat units to about 500 repeat units, such as from about 15 to about 100 repeat units, or from about 20 to about 75 repeat units.

The polymeric moiety is typically connected to the first moiety via a covalent bond to the radical stabilizing moiety, Rad, as: [Si]-A-Z-Rad-[P], wherein [Si] is the silicon particle core,
15 A is the anchoring component, Z is the linker group, Rad is the radical stabilizing moiety, and [P] is the polymer chain.

The remainder of the decorated particle comprises the following moieties covalently bound to the silicon particle core: [Si]-A-Z-FG, and optionally [Si]-A-Z-Rad-LG, wherein [Si] is the
20 silicon particle core, A is the anchoring component, Z is the linker group, Rad is the radical stabilizing moiety, LG is the leaving group, and FG is the functional group, wherein [Si]-A-Z-Rad-LG represents residual amounts of the first moiety that did not undergo polymerization to form a polymer brush.

For completeness, the composite particle prior to formation of the polymer brush may be represented as follows: [Si]-A-Z-FG, and [Si]-A-Z-Rad-LG, wherein [Si] is the silicon particle
25 core, A is the anchoring component, Z is the linker group, Rad is the radical stabilizing moiety, LG is the leaving group, and FG is the functional group.

The polymer brush composite particle is formed from the composite particle by exchanging the leaving groups of the first moiety with propagating polymeric chains through a polymerization reaction. Polymer brush propagation may be accomplished by a method comprising providing a composite particle comprising a silicon core decorated with at least a
30 first moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymerization initiating group, and a second moiety comprising a second anchoring component covalently bonded to the silicon core, and one or more functional groups, forming a polymerization reaction composition comprising one or more polymerization catalysts and
35

one or more monomers, and exposing the composite particle to the polymerization reaction composition.

As set out in the disclosure herein, the exposing of the composite particle to the polymerization reaction composition leads to propagation of a polymer chain via reaction with the polymerization initiating group of the first moiety.

In some embodiments, the polymerization reaction composition may be formed from a polymerization composition comprising at least one dormant transition metal catalyst, an activation agent comprising an oxygen scavenger, and one or more monomers, wherein the one or more monomers may be provided as a part of the polymerization composition, a part of the activation agent, or as a discrete composition.

Thus, in some cases, the method of forming a polymer brush decorated composite particle may comprise providing a composite particle comprising a silicon core decorated with at least a first moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymerization initiating group, and a second moiety comprising a second anchoring component covalently bonded to the silicon core, and one or more functional groups, providing a polymerization composition, an activation agent, and one or more monomers, wherein the polymerization composition comprises one or more dormant transition metal catalysts, and wherein the activation agent comprises one or more oxygen scavengers, and wherein the at least one or more monomers may be part of the polymerization composition, part of the activation agent, or as a discrete composition, and combining the polymerization composition, activation agent and one or more monomers to form a polymerization reaction composition, and exposing the composite particle to the polymerization reaction composition.

Monomers, catalysts, ligands, catalyst activators, and solvents and amounts are described above.

The composite particle having polymerization initiators immobilized thereon and the polymerization reaction composition may be kept in contact with each other for a suitable period of time (residence time). The residence time includes, but is not limited to, from 0.1 seconds to 5 hours. The residence time may i.a. depend on the desired thickness of the formed polymer brush and the rate of formation.

The polymer brush formation may take place at ambient temperature (room temperature), or with cooling or heating. Suitable temperatures are such from -20°C up to 120°C, such as from room temperature (approximately 20°C) to 120°C.

The residence time and temperature during the residence time may suitably be computer-controlled. Other ways of adjusting residence time and temperature may be based on conditions in the compartment holding the polymerization reaction composition (bath
5 conditions) and/or measurements.

Notably, the chemical structure and functionality of the non-initiating species in the base layer impact the surface chemistry of the final material. The chemistry and chemical functionality of the non-initiating species in the base layer and that of the repeating units of the polymer
10 brushes can be similar or different from each other. This entails that orthogonal chemistries such as hydrophobic and hydrophilic moieties can be present on the surface at the same time, with one type residing in the non-initiating part of the base layer, and other(s) in the polymer brush part of the architecture.

15 When considering the polymer brushes grown from the first moieties of the composite particle, several different types can be included, such as block co-polymers, polymers capable of reacting in subsequent steps such as cross-linking, or incorporation of other functional moieties that alter the polymer brush functionality. If the base layer consists of two different initiating species designed for different polymerization reactions, e.g. RAFT and ATRP, two
20 different types of polymers may be anchored to the surface to give a hybrid polymer brush composite particle.

The composite particle may be decorated with one or more first moieties. The introduction of more than one type of initiator opens the possibility of having e.g. first an ATRP-like
25 polymerization from the ATRP-initiators in the base layer, and subsequently growing a different polymer brush structure under RAFT-conditions from the RAFT initiator, enabling formation of a mixed species polymer brush. Furthermore, the base layer may be modified chemically both before and after the polymerization step, to introduced desired chemical structures and properties.

30

In the present disclosure, suitable solvents include alcohols such as methanol, ethanol, and isopropanol. Aprotic solvents such as dimethyl sulfoxide (DMSO), acetone, dimethylform-
amide, tetrahydrofuran, propylene carbonate, methylene carbonate, ethylene carbonate, ethyl lactate alcohol, and ionic liquids may also be used in the present method. In some
35 embodiments, the solvent may be a mixture with water. The solvent may in some cases be a mixture of water and an alcohol.

In the method of the disclosure, polymer brushes are formed on the surface of a Si-particle. The surface has immobilized thereon first moieties with polymerization initiating groups. The first moieties function as initiators for the polymerization reaction.

- 5 After formation of the polymer brushes, the functionalized particles are removed from the polymerization medium.

The brush polymer may be formed from one or more monomers. That is the brush polymer may comprise one or more repeat units. For example, the brush polymer may be a block copolymer comprising two different repeat units. To form a block copolymer, first the
10 composite particle is reacted with one type of monomer, then the composite particle is reacted with another type of monomer. Another example is the formation of random block-co-polymers, where two or more monomers are comprised in the polymerization reaction composition.

15

Composite Aggregates

When seeking to uniformly decorate the surface of the particles with at least one type of first moiety and one type of second moiety, the particles may be fully dispersed in the reaction medium, whether that be the reaction medium used to decorate the silicon particles, or the
20 polymerization reaction composition used to form the polymer brushes on the composite particles.

Silicon particles and/or composite particles may be dispersed by a number of methods, for instance by vigorous stirring in a suitable solvent. Stirring the particles for a sufficient time
25 may lead to full dispersion, for instance at least 10 minutes, such as from 1 hour to 24 hours, typically from 4 hours to 18 hours. Increasing the temperature may reduce the time to achieve full dispersion of the particles. If necessary, dispersion may be facilitated by sonic agitation, for instance using a sonicator or an ultrasonic horn.

30 In some embodiments, the silicon particles and/or composite particles may not fully disperse when they are subjected to the conditions leading to decoration of the Si-core, and/or the formation of polymer brush. In other words, the silicon particles may be in the form of aggregates while being decorated. This may lead to decorated aggregates having an outer surface which is functionalized, and an inner surface which may have different surface
35 properties. In some circumstances, formation of such decorated aggregates may be desirable, as the resultant aggregates may have a useful mixture of surfaces that provide interesting properties. For instance, an aggregate having a functionalized outer surface and at least some of its inner surface comprised of unreacted silicon (for instance silicon hydride or silicon oxide)

may be a useful way to deliver reactive silicon surfaces to a particular environment. The outer surface of the aggregate could be designed such that the aggregate is stable under certain conditions, but more readily breaks apart under other conditions (such as a change in pH or solvent polarity). This may allow reactive silicon surfaces to be selectively delivered at a
5 desired locality by controlling and manipulating the conditions that impact the stability of the aggregate. An example of aggregated silicon nanoparticles is shown in the TEM image of Figure 21.

It is also notable that aggregates may form from reaction of the silicon core after decoration
10 of the surface. For example, oxidation of the silicon core over time may lead to cracking of the core. Likewise, the expansion and subsequent contraction due to alloying/dealloying of lithium when used in an electrochemical cell may lead to cracking of the core. In such circumstances, the surface decoration and particularly the polymer brush layer may continue to contribute towards the stabilization of the core despite crack formation.

15 Thus, in some cases, the Si-core may be an aggregate of particles, the aggregate having an outermost surface and a plurality of internal surfaces, and comprising external composite particles and optionally internal particles, wherein the optional internal particles comprise a silicon core, the external composite particles comprise a silicon core, and an external surface
20 region, which is decorated with at least first and second moiety covalently bonded to the silicon core through first and second anchoring components, wherein the first moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymerization initiating group, and the second moiety comprising a second anchoring component covalently bonded to the silicon core, and one or more functional groups, wherein
25 the external surface region of the external composite particles forms the outermost surface of the aggregate, and wherein none of the surface of the optional internal particles forms part of the outermost surface of the aggregate.

In some cases, the disclosure relates to a brush polymer aggregate of particles, the aggregate
30 having an outermost surface and a plurality of internal surfaces, and comprising external composite particles and optionally internal particles, wherein the optional internal particles comprise a silicon core, the external composite particles comprise a silicon core, and an external surface region which is decorated with first and second moiety covalently bonded to the silicon core through first and second anchoring components, wherein the first moiety
35 comprising a first anchoring component covalently bonded to the silicon core, and a polymeric moiety, and the second moiety comprising a second anchoring component covalently bonded to the silicon core, and one or more functional groups, wherein the external surface region of the external composite particles forms the outermost surface of the aggregate, and wherein

none of the surface of the optional internal particles forms part of the outermost surface of the aggregate.

5 The external composite particles may comprise an internal surface region, i.e. a surface of a particle that does not form part of the outermost surface of the aggregate. Said internal surface region of the external composite particle may be in contact with an internal surface region of an adjacent external composite particle, and/or a surface of an internal particle.

10 The internal surface region of the external composite particle and/or the surface of the internal particles may or may not be functionalized. Whether these surfaces are functionalized will depend on the conditions used to anchor the first and second moieties, as well as the conditions used to form the polymer brush.

15 For instance, if the aggregate is present when the first and second moieties are covalently bonded to the silicon surface, it may be that the internal surface of the aggregate are not exposed to the first and second moieties. In such cases, the internal surfaces of the aggregate (that is internal surface region of the external composite particle and/or the surface of the internal particles) may not be functionalized, i.e. at least 80%, such as at least 90%, such as at least 95% of the surface comprises silicon oxide and/or silicon hydride.

20 Other constructions may be possible. For instance, the particles may be fully dispersed when reacting with the first and second moieties. Thereafter, the particles may be in the form of aggregates when forming the polymers brushes. This is easily achievable by removing the dispersing medium, partially redispersing the composite particles such that at least some are
25 in the form of aggregates of composite particles, and exposing the aggregates of composite particles to a polymerization reaction composition to form a brush polymer on the external surface of the aggregates.

30 By such methods polymer brush aggregate of particles are obtained, wherein the internal surface of the aggregates comprises a first moiety comprising a first anchoring component covalently bonded to the silicon core of the internal particle or external composite particle, and a polymerization initiating group, and a second moiety comprising a second anchoring component covalently bonded to the silicon core of the internal particle or external composite particle, and one or more functional groups.

35 The various options described herein allow a high level of control over the functionalization of the surfaces of silicon particles.

Measurement methods

The nature of surface-grafted polymer brushes may be analyzed through means such as infrared spectroscopy or Raman spectroscopy for verification of functional groups. Dynamic light scattering may be employed for determination of the brush polymer composite particle diameter. Thermogravimetric analysis may be used to determine the total mass of surface-grafted polymeric material and, in conjunction with gel permeation chromatographic analysis of cleaved polymer brush chains, quantify the number of grafted polymer chains per surface area.

Electrochemical cell applications

Development of silicon (Si) active anode material for lithium ion cells (LICs) holds promise for larger capacities than current state of the art, e.g. graphite anodes, but is held back by fundamental issues such as extreme volume expansion during charge/discharge cycles. The extreme volume expansion typically results in loss of contact between the Solid Electrolyte Interphase (SEI) and the Si surface, when the material expands and contracts, resulting in repeated exposure of native Si surface, formation, and loss of the SEI layer. This may in turn result in rapid consumption of electrolyte and charge carriers, ultimately causing premature loss of capacity and battery function. Grafted polymer chains may be introduced to the surface of the silicon active material to alleviate these issues.

Without wishing to be bound by theory, it is believed that covalent attachment of polymeric species to the surface of active anode materials (enables the polymer brushes to remain attached to the surface through each cycle of charge/discharge-induced volume expansion and contraction. To ensure efficient ionic conductivity, the polymer brushes are created in a density regime that allows space for ion penetration. To ensure greater stability of the Si-particle, the particle itself may be heavily decorated. Heavy decoration of the Si-particles is defined as protection of the surface sufficient to stop the surface from reacting with the electrolyte thus hindering formation of an undesirable and destructive SEI-layer. In effect, the functional group on the second moiety bonded to the silicon particle may act as a pre-formed SEI-layer, protecting the underlying silicon from reacting with and consuming excessive amounts of electrolyte during charge/discharge. In particular, this approach enables presence of 'orthogonal' properties on the surface such as very low surface energy in the moieties bound to the Si-core and a polymer brush layer capable of interacting strongly with the matrix binder polymer. By engineering the chemistry of the moieties in combination with the chemistry of the polymer brushes, the Si-polymer brush interface can be designed to e.g. stabilize the Si surface but maintain ionic conductivity.

In some cases, the polymer brushes may be hydrophilic, while the second moieties within the base layer (i.e. the functional groups of the second moiety) are hydrophobic. In some cases, the polymer brushes may be hydrophobic, while the non-initiation moieties within the base layer (i.e. the functional groups of the second moiety) may be hydrophobic. In some cases, the polymer brushes may be hydrophilic, while the non-initiation moieties within the base layer (i.e. the functional groups of the second moiety) may be hydrophilic.

The Si-particles comprising second moieties and first moieties from which the polymer brushes are grafted may be useful as anode active materials.

To produce a negative electrode of a battery, a slurry with all the necessary components may be formed. Typically, this means that the one or more anode active materials, one or more binders, a solvent, and optionally conductive additives may be mixed. By fine-tuning the polymer brushes, for example the length and the polarity, the polymer brushes may improve adhesion to such an extent that the addition of binder is redundant.

In some cases, the anode may be substantially free of binder. For example, the substantially binder-free anode may comprise and/or include less than or equal to about 3 wt% binder, for example less than or equal to about 2 wt% binder, such as less than or equal to about 1 wt% binder, for example less than or equal to about 0.5 wt% binder, such as less than or equal to about 0.3 wt% binder, for example less than or equal to about 0.1 wt% binder, such as less than or equal to about 0.05 wt% binder, based on the total weight of anode active material, conductive additives and binder.

In some cases, the anode may not comprise any binder.

In some cases, the silicon particles decorated with polymer brushes may form a network connected by the polymer brushes, and the polymer brush connections may provide elasticity to the connected network throughout the anode, thus protecting the structural integrity of the anode during battery cycling as well as protecting the structural integrity of the individual silicon particles. The nature of the connection between polymer brushes may include one or more of covalent bonding, ionic bonding, Van der Waals interaction, etc.

In some cases, the silicon particles decorated with polymer brushes may form a network connected by the polymer brushes and polymeric binder, and the polymer brush and polymeric binder connections may provide elasticity to the connected network throughout the anode, thus protecting the structural integrity of the anode during battery cycling as well as protecting the structural integrity of the individual silicon particles. The nature of the

connection between polymer brushes and polymeric binder may include one or more of covalent bonding, ionic bonding, Van der Waals interaction, etc.

Likewise, similar improvements may be made for the following anode materials: graphite particles, carbon-coated silicon particles and Si/C composite particles. In current baseline energy storage devices, the anode composition contains a component that enhances the electrical conduction, e.g., carbon black, and a binder component, e.g., PVDF, that functions to maintain the whole anode structure, to keep particles in close proximity and through the carbon black network, to maintain the electrical conduction paths for the particles. In the baseline composition, the binder, e.g., PVDF, is just a free-standing additive. On the other hand, polymer brush would be covalently bonded to the particle, entangled with the adjacent particles, providing a self-healing property through the cycling induced volume expansion and contraction phenomena, and thereby, providing a more robust, chemically bound overall structure than the baseline, PVDF types of binders. Incorporating organic functional groups for electrical conduction in the PB, e.g., those with overlapping p-bonding (sp and sp²), would further enhance the properties of the anode functions. Given such graphite architectures, a more robust composite anode architectures of varying Si-Graphite compositions can be created. The composite anode architecture can be expressed as:

(Si-O-C-PB)_x (Si-C-PB)_y (graphite-PB)_z + Electrical Conduction enhancer

As expressed above, conventional binders, like, PVDF, may be replaced completely by PBs.

The slurry may comprise the one or more anode active materials, a solvent, optionally a binder and optionally conductive additives. The addition of solvent allows for easy preparation of the electrode. The slurry composition may be formulated to a suitable viscosity to allow it to be processed into a cathode, for example by slot-die coating. The slurry composition may typically have a dynamic viscosity of from about 2 to about 50 Pa·s, for instance from about 5 to about 40 Pa·s or from about 5 to about 25 Pa·s, as measured at 25°C. The slurry composition may typically contain from about 50 to 90 wt% solids, such as from about 60 to 80 wt% solids, or from about 68 to 73 wt% solids, with the remainder being dispersing medium. The method of formation of the slurry composition may not be critical, and once formed it may typically stable at room temperature for at least one day, or at least one week. By "stable" in this context is meant that the solid particles do not settle. While it may be possible to form the slurry composition by combining the ingredients in any order, best results may be obtained when following a method comprising providing a composition comprising composite particles of the disclosure, binder, optionally conductive additives, and optionally

a dispersing medium, adding dispersing medium to the composition, and mixing to provide a slurry composition having a suitable viscosity.

The present disclosure also relates to electrochemical cells comprising the anode of the disclosure, for example a secondary lithium-ion cell. Such cells may comprise a cathode, a separator disposed between the anode and cathode, said cathode, anode and separator forming an electrode assembly, the cell further comprising a housing for the electrode assembly. See Figure 22 for a schematic of a battery. The non-aqueous electrolyte facilitates the transport of lithium ions between the composite cathode and anode. The housing is typically sealed to ensure the electrolyte is retained within the housing. The housing may include terminals in electrical contact with the anode and composite cathode.

These cells may be combined to form a battery system (i.e. an array of cells).

The disclosure also relates to an electrical device comprising a cell of the disclosure. For instance, the disclosure relates to a vehicle comprising a cell (or battery system) of the disclosure. The vehicle may be an electric vehicle, such as a car, truck, bus, scooter, motorbike, bicycle or the like.

Furthermore, the present disclosure relates broadly to electrochemical cells, and more specifically to polymer brushes designed for electrodes within these cells. In particular, it introduces polymer brush structures and arrangements aimed at enhancing uniform lithium deposition and promoting a strong adhesive bond between an electroactive layer and electrically conductive support. In some embodiments, a polymer brush layer described herein includes first and second moieties, which may be co-immobilized.

Functional atoms within polymers, including -N, -O, -S, and -F, have been shown to exhibit the ability to interact with Li, thereby reducing local Li⁺ concentration and promoting uniform rearrangement of Li⁺ distribution. This leads to a decrease in nucleation overpotential and facilitates planar Li deposition. Notably, He *et al.* utilized polydopamine (pDA) to stabilize Li deposition, where the hydroxyl group of the pDA serves as favorable nucleation sites for subsequent Li deposition (Energy Stor. Mater. 2019, 23, 418-426). Additionally, N-containing functional groups such as -NH₂ act as lithiophilic sites. The abundance of functional groups in pDA effectively mitigates uncontrolled dendritic growth during repeated Li plating and stripping cycles. Conversely, Liu *et al.* synthesized an organic supramolecular protective layer (OSPL) via polycondensation of melamine and cyanuric acid on Cu foam (Energy Stor. Mater. 2020, 32, 261-271). The uniformly distributed amino, carbonyl, and triazine groups within OSPL facilitate the rearrangement of concentrated Li⁺ flux. Also, Li *et al.* utilized poly(N-

isopropylacrylamide) brushes anchored to current collector using dopamine for normalized lithium growth for lithium metal anodes (Agew. Chem. 2019, 131, 18414-18419). Furthermore, the presence of abundant polar groups enables the formation of hydrogen bonds, imparting elasticity and accommodating volume expansion during Li plating. In addition, various other polymers have been utilized to enhance current collectors (CCs) and overall cell performance. To address the inherent low conductivity of polymers, diverse strategies are explored, including the incorporation of conductive agents or the utilization of conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) (Electrochem. Commun. 2019, 102, 1-4 and Angew. Chem. Int. Ed. 2011, 50, 6884-6887).

A typical battery comprises essential elements such as an anode, cathode, separator, electrolyte, outer casing, and sealing components. CCs (current collectors) fulfill vital functions within battery systems. Firstly, they support the electroactive layer (anode or cathode) by serving as a substrate for the casting of slurry, a mixture containing an active material, a polymeric binder, and a conductive additive. Secondly, CCs facilitate electron flow between the electrode materials and the external circuit. By manipulating CC properties, various advantages can be achieved. Additionally, strengthening the interface between the active material and CC through a broader contact area creates additional electron pathways, thus reducing internal resistance within the cell.

This disclosure focuses on enhancing the performance, stability, and efficiency of current collectors in lithium-ion batteries (LIBs) and lithium metal batteries (LMBs) by introducing polymer brushes (PB) to improve properties. By incorporating PB into CCs, the goal is to meet the evolving demands of next-generation LIB applications across diverse industries. The present disclosure pertains to scalable techniques for manufacturing polymer brushes on current collectors tailored for electrochemical cells, including alkali-metal-based or anode-free systems. These techniques enable the creation of multifunctional current collectors with various polymer brush configurations. Moreover, this disclosure introduces methods for producing multifunctional current collectors that capitalize on the enhanced lithiophilicity imparted by the polymer brushes, thereby in some embodiments promoting uniform lithium deposition and optimizing performance in alkali-metal-based or anode-free configurations.

Electrically conductive support

In general, copper (Cu) and aluminum (Al) are most commonly employed as electrically conductive supports for the anodic (0–1.5 V vs. Li/Li⁺) and cathodic (3–4.7 V vs. Li/Li⁺) layers, respectively. This preference is based on their electrochemical stability within each respective potential range. Specifically, Al cannot be utilized as anodic electrically conductive support due to its tendency to undergo alloying reactions with Li at 0.26 V (vs. Li/Li⁺). Conversely,

Cu is susceptible to dissolution above 3.5 V (vs. Li/Li⁺), which is within the operational voltage window of cathode active materials. However, various electrically conductive supports are available, including but not limited to other metal foils (e.g., nickel and stainless steel), metalized polymer films (e.g., aluminized polyester film), electrically conductive polymer films, polymer films coated with an electrically conductive material, electrically conductive polymer films coated with a conductive metal, and polymer films containing dispersed conductive particles. Other possible electrically conductive supports encompass expanded metals, metal meshes, metal grids, expanded metal grids, metal wool, woven carbon fabric, woven carbon mesh, non-woven carbon mesh, and carbon felt.

10

In the method of this disclosure, polymer brushes are formed on the surface of an electrically conductive support. The surface has immobilized thereon first moieties with polymerization initiating groups. The first moieties function as initiators for the polymerization reaction.

15 After the formation of the polymer brushes, the resulting electrically conductive support is removed from the polymerization medium.

The brush polymer may be formed from one or more monomers. That is the polymer brush may comprise one or more repeat units. For example, the polymer brush may be a block copolymer comprising two different repeat units. To form a block copolymer, first, the electrically conductive support is reacted with one type of monomer, then the electrically conductive support is reacted with another type of monomer. Random block copolymers may be formed by reacting the electrically conductive support with two or more different monomers at the same time.

25

The present disclosure pertains to scalable techniques for manufacturing polymer brushes on current collectors tailored for electrochemical cells, including alkali-metal-based or anode-free systems. These techniques enable the creation of multifunctional current collectors with various polymer brush configurations. Moreover, this disclosure introduces methods for producing multifunctional current collectors that capitalize on the enhanced lithiophilicity imparted by the polymer brushes, thereby in some embodiments promoting uniform lithium deposition and optimizing performance in alkali-metal-based or anode-free configurations.

35 Example embodiment 1 -immobilization of (p-chloromethyl)phenyltrimethoxysilane (CPTMS) and 4-aminopropyltrimethoxysilane (APTMS)

This example illustrates a procedure for covalently attaching CPTMS (first moiety precursor) and APTMS (second moiety precursor) to an electrically conductive support as illustrated in process 506 of FIG. 32.

The surface modification process will begin with the utilization of clean Cu foil, onto which CPTMS and APTMS polymerization initiators will be applied using a chemical vapor deposition method. Substrates will be arranged on a rack and introduced into a vacuum oven containing
5 8 vials of 100 μ L CPTMS (Gelest) and 8 vials of 100 μ L APTMS (Sigma-Aldrich) at approximately 45°C for 150 minutes. The pressure gauge will be adjusted to reach -1.0 bar, causing the CPTMS and APTMS to evaporate and chemically deposit onto the electrically conductive support. Following this, the electrically conductive support will be removed from the oven and will be subjected to an annealing process at around 100°C for 1 hour.

10

Example embodiment 2: Wet chemical deposition of CPTMS on Cu

An alternative wet chemical approach for surface immobilization of polymerization initiators onto an electrically conductive support is disclosed, comprising the following steps. First, a solution composed of 1% acetic acid and 1% CPTMS will be thoroughly mixed in ethanol.
15 Subsequently, the electrically electrically conductive support will be immersed in the resultant solution for 15 minutes, immobilizing the polymerization initiators on the Cu surface. Next, modified electrically conductive support will undergo a thorough washing with acetone to eliminate excess reagents, which will then be subjected to annealing at 100°C for 3 minutes. Post-annealing, a comprehensive cleaning process utilizing acetone will be conducted to
20 eliminate any residual contaminants. Finally, the samples will be left to air dry. Verification of the surface modification can be conducted through water contact angle measurements using a Krüss Mobile Surface Analyzer. Additionally, Fourier-transform infrared spectroscopy (FT-IR) can be used to validate the existence of CPTMS on the surface.

25 Example embodiment 3: Chemical vapor deposition of APTMS and derivatization with BiBB

A clean Cu foil sample will be positioned within a glass container along with two sample vials containing 100 μ L of APTMS each. The container will be sealed with a lid and placed in an oven set at 30°C for 1 hour. Subsequently, the resulting sample will be annealed at 100°C for 1 hour. The APTMS-grafted Cu foil will then be added to a solution containing
30 dichloromethane, triethylamine, and BiBB. The sample will be agitated on a shaking table at 80 rpm for 1 hour. The resulting sample will be rinsed with acetone and then sonicated sequentially in dichloromethane and acetone for 5 minutes each.

35 Example embodiment 4: Chemical vapor deposition of 3-trimethoxysilylpropyl 2-bromo-2-methyl-propionate (BPTMS)

Similar to Example embodiment 1, a clean Cu foil will be placed in an enclosure alongside a small vial containing 50 μ L of BPTMS and 50 μ L of APTMS. This sealed container, housing both

the Cu foil and BPTMS, will subsequently be placed in an oven set at 45°C for 2.5 hours. Following this, the sample will undergo annealing in an oven at 100°C for 1 hour.

Example embodiment 5: Preparation of reaction composition for polymer brush formation

- 5 This example illustrates the preparation of a reaction composition (process 505 of FIG. 5) for the method as disclosed herein.

As illustrated in Process 502 of FIG. 5, 16 mL of a catalyst solution comprising 76 μ L of tris[2-(dimethylamino)ethyl]amine (Me6TREN, a ligand commercially available at >98% grade from Alfa Aesar), 15.9 mL of water, and 324 mg/L of Cu(II) sourced from solid Cu will be added to a glass container. Afterward, an additional 484 mL of water, 410 mL of ethanol (96% grade from Sigma-Aldrich), and 75 mL of the acrylamide monomer (Sigma-Aldrich) will be added and mixed. In a separate container, Process 503 of FIG. 5 will involve dissolving 4,000 mg of sodium ascorbate (a catalyst activator from Sigma-Aldrich) in 15 mL of water. Immediately after dissolution, this solution will be combined with the first solution. After 5 minutes, the resultant reaction composition solution will be employed for polymer brush formation.

Example embodiment 6: Preparation of poly(acrylamide) brush decorated electrically conductive support

- 20 CPTMS and APTMS co-immobilized Cu foil from Example 1 will be used as the substrate for growing poly(acrylamide) brushes. In a conical flask, 15 mL of acrylonitrile and 50 mL of DMSO will be combined and purged with N₂. Separately, 2 mg of anhydrous CuCl₂ and 3.2 mg of tris(2-pyridyl-methyl)amine (TPMA) will be dissolved in DMF and purged with N₂. Then, 0.75 mL of this solution will be added to the acrylonitrile/DMSO mixture. Additionally, 0.9 mL of tin(II) 2-ethylhexanoate (Sn(EH)₂) dissolved in 50 mL of DMSO will be prepared, and 1 mL of this mixture will be added to the acrylonitrile/DMSO solution, constituting the reaction composition for the poly(acrylamide) brush growth. The BPTMS-anchored Cu foil will be submerged in this reaction composition overnight to facilitate the growth of the poly(acrylamide) brush on the Cu foil. Ellipsometer measurements can be used to measure the thickness and uniformity of the poly(acrylamide) brush layer.

Example embodiment 7: Preparation of poly(acrylamide) brush decorated electrically conductive support

- 35 Various batches of CPTMS precursor will be tested, with subsequent polymerization of acrylamide to form poly(acrylamide) brush. The polymerization initiator anchored electrically conductive support prepared in Example embodiment 2 will be used to grow poly(acrylamide) on the surface of the electrically conductive support. The reaction composition solution from Example 5 will be transferred to a three-neck round bottom flask and degassed with an inert

gas for 10 minutes. Afterward, the initiator decorated electrically conductive support will be left in the solution for 2 hours to grow poly(acrylamide) brush. The resulting sample will be cleaned by sonication in water and acetone for 5 minutes each.

5 Example embodiment 8: Preparation of poly(acrylonitrile) brush decorated electrically conductive support

The BPTMS and APTMS co-immobilized foil from Example embodiment 4 will be used as the substrate for growing poly(acrylonitrile) (PAN) brushes. In a conical flask, 15 mL of acrylonitrile and 50 mL of DMSO will be combined and purged with N₂. Separately, 2 mg of anhydrous CuCl₂ and 3.2 mg of tris(2-pyridyl-methyl)amine (TPMA) will be dissolved in DMF
10 and purged with N₂. Then, 0.75 mL of this solution will be added to the acrylonitrile/DMSO mixture. Additionally, 0.9 mL of tin(II) 2-ethylhexanoate (Sn(EH)₂) dissolved in 50 mL of DMSO will be prepared, and 1 mL of this mixture will be added to the acrylonitrile/DMSO solution, constituting the reaction composition for the PAN brush growth. The BPTMS and
15 APTMS co-immobilized Cu foil will be submerged in this reaction composition overnight to facilitate the growth of the PAN brush on the Cu foil. Ellipsometer measurements can be used to measure the thickness and uniformity of the polymer brush layer.

20 Example embodiment 9: Preparation of fluorinated polymer brush decorated electrically conductive support

A mixture comprising 25 mL of water, 25 mL of isopropanol, 0.6 mL of a mixture comprising 25 mL of water, 25 mL of isopropanol, 0.6 mL of PMDETA, 7.6 mL of 1H,1H,2H,2H-Heptadecafluorodecyl methacrylate (HFDMA), and 0.4 mL of ethylene glycol dimethacrylate (EDGMA) will be prepared in a round bottom flask. After mixing, the reaction mixture is
25 expected to form two phase-separated layers, with the top layer selected for further use. The initiator-anchored electrically conductive support from Example 3 will be employed with the polymerization solution to undergo a reaction for one hour. The water contact angle of the resulting substrate can be used to indicate the successful coating by fluorinated polymer brushes.

30

Example embodiment 10: Assembly and evaluation of coin cells using a Cu electrically conductive support decorated with fluorinated polymer brushes

A composite NMC cathode will be fabricated by compressing NMC₁₁₁ materials, Super P, and polyvinylidene fluoride (PVDF) at a weight ratio of 90:5:5 with N-methyl-2-pyrrolidone (NMP)
35 as the solvent over an Al current collector. The cathode will be thoroughly dried to remove residual solvent before cell assembly. The loading of the active materials on an aluminum current collector will be about 8 mg/cm². Cell assembly will be carried out in an argon-filled glovebox (oxygen and moisture both below 0.1 ppm) with a 16 mm diameter fluorinated

polymer brush decorated copper foil from Example 9, 12 mm diameter cathode disc, and 19 mm diameter Celgard 2400 separator. 1M LiTFSI (Lithium bis(trifluoromethanesulfonyl)imide) in DME/DOL (1,2-dimethoxyethane/1,3-dioxolane) 1:1(v/v) with 2 wt% LiNO₃ will be used as an electrolyte. Approximately 150 μ l of electrolyte will be added to each coin cell. A cell with the bare Cu current collector will be fabricated following the identical procedure as outlined above. All the cells will be tested using a Maccor battery tester. The anode-free cells will undergo formation cycles for 3 cycles at C/10 rate (1C=180 mA/g) and subsequently cycling will be carried out with C/5 charge and C/3 discharge. The potential window is between 3.5 and 4.4 V vs. Li/Li⁺. Specific capacity and capacity retention curves of cells with and without polymer brush decoration will be compared.

Example embodiment 11: Assembly and evaluation of coin cells using a Cu electrically conductive support decorated with poly(acrylonitrile) brushes

The coin cell battery will be assembled using the identical procedure outlined in Example embodiment 8, albeit utilizing PAN brush decorated Cu electrically conductive support. Cell performances, including specific capacity and capacity retention curves, will be generated.

Example embodiment 12: Assembly and evaluation of coin cells using a Cu electrically conductive support decorated with polyacrylamide brushes

The coin cell battery will be assembled using the identical procedure outlined in Example embodiment 6, albeit utilizing polyacrylamide brush decorated Cu electrically conductive support. Cell performances, including specific capacity and capacity retention curves, will be generated.

25 Si/C Composite Particles

Example embodiment 13: Synthesis of a Si/C composite from Si micropowder using mechanical milling technique.

A general method for the synthesis of a Si/C composite from silicon micropowder is described herein, and a process flow diagram for mechano-chemical synthesis of Si/C composite is shown in Figure 26. Micron-sized silicon powder will be mixed with a polymer powder. In dry milling of Si and polymer powders, 8,500 mg of 325 mesh Si powder and 1,000 mg polyvinylidene chloride (PVDC) will be ground with agate mortar and pestle. The powders will be mixed with yttria-stabilized zirconia (YSZ) media in a 12:1 ratio by mass and sealed in an attrition- or ball-milling jar under argon atmosphere. The sealed jar will then be milled at speeds ranging from 500 rpm for 4 hours. The product will be harvested and loaded into an alumina crucible and placed at the center of a quartz tube furnace with a cross-sectional diameter of 4 inches. The system will then be evacuated to a base pressure of <0.05T, and backfilled to atmospheric pressure with argon. The furnace will be heated to 900°C at a ramp

rate of 1°C/min and held at that temperature for 2 hours in argon gas, producing a Si/C composite. The resulting Si/C composite product will then be coated with a graphitic carbon layer via chemical vapor deposition (CVD). Pyrolysis of a hydrocarbon precursor, acetylene, will be carried out at 600°C in an inert diluent/carrier gas. This step will result in the formation of Si/C composite particles with a graphitic carbon layer (Compound 1).

Example embodiment 14: Synthesis of a Si/C composite from metallurgical grade Si (MG-Si). A process flow diagram for MG-Si-based synthesis of Si/C composite is shown in Figure 27. MG-Si chips will be crushed into a powder using an agate mortar and pestle. The MG-Si powder will be mixed with YSZ media in a 12:1 ratio by mass and sealed in an attrition- or ball-milling jar under an argon atmosphere. The sealed jar will then be milled at 1,000 rpm for 6 hours. The milled MG-Si powder can be etched to remove metallic impurities using a ferric etchant. 50 mM $\text{Fe}(\text{NO}_3)_3$ will be mixed with 3M HF in ethanol under constant magnetic stirring. After 2 hours, the precipitate product will be collected via centrifugation and washed with DI- H_2O until neutralized. The etched product will then be coated with polyvinylidene chloride (PVDC) via emulsion polymerization in methyl-ethyl ketone and DI- H_2O using sodium dodecylbenzenesulfonate as a surfactant. The emulsion will be obtained through probe sonication and magnetic stirring for 6 hours. Afterward, the product will be collected through centrifugation and dried. Once dried, the product will be harvested and loaded into an alumina crucible and placed at the center of a quartz tube furnace with a cross-sectional diameter of 4 inches. The system will then be evacuated to a base pressure of $<0.05\text{T}$, and backfilled to atmospheric pressure with argon gas. The furnace will then be heated to 900°C at a ramp rate of 1°C/min and held at that temperature for 2 hours in an argon atmosphere. The resulting Si/C composite material will then be coated with a graphitic carbon layer via CVD as described in Example embodiment 13, to produce Si/C composite particles with a graphitic carbon layer (Compound 2).

Example embodiment 15: Synthesis of a Si/C composite from silica using a magnesiothermic reduction method. A general method for the synthesis of a Si/C composite from silica microparticles is described herein, and a process flow diagram is shown in Figure 28. 3,000 mg of silica microparticle powder and 6,000 mg of magnesium powder will be ground together in an agate mortar and pestle in an inert environment. While still in an inert environment, the ground mixture will be loaded into an alumina crucible and placed at the center of a quartz tube furnace with a cross-sectional diameter of 4 inches. The system will then be evacuated to a base pressure of $<0.05\text{T}$, and backfilled to atmospheric pressure with argon. The furnace will then be heated to 600°C at atmospheric pressure, under constant flow, at a ramp rate of 5°C/min. Once the temperature setpoint is reached, the furnace will be held at the setpoint of 600°C for 30

minutes to allow the system to equilibrate. The reaction will be held at this temperature, pressure, and flow rate setpoint for 4 hours. Once the reaction is done, the furnace will be cooled in an inert gas environment, under constant flow, before the product material is harvested. The harvested material will then be treated with 1M HCl in ethanol under constant stirring for 12 hours. Afterward, the product will be collected through centrifugation and drying. The resulting porous silicon material will then be coated with a graphitic carbon layer via CVD as described in Example 13, to produce Si/C composite particles with a graphitic carbon layer (Compound 3).

10 Example embodiment 16: Synthesis of a Si/C composite from silicon nanoparticles.

A general method for the synthesis of a Si/C composite from silicon nanoparticles is described herein, and the process flow diagram is shown in Figure 29. 1,0000 mg of silicon nanoparticles will be loaded into a graphite crucible and placed at the center of a quartz tube furnace with a cross-sectional diameter of 4 inches. The system will then be evacuated to a base pressure of <0.05T, and backfilled to atmospheric pressure with an inert gas such as N₂ or Ar. The furnace will then be heated to 600°C at atmospheric pressure in an inert gas environment, under constant flow, at a ramp rate of 5°C/min. Once the temperature setpoint is reached, the furnace will be held at the setpoint of 600°C for 30 minutes to allow the system to equilibrate. Then, the hydrocarbon precursor will be introduced at atmospheric pressure at a flow of 10% of the total flow rate including the inert diluent. The reaction will be held at this temperature, pressure, and flow rate setpoint for 8 hours. Once the reaction is done, the furnace can be cooled in an inert gas environment, under constant flow, before the product material is harvested as Compound 4.

25 Example embodiment 17: Immobilization of 4-(chloromethyl)benzenediazonium tetrafluoroborate on Compound 1

A Si/C composite material will be decorated using 4-(chloromethyl)benzenediazonium tetrafluoroborate (CBD) as the first moiety precursor.

First, CBD will be synthesized by the addition of 5 g 4-aminobenzyl alcohol with 50 mL of 37% HCl and will be reacted for 24 hours in the dark. Afterward 35 mL of 48% tetrafluoroboric acid will be added to the reaction mixture at 0°C and stirred for 15 minutes. A 15 mL of 20 wt.% sodium nitrite solution will slowly be added to the reaction mixture and left to react for 20 minutes. The reaction mixture will then be placed in a freezer overnight and will then be washed with cold DI water, methanol, and diethyl ether and will be dried under vacuum for 1h followed by storage in a freezer until use. CBD can be used in a chemically reductive environment for attachment to graphitic surfaces.

The reaction to immobilize CBD as the ATRP initiator on the surface of the graphitic carbon coating of the Si/C composite material will be carried out using Compound 1. 17.2 g of

Compound 1 will be dispersed in DI water by sonication and stirred, which will be followed by the addition of 2.5 g of CBD. Sodium ascorbate will slowly be added for 3 hours and the reaction mixture will be stirred for an additional 5 hours. The final product (Compound 5) will then be washed with DI water by centrifugation or filtration.

5

Example embodiment 18: Co-immobilization of 4-(chloromethyl)benzenediazonium tetrafluoroborate and 4-carboxybenzenediazonium tetrafluoroborate on Compound 1

A Si/C composite material will be decorated using 4-(chloromethyl)benzenediazonium tetrafluoroborate (CBD) and 4-carboxybenzenediazonium tetrafluoroborate as first and second moiety precursors.

First, CBD will be prepared as described in Example 17. For the second moiety precursor, 0.5 g of 4-aminobenzoic acid will be used instead and the identical procedure for the CBD synthesis will be followed. The reaction to immobilize both the first and second moieties on the surface of the graphitic carbon coating of the Si/C composite material will be carried out using Compound 2. 7.5 g of Compound 1 will be dispersed in DI water by sonication and stirred, which will be followed by the addition of 1.0 g of CBD and 0.1 g of 4-carboxybenzenediazonium tetrafluoroborate. Sodium ascorbate will be slowly added over 3 hours and the reaction mixture will be stirred for an additional 5 hours. The final product (Compound 6) will then be washed with DI water by centrifugation or filtration.

20

Example embodiment 19: Immobilization of 4-(chloromethyl)benzenediazonium tetrafluoroborate on Compound 2

CBD will be immobilized on the surface of the graphitic carbon coating of Compound 2 using the identical procedure outlined in Example 17. The final product (Compound 7) will be collected and used for the following polymerization step.

25

Example embodiment 20: Immobilization of 4-(chloromethyl)benzenediazonium tetrafluoroborate on Compound 3

CBD will be immobilized on the surface of the graphitic carbon coating of Compound 3 using the identical procedure outlined in Example 17. The final product (Compound 8) will be collected and used for the following polymerization step.

30

Example embodiment 21: Immobilization of 4-(chloromethyl)benzenediazonium tetrafluoroborate on Compound 4

CBD will be immobilized on the surface of the graphitic carbon coating of Compound 4 using the identical procedure outlined in Example embodiment 17. The final product (Compound 9) will be collected and used for the following polymerization step.

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Example embodiment 22: Polyacrylic acid polymer brush formation on Compound 5

Polymer brushes will be grown from the attached initiator site by dispersing the Si/C composite material decorated with CBD (Compound 5) in a mixture of DI water and isopropanol. The dispersion will first be stirred for 10 minutes and then sonicated for 10 minutes. A *tert*-butyl acrylate monomer solution will be prepared in the presence of an ATRP catalyst and then added to the dispersion containing the Si/C composite material. Sodium ascorbate dissolved in water will then be added to the reaction mixture containing the dispersed Si/C composite material to initiate the polymerization, which reaction will be run for 2 hours. The Si/C composite material containing attached poly(*tert*-butyl acrylate) brushes will be purified by washing with dichloromethane and centrifugation. The polymer brush attachment on the surface of the Si/C composite material can be confirmed by XPS. (The composite material is irradiated with X-rays, causing the emission of electrons whose energy is analyzed to determine the elemental composition and chemical bonding.) XPS should clearly show the ester bonds of the acrylate present as well as the graphitic coating. To produce polyacrylic acid brushes, the Si/C composite material containing PtBA polymer brushes will be dispersed in dichloromethane and 0.5 wt.% vs the weight of Si/C composite material of methanesulfonic acid will be added and left to react for 2 hours. The material will be washed with dichloromethane twice by centrifugation to produce polyacrylic acid polymer brushes on the surface of the Si/C composite material (Compound 10), which can be confirmed by FT-IR.

Example embodiment 23: Polyacrylic acid polymer brush formation on Compound 6

Polyacrylic acid polymer brush will be grafted on Compound 6 using the identical procedure outlined in Example 22. The final product will be collected as Compound 11 as depicted in Figure 25.

Example 24: Polyacrylic acid polymer brush formation on Compound 7

Polyacrylic acid polymer brush will be grafted on Compound 7 using the identical procedure outlined in Example embodiment 22. The final product will be collected as Compound 11 as depicted in Figure 25.

Example embodiment 25: Polyacrylic acid polymer brush formation on Compound 8

Polyacrylic acid polymer brush will be grafted on Compound 8 using the identical procedure outlined in Example embodiment 21. The final product will be collected as Compound 13.

Example embodiment 26: PPFS polymer brush formation on Compound 5

Seems An example of Si/C composite material containing poly(pentafluorostyrene) (PPFS) polymer brushes is described herein. Using the same technique described in Example

embodiment 17 for the synthesis of polyacrylic acid polymer brushes, a Si/C composite material containing ATRP initiators on the surface will be dispersed in DI water and isopropanol. A pentafluorostyrene monomer solution will be prepared in the presence of an ATRP catalyst and then added to the dispersion containing the Si/C composite material.

- 5 Sodium ascorbate dissolved in water will then be added to the reaction mixture containing the dispersed Si/C composite material to initiate the polymerization, which reaction will be run for 2 hours. The material will be washed with dichloromethane twice by centrifugation to produce PPFS polymer brushes on the surface of the Si/C composite material (Compound 14), which can be confirmed by FT-IR.

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Example embodiment 27: Battery electrode preparation using polymer brush decorated Si/C composite materials (Compound 10) and coin cell assembly

A slurry will be prepared utilizing Si/C composite materials bonded with polymer brushes, as detailed in Example embodiment 22, to make anode electrode sheets. Polymer brush-coated

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Si/C composite material (Compound 5, 0.5 grams), conductive carbon (Kappa 10, 15 mg), 1% CNT dispersion in water (Tuball, 0.5 g), 5% polyacrylic acid solution in H₂O (0.5 g), and additional H₂O (2.1 g). This slurry will undergo thorough mixing using a planetary mixer. Subsequent Hegman gauge characterization can be used to confirm no agglomerated particle size >20 µm. The resultant slurry will be used to coat electrode sheets with a doctor blade

20 set with a 150 µm gap. The coated foil will then be dried in a vacuum oven set to 50°C for at least 12 hours. Coin cells will be assembled within a glovebox for the assessment of the resulting electrode's performance. Lithium metal will be used as a counter electrode, and a 1 M lithium hexafluorophosphate solution in EC/EMC with 5% FEC will be used as an electrolyte. Specific capacity and capacity retention curves can be compared to electrodes prepared

25 without polymer brush decoration.

Example embodiment 28: Battery electrode preparation using Si/C composite materials (Compound 14) and coin cell assembly

- 30 The coin cell battery will be assembled using the identical procedure outlined in Example embodiment 26, albeit utilizing Si/C composite material with poly(pentafluorostyrene) brush decoration (Compound 14). Cell performances, including specific capacity and capacity retention curves, will be measured.

Example embodiment 29: Battery electrode preparation using Si/C composite materials (Compound 13) and coin cell assembly

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The coin cell battery will be assembled using the identical procedure outlined in Example embodiment 27, albeit utilizing Si/C composite material with polyacrylic acid brush decoration

(Compound 13). Cell performances, including specific capacity and capacity retention curves, will be measured.

Example embodiment 30: Battery electrode preparation using Si/C composite materials (Compound 1) and coin cell assembly

The coin cell battery will be assembled using the identical procedure outlined in Example embodiment 27, albeit utilizing Si/C composite material lacking polymer brush decoration (Compound 1). Cell performances, including specific capacity and capacity retention curves, will be measured. The inventors expect superior performance from the cells with polymer brush decorated Si/C composite materials.

The disclosure herein is further illustrated by the below non-limiting Examples.

Examples

The present disclosure is further illustrated by the following non-limiting examples. The following reagents and abbreviations are used in the examples:

Methanol (MeOH, 99.85%, HPLC-grade, Chemsolute), ethanol (EtOH, 96%), toluene (99.8 %, HPLC grade, Chemsolute), dichloromethane (DCM, 99.9%, HPLC grade, Chemsolute), hydrofluoric acid (HF, 48% in water, Sigma-Aldrich), silicon nanomaterial (SkySpring Nanomaterials, $D_{50} = 100$ nm), silicon nanomaterial (MTI, $D_{50} = 100$ nm) *tert*-butyl acrylate (tBA, 98%, Sigma-Aldrich), 4-vinylbenzyl chloride (4-VBC, 90%, Sigma-Aldrich), pentafluorostyrene (PFS, >98%, Tokyo Chemical Industry), allylamine (98%, Aldrich), acrylonitrile ($\geq 99\%$, Aldrich), acetone (>99%), 4-decylbenzenediazonium tetrafluoroborate (synthesized in-house), *tert*-butyl methacrylate (tBMA, >98%, Tokyo Chemical Industry), isopropanol (iPrOH, 99.8%, HPLC grade, Chemsolute), sodium L-ascorbate (NaAsc, $\geq 98\%$, Sigma-Aldrich), DI water (Silhorko with M22-F softening plant, RO B1-2 Reverse Osmosis plant and Silex 2BS mixed bed plant, produced to ensure a conductivity of <0.5 μ S, indicating a low presence of ions i.e. around <0.1 mg/l), methanesulfonic acid ($\geq 99\%$, Sigma-Aldrich), potassium bromide (KBr, spectroscopy grade, Roth), aluminum oxide (Al_2O_3 , Supelco), Graphite (SLC1520T, Superior Graphite), lithium hydroxide (LiOH), sulfuric acid (1%).

"Sonicator" refers to a Bandelin Sonorex Super RK100 sonicator (35 kHz ultrasound frequency, 80 W nominal ultrasonic power).

"Centrifuge" refers to a Centrifuge 5810 (Eppendorf).

XPS measurements were taken using a Kratos Axis Ultra-DLD spectrometer using a monochromatic Al K-alpha X-ray source. Survey spectra were obtained by averaging two measurements from 0 to 1400 eV at a pass energy of 160 eV. Data processing was carried out using CasaXPS v2.3.15 software.

ATR IR spectra were recorded on a Spectrum Two FT-IR Spectrometer (PerkinElmer).

"Shakerboard" refers to an orbital shakerboard PSU-10i (Grant Instruments Ltd).

Water contact angles (WCA) were measured on a Krüss Mobile Surface Analyzer. In 5 separate points, the contact angle of a DI-water and a CH₂I₂ drop is measured. Using the software ADVANCED v. 1.14, the surface free energy (SFE) can be calculated. The SFE indicates the maximum surface tension of a liquid that wets a solid surface, under ideal conditions. Accordingly, a material with a high SFE is easier to wet than a material with a lower SFE, and low SFE materials will generally exhibit higher water contact angles than those materials with a higher SFE.

Example 1: Co-immobilisation of 4-vinylbenzyl chloride and tert-butyl acrylate

A Si-particle was decorated using 4-vinylbenzyl chloride (4-VBC) and *tert*-butyl acrylate (tBA) as first and second moiety precursors.

- 15 First, the Si-particle was treated with HF to form a H-terminated Si-surface: In a polypropylene conical flask equipped with a magnetic stirbar, 20 g silicon nanomaterial (SkySpring Nanomaterials, D50 = 100 nm) was suspended in 920 mL methanol by stirring it for 10 minutes and sonicating in a bath sonicator for 10 minutes. The suspension was returned to a stirplate and 80 mL hydrofluoric acid was added to the flask. The contents of the flask
20 were then stirred for 10 min (500 RPM), sonicated in a bath sonicator for 10 minutes, and stirred for 10 minutes (500 RPM). The suspension containing the Si nanomaterial was divided evenly between two centrifuge bottles and recovered by centrifugation (5 min at 3900 RPM, Eppendorf 5810 centrifuge). The supernatant was discarded, and the obtained Si nanomaterial recovered. The recovered nanomaterial was suspended in 0.5 % HF in methanol (10
25 mL 48% HF (aq) in 990 mL MeOH) by sonication in a bath sonicator (5 minutes), shaking on an orbital shaker table (MaxQ 2000, Thermo Scientific) (5 minutes) and sonication in a bath sonicator (10 minutes). The suspended nanomaterial was then recovered by centrifugation (5 min at 3900 RPM), by discarding the supernatant. Finally, the nanomaterial was suspended in Ar purged toluene (900 mL) by sonication in a bath sonicator (5 minutes), shaking on an
30 orbital shaker table (5 minutes), and sonication in a bath sonicator (10 minutes).

To immobilise 4-VBC and tBA, the HF-treated Si nanomaterial suspended in toluene was parted evenly between 4 glass bottles with screw cap lids (250 mL, Labsolute) which were equipped with magnetic stirbars and placed on magnetic stirplates and stirred at 300 RPM.

- 35 tBA and 4-VBC was passed through Al₂O₃ columns. The Bluecap bottles were closed with septa while keeping an argon-flow in the bottles.

Different amounts of tBA and 4-VBC were added to the reactions 1 to 4 as shown in *Table 1*, along with 4-decylbenzyl diazonium tetrafluoroborate (416 mg in each reaction).

5 *Table 1*: Overview of experiment structure and reaction mixture composition with respect to concentration and relative ratio of the two reactive species which are being co-grafted.

Reaction number	Concentration of reactive tBA (mM)	tBA (mL)	Concentration of 4-VBC (mM)	4-VBC	Relative ratio of tBA to 4-VBC
1	1000	36.6	0	0	0:100
2	900	33.0	100	3.5	10:90
3	500	18.3	500	17.6	50:50
4	100	3.7	900	31.7	90:10
5	0	0	1000	142.5	100:0

After 2 hours the suspended particles were transferred to centrifuge bottles and recovered by centrifuging (5 min at 3900 RPM). The supernatants were discarded, and the nanomaterials were resuspended by adding 25 mL DCM to each centrifuge bottle and the bottles were
10 sonicated for 10 min in a bath sonicator and shaken on an orbital shakerboard until the Si nanomaterial was well resuspended. Then, 250 mL methanol was added to each of the centrifuge bottles, which were then centrifuged (5 min at 3900 RPM). The supernatant was discarded and the DCM suspension, MeOH addition, and centrifugation steps repeated once again. The Si nanomaterial was then dried to obtain the final product.

15 The reaction to immobilise just 4-vinylbenzyl chloride (Reaction number 5 in *Table 1*) was carried out using 20 g HF-treated Si nanomaterial suspended in 1000 mL toluene. 142.5 mL vinylbenzyl chloride was passed through an Al₂O₃ column and added. While keeping the reaction under a flow of argon, 4-decylbenzyl diazonium tetrafluoroborate (1667.1 mg) was
20 added. After 2 hours the suspended nanomaterial was transferred to two centrifuge bottles and recovered by centrifuging (5 min at 3900 RPM). The supernatants were discarded, and the nanomaterials were resuspended by adding 50 mL DCM to each centrifuge bottle and the bottles were sonicated for 10 min in a bath sonicator and shaken on an orbital shakerboard until the Si nanomaterial was well resuspended. Then, 500 mL methanol was added to each
25 of the two centrifuge bottles, which were then centrifuged (5 minutes at 3900 RPM). The supernatant was discarded and the DCM suspension, MeOH addition, and centrifugation steps repeated once again. The Si nanomaterial was then dried to obtain the final product.

To determine the ratio of 4-VBC and tBA immobilised on the surface, Fourier-transform infrared spectroscopy-spectroscopy (FTIR-spectroscopy) was used. A Spectrum Two (PerkinElmer) instrument was used.

- 5 The FTIR-peaks obtained upon immobilisation of 4-VBC and tBA on a Si-particle comprises the peaks specified in Table 2, below:

Table 2: FTIR peak assignments for spectra obtained co-grafting tBA and 4-VBC.

Wavenumber (cm ⁻¹)	Functional group Assignment	Grafted molecule
2981	CH ₃ stretching vibration	tBA
1514	C=C aromatic ring vibration	4-VBC
1481	CH ₃ asymmetric deformation vibration	tBA
1369	C(CH ₃) ₃ CH ₃ symmetric bending vibration	tBA
1266	Ar-CH ₂ -Cl wag motion	4-BvBC

- 10 By integrating the peaks listed in Table 2 above, and which may be seen in Figure 2, and normalizing each obtained peak area to the peak area obtained for a particle which is decorated with the pure compound (that is decorated with only tBA or only 4-VBC), the relative density of each molecule is obtained. Since several peaks are integrated for both tBA (three different peaks) and 4-VBC (two different peaks), several series of *relative densities*
- 15 are obtained. To give the most representative view of the data, the average of these series is taken, and used to indicate the relative amount of each molecule immobilised.

For this set of co-immobilisation reagents, several more experiments were carried out, with concentrations and relative reagent amounts and ratios for all experiments given in Table 3.

Table 3: Experiment overview for co-grafting of tert-butyl acrylate and 4-vinylbenzyl chloride spectra shown in Figure 2.

Concentration of reactive tBA (mM)	Concentration of 4-VBC (mM)	Relative ratio of tBA to 4-VBC
1000	0	100:0
900	100	90:10
750	250	75:25
650	350	65:35
500	500	50:50
400	600	40:60
250	750	25:75
100	900	10:90
0	1000	0:100

- 5
- The FTIR data obtained based on the experiments listed in Table 3 was analyzed as described above, and the averaged *relative surface stoichiometry* of 4-vinylbenzyl chloride was determined as $\frac{n_2}{n_1+n_2}$, wherein n_1 is the *relative grafting density* of tBA, and n_2 is the relative grafting density of 4-VBC.
- 10
- The *relative densities* were then used to calculate the averaged *relative surface stoichiometry* for each moiety precursor.

The *relative surface stoichiometry* of 4-VBC was fitted with an expression based on work by Faucheux *et al.* (see “*Langmuir* 2006, 22, 1, 153–162”) describing the grafting of two species with different rate constants to a surface with reactive sites which are consumed upon grafting of molecules. See the equation below:

15

$$\frac{n_2}{n_1 + n_2} = \frac{\frac{k_2}{k_1} \cdot c_2}{1 + \left[\left(\frac{k_2}{k_1}\right) - 1\right] \cdot c_2}$$

Wherein n_1 and n_2 denominates the *relative grafting density* of species 1 and 2, and thus $\frac{n_2}{n_1+n_2}$ is the relative surface stoichiometry of species 2, k_1 and k_2 are the rate constants for reaction of species 1 and 2 to the surface, c_2 is the fraction of reactive species 2 in the reaction mixture (i.e. the ratios given in Table 2 rightmost column).

20

Figure 3 shows the experimental data as well as the fit to the analytical expression, while the data from the fit are collected in *Table 4*.

Table 4: Values for fitted parameters (k_1, k_2), the relative reaction rate, the R-squared value for the fit, as well as the p-value for the fitted model.

k_1 (tBA)	k_2 (4-VBC)	k_2/k_1	R^2	p-value
2.17	2.72	1.25	0.99	1.76e-09

As is evident from *Table 4*, 4-VBC reacts slightly faster than tert-butyl acrylate, given its higher relative rate constant.

- 10
- Example 2: Polymer brush formation on composite particle

Polymer brushes based on tBA were grafted from the Si-particles decorated using a reaction composition containing a 10:90 ratio of 4-VBC/tBA (The product of Reaction number 4, as seen in *Table 1*).
- 15
- 3.08 g Si-particles decorated using a reaction composition containing a 10:90 ratio of 4-VBC/tBA (Reaction number 4, as seen in *Table 1*) and 129 mL isopropanol (iPrOH) was added to a glass bottle containing a magnetic stirbar. The contents were stirred for 10 min and sonicated in a bath sonicator for 10 minutes. Then tert-butyl methacrylate (18 mL), inactivated polymerization catalyst (7.49 mL), and DI water (85.9 mL) was added to the flask,
- 20
- and the contents were purged with argon for 8 minutes. In a separate glass flask sealed with a septum, ascorbic acid (108.5 mg) and sodium ascorbate (842.4 mg) was mixed under an argon blanket. Then, via a syringe, argon purged deionised water (DI water) (3.6 mL) was transferred to the flask containing ascorbic acid and sodium ascorbate, and the flask was shaken until the solids were dissolved. The solution of ascorbic acid and sodium ascorbate
- 25
- was then transferred to the flask containing the particle suspension to activate the polymerization reaction. Over 60 min, the flask with the polymerization reaction was then sequentially sonicated for 10 minutes and stirred for 10 minutes, for a total of 30 minutes of sonication and a total of 30 minutes of stirring.
- 30
- The polymer brush particles were then recovered by centrifugation (5 minutes at 3900 RPM), the supernatant decanted and discarded while the obtained polymer brush modified nanomaterial was resuspended in dichloromethane (40 mL) placing it on an orbital shaker board for 10 min and sonicating in a bath sonicator for 5 min. MeOH (400 mL) was then added to the suspended particles, which were then recovered by centrifugation (5 minutes at 3900
- 35
- RPM). This step was repeated twice in total. The obtained polymer brush modified nanomaterial was then dried in an ambient atmosphere at room temperature for 16 hours,

after which it was placed in a regular oven at 60°C for 90 minutes, after which the product was obtained (3.68 g).

5 Upon formation of polymer brushes based on tBMA, the tert-butyl group may be removed to reveal polymer brushes based on methacrylic acid.

2.97 g of formed product was suspended in dichloromethane (149 mL) by stirring for 10 minutes and sonicating in a bath sonicator for 10 minutes. Methanesulfonic acid (0.39 mL) was added and the suspension stirred for 2 hours. The Si nanomaterial was recovered by
10 centrifugation (5 minutes at 3900 RPM), resuspended in DCM (160 mL) by 10 minutes sonication, and recovered by centrifugation (5 minutes at 3900 RPM). This step was repeated twice, to obtain the final product.

Then, the particles without polymer brushes, the particles with tBMA polymer brushes, and
15 the particles with methacrylic acid (MAA) polymer brushes were subjected to thermogravimetric analysis (TGA).

As shown in Figure 4, the thermogravimetric analysis (TGA) indicates formation of poly(tert-butyl methacrylate) PBs with the organic fraction comprising 31 wt.%, and the removal of the
20 tert-butyl methacrylate group resulting in a reduced organic mass fraction of 21 wt.% due to the loss of mass from the removed tert-butyl group. Note that the organic fraction for the composite particle without polymer brushes is close to 0 wt.%, indicating a monolayer-like structure before the formation of PBs.

25 Furthermore, ATR FTIR measurements were made of the particles with polymer brushes based on tBMA and MAA. The FTIR transmission spectra may be seen in Figure 5, wherein the top line corresponds to the spectrum from the particles with polymer brushes based on methacrylic acid, while the lower line corresponds to the spectrum from the particles with polymer brushes based on tBMA.

30

The peak assignments are shown in *Table 5*, below.

Table 5: ATR FTIR Peak assignments for PtBMA and PMAA PBs grown from a particle decorated with a solution of tBA/4-VBC in a 90:10 ratio.

Wavenumber (cm ⁻¹)	Functional group Assignment	Grafted molecule
1365	<i>Tert</i> -butyl C(CH ₃) ₃ symmetric bending vibration	PtBMA
1717	C=O stretching vibration	PtBMA
1694	C=O stretching vibration	PMAA
1248	C-O stretching	Both PtBMA and PMAA
3500 (broad)	O-H stretching vibrations	PMAA and/or H ₂ O residuals

- 5 The ATR FTIR measurements further support the formation of PBs from Si-particles which are decorated using a solution comprising tBA and 4-VBC.

Example 3: Co-immobilisation of 4-vinylbenzyl chloride and pentafluorostyrene

- 10 A composite particle was decorated using 4-vinylbenzyl chloride (4-VBC) and pentafluorostyrene (PFS) as first and second moiety precursors.

First, the Si-particle was treated with HF to form a H-terminated Si-surface:

- 15 Four screwcap polypropylene tubes equipped with magnetic stirbars, were charged with 0.5 g silicon nanomaterial (SkySpring Nanomaterials, D50 = 100 nm) each. Methanol (23 mL) was added to each tube, and the contents stirred for 10 minutes and sonicated in a bath sonicator for 10 minutes. The suspensions were returned to a stirplate and hydrofluoric acid (2 mL) was added to each screwcap tube. The contents of the screwcap tubes were then stirred for 10 min (500 RPM), sonicated in a bath sonicator for 10 minutes, and stirred for 10 minutes (500 RPM). The HF-treated Si nanomaterial was recovered by centrifugation (5 min at 3900 RPM, Eppendorf 5810 centrifuge). The supernatants were discarded, and the obtained Si nanomaterial recovered. In four separate screwcap vials, the recovered nanomaterials were suspended in 25 mL 0.5 % HF in methanol (1 mL 48% HF (aq) in 99 mL MeOH) by sonication in a bath sonicator (5 minutes), shaking on an orbital shaker table (MaxQ 2000, Thermo Scientific) (5 minutes) and sonication in a bath sonicator (10 minutes). The suspended nanomaterials were then recovered by centrifugation (5 min at 3900 RPM), by discarding the supernatant. Finally, the nanomaterials were suspended in argon-purged toluene (25 mL in each of the four separate tubes) by sonication in a bath sonicator (5 minutes), shaking on an orbital shaker table (5 minutes), and sonication in a bath sonicator (10 minutes), resulting in 30 four screwcap tubes each containing HF-treated Si nanomaterial suspended in toluene (25 mL).

5 The four screwcap vials each containing HF-treated Si nanomaterials suspended in argon-purged toluene (25 mL) were equipped with magnetic stirbars and placed on magnetic stirplates and stirred at 300 RPM. PFS and 4-VBC were passed through Al₂O₃ columns. The vials were closed with septa while keeping an Ar-flow in the vials. 4-VBC and PFS was added to the four screwcap vials according to Table 6 (Reaction number 1-4), along with 4-decylbenzyl diazonium tetrafluoroborate (41.6 mg in each reaction).

Table 6: Reagent concentrations for PFS and 4-VBC co-grafting experiments.

Reaction number	Concentration of PFS (mM)	PFS (mL)	Concentration of 4-VBC (mM)	4- VBC (mL)	Relative ratio of PFS to 4-VBC
1	1000	3.45	0	0	100:0
2	500	1.73	500	1.76	50:50
3	300	1.04	700	2.47	30:70
4	100	0.35	900	3.17	10:90
5	0	0	1000	142.5	0:100

10 After 2 hours the suspended nanomaterial was recovered by centrifuging (5 minutes at 3900 RPM). The supernatants were discarded and the nanomaterials were resuspended by adding 2.5 mL DCM to each screwcap vial and sonicating for 10 minutes in a bath sonicator and shaking on an orbital shakerboard until the Si nanomaterial was well resuspended. Then, 25
15 mL MeOH was added to each of the four screwcap vials, which were then centrifuged (5 min at 3900 RPM). The supernatant was discarded and the DCM suspension, MeOH addition, and centrifugation steps repeated once again. The Si nanomaterial was then dried to obtain the final products.

20 Using the same procedure, a particle decorated only with 4-VBC was made (reaction number 5, in Table 6).

The co-immobilisation of pentafluorostyrene (PFS) and 4-VBC under the conditions indicated in Table 6 resulted in the spectral data shown in Figure 6A. From the top-curve to the curve
25 furthest down is seen the product of Reaction Number 1, 2, 3, 4 and lastly the reaction wherein the particle has been decorated only with 4-VBC.

The analysis of peak areas here is carried out on the peaks found in the aromatic region from 1475 to 1550 cm⁻¹.

30

As shown in Figure 6B, which is a zoom in of Figure 6A, pure 4-VBC has a single peak in this region at 1513 cm⁻¹, whereas PFS presents with 2 peaks at 1504 and 1523 cm⁻¹.

These peaks are specified in Table 7 below:

5

Table 7: FTIR peak assignments for spectra obtained by co-grafting 4-VBC and PFS.

Wavenumber (cm ⁻¹)	Functional group Assignment	Grafted molecule	Peak no.
1504	C=C aromatic ring vibration.	PFS	1
1513	C=C aromatic ring vibration.	4-VBC	2
1524	C=C aromatic ring vibration.	Pentafluorostyrene	3

As the three peaks overlap, peak-fitting was used to obtain the relative density and the relative surface stoichiometry of the two moieties.

10

Figure 7 shows an example of the data fitting, here for the 30:70 ratio of PFS/4-VBC. The raw data is fitted with three components in total, one for each of the peaks listed in Table 7.

Then, the densities of each of the two moieties can be calculated at the various ratios.

15

Subsequently, *relative surface stoichiometry* and *relative grafting density* can be calculated as shown in Example 1.

Figure 8 shows the relative surface stoichiometry of 4-VBC as a function of the fraction of 4-VBC in solution, determined in the same fashion as was described for the co-grafting of tBA and 4-VBC in the previous section.

20

The data was fitted to the same equation as mentioned in Example 1 to arrive at the following data:

25

Table 8: Values for fitted parameters (k₁,k₂), the relative reaction rate(k₂/k₁), the R-squared value for the fit, as well as the p-value for the fitted model.

k ₁ (PFS)	k ₂ (4-VBC)	k ₂ /k ₁	R ²	p-value
1.42	2.82	1.98	0.978	5.8 · 10 ⁻⁴

Table 8 shows the data obtained by fitting the model to the data and indicates that 4-VBC reacts faster than PFS, by about a factor of 2.

30

Example 4: Polymer brush formation on composite particle

Polymer brushes based on tert-butyl methacrylate were grafted from the Si-particles decorated using a reaction composition containing a 50:50 ratio of 4-VBC/PFS (The product of Reaction number 2, as seen in *Table 6*, Example 3).

5 297 mg particles decorated using a reaction composition containing a 50:50 ratio of 4-VBC/PFS and iPrOH (17.5 mL) was added to a screwcap glass bottle containing a magnetic stirbar. The contents were stirred for 10 minutes and sonicated in a bath sonicator for 10 minutes. Then tert-butyl methacrylate (1.9 mL), inactivated polymerization catalyst (0.8 mL),
10 and DI water (4.9 mL) was added to the flask. In a separate glass vial sealed with a septum, sodium ascorbate (103 mg) and DI water (0.4 mL) was mixed, and the vial was shaken until the solids were dissolved. The solution of sodium ascorbate was then transferred to the flask containing the particle suspension to activate the polymerization reaction. Over 40 minutes, the flask with the polymerization reaction was sequentially sonicated for 10 minutes and
15 stirred for 10 minutes, for a total of 20 minutes of sonication and a total of 20 minutes of stirring.

The polymer brush particles were then recovered by centrifugation (5 min at 3900 RPM), the supernatant decanted and discarded while the obtained polymer brush nanomaterial was
20 resuspended in dichloromethane (4 mL) placing it on an orbital shaker board for 10 minutes and sonicating in a bath sonicator for 5 minutes. MeOH (40 mL) was then added to the suspended particles, which were then recovered by centrifugation (5 min at 3900 RPM). This step was repeated twice in total. The obtained polymer brush nanomaterial was then dried in an ambient atmosphere at room temperature for 16 hours, after which the final product was
25 obtained (317 mg).

Upon formation of polymer brushes based on tBMA, the tert-butyl group may be removed to reveal polymer brushes based on MAA by the following method:

30 317 mg Si nanoparticle decorated with PFS and 4-VBC, the latter from which a PtBMA polymer brush is formed was suspended in dichloromethane (17.5 mL) by stirring for 10 min and sonicating in a bath sonicator for 10 minutes. Methanesulfonic acid (44.5 μ L) was added for deprotection and the suspension was stirred for 2 hours. The Si nanomaterial was recovered by centrifugation (5 minutes at 3900 RPM) and resuspended in DCM (25 mL) by 10 minutes
35 sonication, and recovered by centrifugation (5 minutes at 3900 RPM). This step was repeated twice, to obtain the final product.

Then, the particles without polymer brushes, the particles with tert-butyl methacrylate polymer brushes, and the particles with methacrylic acid polymer brushes were subjected to thermogravimetric analysis (TGA).

- 5 As shown in Figure 9, thermogravimetric analysis (TGA) indicates formation of poly(tert-butyl methacrylate) PBs with the organic fraction comprising 43 wt%, and the removal of the tert-butyl methacrylate group resulting in a reduced organic mass fraction of 30wt%.

Furthermore, KBr FTIR measurements were made for the Si nanomaterial decorated with 4-VBC/PFS, the same material with PtBMA polymer brushes grown from the VBC-initiation sites, and the same material with PMAA polymer brushes.

The FTIR transmission spectra may be seen in Figure 10, wherein the top line corresponds to the spectrum from the particles with polymer brushes based on methacrylic acid, while the lower line corresponds to the spectrum from the particles with polymer brushes based on tBMA, and the lowest line correspond to the particles prior to polymer brush formation.

The peak assignments are shown in Table 9, below.

20 Table 9: Assignment of peaks for the data shown in Figure 10.

Wavenumber (cm ⁻¹)	Functional group assignment	Grafted molecule
1504	C=C aromatic ring vibration.	PFS
1524	C=C aromatic ring vibration.	PFS
1365	Tert-butyl C(CH ₃) ₃ symmetric bending vibration	PtBMA
1719	C=O stretching vibration	PtBMA
1700	C=O stretching vibration	PMAA
1248	C-O stretching	Both PtBMA and PMAA
2500 - 3600 (Broad)	O-H stretching	PMAA

This demonstrates that the tert-butyl group from the polymer brush can be removed, to reveal PMAA polymer brushes, resulting in a fluorinated, hydrophobic layer and a hydrophilic polymer brush structure.

25

Example 5: Co-immobilisation of 4-VBC and acrylonitrile

A composite particle was decorated using 4-VBC and acrylonitrile (AN) as first and second moiety precursors.

First, the Si-particle was treated with HF to form a H-terminated Si-surface using the procedure seen in Example 3.

The four screwcap vials each containing HF-treated Si nanomaterials suspended in argon purged toluene (25 mL) were equipped with magnetic stirbars and placed on magnetic stirplates and stirred at 300 RPM. 4-VBC and AN was passed through Al₂O₃ columns. The screwcap vials were closed with septa while keeping an Ar-flow in the vials. 4-VBC and AN was added to the four screwcap vials according to Table 10, along with 4-decylbenzyl diazonium tetrafluoroborate (41.6 mg in each reaction).

Table 10: Reagent concentrations for AN and 4-VBC co-grafting experiments.

Reaction number	Concentration of AN (mM)	AN (mL)	Concentration of 4-VBC (mM)	4-VBC (mL)	Relative ratio of AN to 4-VBC
1	500	0.82	0	0	100:0
2	250	0.41	250	0.88	50:50
3	50	0.082	450	1.56	10:90
4	5	0.0082	495	1.74	1:99
5	0	0	1000	142.5	0:100

0.082 mL acrylonitrile was measured by taking 0.82 mL from a 10% (by volume) solution of acrylonitrile in toluene. The 0.0082 mL acrylonitrile was measured by taking 82 μL from a 10% (by volume) acrylonitrile in toluene solution.

After 2 hours the suspended nanomaterial was recovered by centrifuging (5 minutes at 3900 RPM). The supernatants were discarded, and the nanomaterials were resuspended by adding 2.5 mL DCM to each screwcap vial and sonicating for 10 min in a bath sonicator and shaking on an orbital shakerboard until the Si nanomaterial was well resuspended. Then, 25 mL methanol was added to each of the four screwcap vials, which were then centrifuged (5 minutes at 3900 RPM). The supernatant was discarded and the DCM suspension, MeOH addition, and centrifugation steps repeated once again. The Si nanomaterial was then dried to obtain the final products.

Using the same procedure, a particle decorated only with 4-VBC was made.

The co-grafting of AN and 4-VBC under the conditions indicated in Table 10 resulted in the spectral data shown in Figure 11 where the curve number pertains to the Reaction number in Table 10. The analysis of peak areas here is carried out on the peaks listed in Table 11.

Table 11: FTIR peak assignments for spectra obtained by co-grafting 4-VBC and AN.

Wavenumber (cm ⁻¹)	Functional group Assignment	Grafted molecule
471	C-CN deformation vibration.	AN
471	Si-O-Si rocking vibration	SiO _x layer on Si nanomaterial due to oxidation
1513	C=C aromatic ring vibration.	4-VBC
2259	C≡N Stretching vibration.	AN
2259	SiO _x -H stretching vibration	Residual Si-H in an oxidized environment
3026	Aryl C-H stretching vibration.	4-VBC

Then, the densities of each of the two moieties can be calculated at the various ratios. Subsequently, *relative surface stoichiometry* and *relative grafting density* can be calculated as shown in Example 1.

Figure 12 shows the relative surface stoichiometry of 4-VBC as a function of the fraction of 4-VBC in solution, determined in the same fashion as was described for the co-grafting of tBA and 4-VBC in the previous section.

The data was fitted to the same equation as mentioned in Example 1 to arrive at the following data, seen in Table 12:

Table 12: Values for fitted parameters (k_1, k_2), the relative reaction rate (k_2/k_1), the R-squared value for the fit, as well as the p-value for the fitted model shown in Figure 12.

k_1 (AN)	k_2 (4-VBC)	k_2/k_1	R ²	p-value
8.38	3.12	0.37	0.924	0.0057

Table 12 shows the data obtained by fitting the model to the data from the peaks at 471 cm⁻¹ for AN, and 1513 and 3026 cm⁻¹ for 4-VBC. AN appears to react faster than 4-VBC by a factor of roughly 2.5.

Comparative Example 6: Co-immobilisation of 4-VBC and allylamine

A composite particle was decorated using 4-VBC and A) as first and second moiety precursors.

First, the Si-particle was treated with HF to form a H-terminated Si-surface using the procedure seen in Example 3.

The four screwcap vials each containing HF-treated Si nanomaterials suspended in argon purged toluene (25 mL) were equipped with magnetic stirbars and placed on magnetic stirplates and stirred at 300 RPM. 5 mL 4-vinylbenzyl chloride and 5 mL allylamine were passed through Al₂O₃ columns. The screwcap vials were closed with septa while keeping an argon-flow in the vials. 4-VBC and allylamine was added to the four screwcap vials according to *Table 13*, along with 4-decylbenzyl diazonium tetrafluoroborate (41.6 mg in each reaction).

Table 13: Reagent concentrations for allylamine and 4-VBC co-grafting experiments.

Concentration of allylamine (mM)	Concentration of 4-VBC (mM)	Relative ratio of allylamine to 4-VBC
500	0	100:0
450	50	90:10
250	250	50:50
50	450	10:90

0.09 mL allylamine was measured by taking 0.9 mL from a 10% (by volume) solution of allylamine in toluene.

After 2 hours the suspended nanomaterial was recovered by centrifuging (5 minutes at 3900 RPM). The supernatants were discarded and the nanomaterials were resuspended by adding 2.5 mL DCM to each screwcap vial and sonicating for 10 minutes in a bath sonicator and shaking on an orbital shakerboard until the Si nanomaterial was well resuspended. Then, 25 mL MeOH was added to each of the four screwcap vials, which were then centrifuged (5 minutes at 3900 RPM). The supernatant was discarded and the DCM suspension, MeOH addition, and centrifugation steps repeated once again. The Si nanomaterial was then dried to obtain the final products.

The co-immobilization of allylamine and 4-VBC under the conditions indicated in *Table 13* did not proceed.

Notably, no peaks pertaining to 4-VBC are observed in any of the spectra obtained, even for a 10:90 allylamine to 4-VBC ratio.

As such, this experiment demonstrates a limitation in the chemical functional group which can be used in this methodology and shows that allyl amines likely cannot be grafted to the surface, as well as they prevent the grafting of another molecule (4-VBC), which is known to graft under other conditions.

Example 7: Controlling grafting density of 4-VBC by lowering the concentration of 4-VBC in the reaction mixture.

All the above examples (that is example 1-6) were designed to control the density of 4-VBC by diluting with another reactive molecule during the hydrosilylation reaction. However, lowering the concentration of 4-VBC without adding another co-grafting agent can also reduce the amount of grafted material, as will be seen below.

Using the procedure of Example 1, except adding only one type of moiety, namely 4-VBC, in concentrations as specified below in *Table 14*, Si-particles were decorated:

Table 14: Concentrations evaluated for density control using only one reactant, 4-vinylbenzyl chloride.

Experiment ID	Concentration of 4-VBC (mM)
1	50
2	100
3	200
4	500
5	1000

Figure 13 shows the FTIR spectra while Figure 14 indicates the correlation between peak areas from 4-VBC and the solution concentration of 4-VBC. The peaks corresponding to 4-VBC (see *Table 2*) were analyzed in the FTIR-spectrum. The normalized peak areas were then plotted against the 4-VBC concentration as seen in Figure 14.

Example 8: Immobilization of tBA as a protected carboxylic acid, and subsequent de-tert-butylation to reveal the carboxylic acid

This example illustrates how a particle may be decorated with a protic group (carboxylic acid), despite the incompatibility of protic species such as allylamine and the hydrosilylation reaction shown in Comparative Example 6.

First, the Si-particle was treated with HF to form a H-terminated Si-surface using the procedure seen in Example 1.

The HF treated Si nanomaterial suspended in 200 mL argon-purged toluene (corresponding to a starting mass of 4 g Si nanomaterial) was placed in a flask and stirred with a magnetic stirbar. tBA was passed through an Al₂O₃ column, and 14.71 mL tBA was then added to the flask, along with 333.2 mg 4-decylbenzenediazonium tetrafluoroborate.

After 2h, the nanomaterial was recovered by centrifugation (5 minutes at 3900 RPM), and the following purification step repeated twice: The supernatant was decanted and the particles resuspended in 200 mL toluene by ultrasonication in a bath sonicator for at least 10 minutes, after which the Si nanomaterial was recovered by centrifugation (5 minutes at 3900 RPM).

5

After immobilization (covalent bonding) of tBA, a de-*tert*-butylation reaction may be achieved using the following method:

The nanomaterial was resuspended in 200 mL DCM by stirring for 15 minutes with a magnetic stirbar. 1.56 mL methanesulfonic acid was added, and after 20h the Si nanomaterial was recovered by centrifugation and the following purification routine was repeated twice: The supernatant was discarded, and the Si nanomaterial was resuspended in 300 mL DCM by sonication for 10 minutes in a bath sonicator. The Si nanomaterial was then recovered by centrifugation (5 minutes at 3900 RPM), and dried.

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Figure 15A and Figure 15B shows KBr FTIR spectra obtained after grafting tBA, and after the removal of the *tert*-butyl group. The reveal of the carboxylic acid concomitant with the removal of the *tert*-butyl group is evident by the disappearance of the peak at 1366 cm^{-1} which is assigned to the *tert*-butyl C-H bending and the presence of the broad peak from 2500 to 3600 cm^{-1} . The broad peak between 3000 and 3600 cm^{-1} before the removal of the *tert*-butyl group is ascribed to water bound in the KBr (according to Socrates, G., Infrared and Raman Characteristic Group Frequencies – Tables and Charts, 3rd Edition, John Wiley and Sons).

This showcases how a protic species can be grafted to the surface through use of protection group chemistry, in this case the *tert*-butyl ester.

Example 9: Particle sizes

The size of Si nanomaterial decorated with 4-VBC, the same material with PtBMA PBs grown from the 4-VBC decorated Si-nanomaterial, and the same material with PMAA polymer brushes has been evaluated using dynamic light scattering.

First, the Si-particle was treated with HF to form a H-terminated Si-surface using the procedure seen in Example 3.

35

A screwcap bottle with the HF-treated Si nanomaterial suspended in argon-purged toluene (25 mL) was placed on magnetic stirplates and stirred at 300 RPM. 5 mL 4-vinyl benzylchloride was passed through an Al_2O_3 column. The screwcap bottle was closed with septa while keeping

an argon-flow in the reactor. 1.78 mL 4-VBC, along with 4-decylbenzyl diazonium tetra-fluoroborate (41.4 mg) was added to the reaction. After 2 hours the suspended nanomaterial was recovered by centrifuging (5 min at 3900 RPM). The supernatant was discarded, and the nanomaterial resuspended by adding 25 mL toluene to the centrifuge bottle sonicating for 10 min in a bath sonicator and shaking on an orbital shakerboard until the Si nanomaterial was well resuspended. The Si nanomaterial was recovered by centrifugation (5 minutes at 3900 RPM), the supernatant was discarded, and the toluene suspension and centrifugation steps repeated once again, after which the same purification routine was carried out twice, using isopropanol as the solvent. The resulting material was used directly in the following polymer brush formation reaction.

Then polymer brushes were formed using the below methodology:

The 4-VBC modified Si nanomaterial was resuspended in 17.5 mL iPrOH by sonicating for 10 min and the reaction vessel was then equipped with a magnetic stirbar and transferred to a stirplate. 4.9 mL deionized water, 1.9 mL tBA, 0.78 inactivated polymerization catalyst was added to the stirred suspension of particles. 100 mg NaAsc was dissolved in 0.4 mL deionized water and added to the stirred particle suspension, which was then sequentially sonicated and stirred for 10 minutes, for 40 minutes total. The polymer brush modified Si nanomaterial was then recovered by centrifugation (5 minutes at 3900 RPM) and purified by performing the following steps twice: discarding the supernatant, then resuspending the Si nanomaterial in 4 mL DCM by sonicating for 5 minutes, and then adding 10 mL diethyl ether and recovering by centrifugation (5 minutes at 3900 RPM).

Lastly, the tert-butyl group was removed to reveal the PMAA polymer brushes:

The PtBMA-modified Si nanomaterial was resuspended in 25 mL DCM by sonication (10 min) and stirred for 5 min. 195 μ L methanesulfonic acid was added to the particle suspension. After 20h the Si nanomaterial was recovered by centrifugation (5 minutes at 3900 RPM) and purified by repeating the following steps twice: decant the supernatant and resuspend the Si nanomaterial in DCM (25 mL) and recover by centrifugation (5 minutes at 3900 RPM).

Figure 16 illustrates the changes in particle size distributions, as determined by dynamic light scattering (DLS) measurements. Each of the curves are numbered as described below:

- Size distribution of the "as-is" Si nanomaterial (suspended in MeOH, curve no. 1)
- Size distribution after the grafting of 4-VBC (suspended in iPrOH, curve no. 2)
- Size distribution after formation PtBMA polymer brushes (suspended in DCM, curve no. 3)

- Size distribution after removal of the *tert*-butyl protection group to reveal PMAA polymer brushes. (suspended in MeOH, curve no. 4)

The corresponding D₅₀ particle sizes are found in *Table 15*, below.

5

Table 1. D₅₀ (nm) particle sizes for different steps of the Si nanomaterial modification process.

	As received Si nanomaterial	After HF treatment and diazonium hydrosilylation (DHS) reaction	After PtBMA polymer brush formation	After removal of tert-butyl protecting group
D ₅₀ (nm)	382	154.3	1049	409

Evidently, ultrasonic treatment combined with HF etching and grafting of 4-VBC to form a thin organic layer on the surface of the Si nanomaterial results in smaller particles when compared to the “as received” nanomaterial and a lower D₅₀, likely due to the processing breaking up aggregates present in the as-received material. After the formation of polymer brushes, the D₅₀ increases significantly, indicating formation of a thicker organic layer. Finally, after protection group removal, the particle size distribution and D₅₀ decreases, in line with a lower molecular mass of the repeating unit in the polymer, and thus a thinner polymer brush layer.

15

Figure 17 shows the FTIR spectrum obtained after removal of the *tert*-butyl group, to confirm the chemical identity of the polymer brush on the Si nanomaterial. By comparison with the peaks listed and assigned in *Table 9*, the large band at 1699 cm⁻¹ indicates presence of the C=O carbonyl functional group from carboxylic acid, while the lack of a sharp peak at 1366 cm⁻¹ indicates complete removal of the *tert*-butyl group. The broad peak from 2500-3600 cm⁻¹ indicates presence of carboxylic acid as well.

25

Example 10: Changes to the amount of SiO_x and Si-H amounts throughout an exemplary grafting process

This example describes the amount of SiO_x & Si-H bonds present in an exemplary “as-is” Si nanomaterial, HF treated Si Nanomaterial, and after the hydrosilylation reaction with 100% *tert*-butyl acrylate.

30

Si-particles were treated with HF to form a H-terminated Si-surface using the procedure seen in Example 3.

The HF-treated Si nanomaterial suspended in argon-purged toluene (25 mL) was placed on a magnetic stirplate and stirred at 300 RPM. 5 mL tBA was passed through an Al₂O₃ column. The screwcap bottle was closed with septa while keeping an argon-flow in the reactor. 1.84 mL tBA, along with 4-decylbenzyl diazonium tetrafluoroborate (41.2 mg) was added to the reaction. After 2 hours the suspended nanomaterial was recovered by centrifuging (5 minutes at 3900 RPM). The supernatant was discarded, and the nanomaterial resuspended by adding 25 mL toluene to the centrifuge bottle sonicating for 10 minutes in a bath sonicator and shaking on an orbital shakerboard until the Si nanomaterial was well resuspended. The Si nanomaterial was recovered by centrifugation (5 minutes at 3900 RPM), the supernatant was discarded, and the toluene suspension and centrifugation steps repeated once again, after which the Si nanomaterial was dried under a flow of argon in a vessel with an inert atmosphere. After drying, a small sample was immediately fashioned into a KBr pellet to measure the content of Si-H and SiO_x.

Figure 18A shows the full FTIR spectra of the untreated Si Nanomaterial, the HF-etched Si nanomaterial, and the same material after the diazonium initiated hydrosilylation reaction with 100% tert-butyl acrylate to decorate the particle entirely with tBA.

The large peak in the range from 800 to 1300 cm⁻¹ is a composite peak for a series of Si-O-Si and Si-OH species according to *Table 16* (below), compiled based on literature reports (Saputra R.E. et al., Molecular and Biomolecular spectroscopy 199 (2018) 12-20; Sun, X.H., et al. Inorganic chemistry, 42, 2003, 2399; Mawhinney, D.B., et al., J. Phys. Chem. B, 1997, 101, 1202-1206).

Table 16: Peak assignments for SiO_x species.

Region (cm ⁻¹)	Assignment
800	V _{symmetric} Si-O-Si
960	V _{symmetric} Si-OH
1000-1200	V _{asymmetric} Si-O-Si

In Figure 18B the various SiO_xH_{4-x} peaks are assigned for the HF-treated Si Nanomaterial, indicating the presence of a range of SiO_xH_{4-x} species, from the most reduced SiH₃ species to the more oxidized species such as SiH(O)₃ and SiH₂(O)₂ and SiH(O)₂. Also plotted in Figures 18A & 18B is the KBr FTIR after the hydrosilylation reaction showing a diminished amount of Si-H bands after the reaction, in line with their reaction with the grafting agent, tBA in this case.

By normalizing the KBr FTIR intensity to the Si sample mass and subsequent peak integration, the relative amounts of Si-H and SiO_x can be determined as the Si nanomaterial progresses through the process ("As received", HF-etched, Hydrosilylation Reaction).

- 5 Indicated by the data in Table 17, after the HF treatment only 6.3% of the initially present SiO_x peak area remains, indicating almost full removal of the SiO_x species during the HF treatment.

Table 17: Peak areas of the Si-H and SiO_x species right after HF etch, and after the subsequent hydrosilylation reaction with 100% tert-butyl acrylate.

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	SiH peak area pr. mg Si sample [a.u. mg ⁻¹]	SiO _x peak area pr. mg Si sample [a.u. mg ⁻¹]	SiO _x peak area relative to untreated Si nanomaterial
Untreated Si Nanomaterial	0.12	126.5	100%
HF treated Si Nanomaterial	16.2	8.2	6.3%
After decoration of the above Si nanomaterial with 100% tBA	5.9	9.7	7.8%

To determine the amount of Si-H bands which react during the hydrosilylation reaction, the peak area for the HF-treated Si nanomaterial and the same material after hydrosilylation is determined. As indicated by the exemplary data in Table 17, $\frac{16.2-5.9}{16.2} = 64\%$ of the Si-H peak area is gone after the hydrosilylation reaction, indicating that some Si-H species are left after reaction, which is to be expected based on steric considerations, i.e. the grafted molecules are larger than the distance between the two closest SiH bands that could have reacted.

15

Example 11: Qualitative observations regarding the stability of HF treated Si nanomaterial and Si nanomaterials modified with polymer brushes.

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The Si-Si bonds are known to be labile and reactive towards oxidation through reaction with water and/or ambient oxygen.

When the surface is covered with an SiO_x layer a stabilizing effect is observed, although when the surface is Si-H terminated after the HF treatment, vigorous reaction of the Si Nanomaterial with water can be observed. Specifically, when Si-H terminated Si nanomaterial obtained

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through HF treatment is mixed with water, gas bubble formation is observed from the redox reaction between Si-Si bonds and water, resulting in formation of H₂ gas.

5 This contrasts with the observations made when mixing a PMAA polymer brush modified Si nanomaterial with water, where no spontaneous gas formation is observed, indicating that the polymer brushes have a stabilizing effect on the Si nanomaterials.

10 In fact, when modified with PMAA polymer brushes, a suspension of the particles can be pH-adjusted from the initial value (just below pH 2 by virtue of the carboxylic acid groups) to a pH value of 7 by addition of hydroxide ion (Figure 20), without inducing significant oxidation of the Si-Si bonds.

This is indicated by the ATR FTIR spectrum in Figure 19 showing the presence of polymer brushes after the pH adjustment, see Table 18 for peak assignments.

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Table 18. Peak assignments for the ATR FTIR spectra presented in Figure 19.

Peak position (cm ⁻¹)	Functional group assignment	Polymer brush type
2100 – 3600	Carboxylic acid O-H stretching	PMAA
1691	Carboxylic acid C=O stretching	PMAA
1528	Lithium carboxylate C=O stretching	Poly(lithium methacrylate)
980 - 1221	SiO _x species.	Both

20 In the case of strong oxidation of Si-Si bonds, the particles have been observed to strongly oxidize and present with little to no polymer brush signals in the FTIR spectra after the oxidation reaction. In some cases, for example in basic environment with pH > 7, the reaction with water has been observed to be self-accelerating, with the vigorous reaction constantly revealing fresh Si-Si bonds which are then attacked by more water, resulting in disintegration of the Si nanomaterial. In the case of adjusting pH from an acidic environment to pH 7, while polymer brushes are present on the Si nanomaterial, the peaks pertaining to the polymer
25 brush layer are still present, indicating an improved stability over the HF treated particles.

Unless otherwise indicated, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure
30 pertains.

Example 12: Formation of polymer brushes on graphite powder.

In this example, the inventors demonstrate first covalent attachment of polymerization initiators on graphite particles, followed by formation of surface polymers, grown from the covalently attached polymerization initiators. The graphite substrate is chosen to have a well-defined system and demonstrate that polymer brushes can be formed from the surface of carbonaceous materials.

Attachment of polymerization initiators to graphite powder.

139 g graphite powder (SLC1520T, Superior Graphite) was suspended in DI Water (1375 mL) in a flask by stirring at 1000 RPM on a magnetic stirrer for 10 minutes. The suspended graphite powder was then sonicated for 10 minutes in a small sonicator, and returned to stirring, at 600 RPM. 1654.6 mg 4-(chloromethyl)benzenediazonium tetrafluoroborate (CBD) and 481.3 mg sodium ascorbate was added, and the flask sealed, and left to stir for 150 minutes. After 150 minutes 481.3 mg sodium ascorbate was added, and the suspension was left to stir for another 150 minutes.

The graphite was then recovered by partitioning the graphite suspension in two centrifuge bottles and centrifugating the suspension for 5 minutes at 3900 RPM using an Eppendorf 5810 centrifuge. The supernatant was then decanted, and the graphite resuspended in 500 mL DI water in each bottle by shaking on a shakerboard for 10 minutes and sonicating for 10 minutes, and shaking by hand as necessary to obtain a good suspension of graphite-I. This rinsing process was repeated twice with DI water and twice with acetone after which the graphite was left to dry under ambient conditions, with a resulting product mass of 129 g. The graphite with covalently attached polymerization initiators is referred to as Graphite-I.

Formation of polymer brushes from polymerization initiators attached covalently to graphite particles.

Solution A, consisting of DI water (440.4 mL) and iPrOH (660.6 mL) was mixed in a bottle. 125 g Graphite-I (graphite powder with polymerization initiators covalently attached as described above) was suspended in 367 mL of mixture A by stirring it at 500 RPM for 10 minutes, followed by sonication for 10 minutes. This led to a smooth and homogeneous suspension of Graphite-I particles.

To form Solution B, 633 mL of solution A was combined with *tert*-butyl methacrylate (92.3 mL), and catalyst solution (0.28 mM) comprising Me₆TREN (180 µL), DI-water (38.4 mL), and Cu(II) (324 mg/L, obtained from a solid copper source) (38.4 mL). Sodium ascorbate (4920.3 mg) was dissolved in DI water (18.5 mL), and this solution of sodium ascorbate was added to Solution B, mixed, and left for 5 minutes. After 5 minutes, solution A and solution B was combined to initiate the polymerization reaction, which was left to react for 30 minutes. The

inventors observed that after 2 to 5 minutes of polymerization, the graphite particles started to aggregate and form larger particles, well in line with the formation of quite hydrophobic polymer chains on the surface, leading to aggregation in the aqueous solvent. This is a strong indication of the formation of covalently attached surface polymers on the graphite particles.

- 5 After 30 minutes, the graphite particles with covalently attached PtBMA polymer brushes were recovered by partitioning the graphite suspension into to centrifuge bottles and centrifuging for 5 minutes at 3900 RPM. The supernatant was discarded and the graphite was resuspended in 400 mL DCM in each centrifuge bottle by shaking on shakerboard (10 minutes) and sonicating (10 minutes) and shaking the bottles as necessary to ensure good suspension of
- 10 the Graphite-PtBMA. This process of centrifuging, decanting supernatant, and resuspending in DCM was repeat a total of three times, after which the graphite powder was left to dry under ambient conditions. The resulting material is referred to as Graphite-PtBMA.

Conversion of PtBMA polymer brushes to PMAA polymer brushes

- 15 With the intent of controlling the surface properties and demonstrating binding of lithium ions in the polymer brushes covalently attached to the graphite particles, the inventors here demonstrate conversion of the PtBMA polymer brushes to PMAA polymer brushes through an acid catalyzed de-tertbutylation, i.e., removal of the *tert*-butyl protecting group. This reaction will thus convert Graphite-PtBMA to Graphite-PMAA.

- 20 117 g Graphite-PtBMA with covalently attached PtBMA polymer brushes were suspended in DCM (1250 mL) by stirring (500 RPM, 10 minutes) and sonicating for 10 minutes. This formed a smooth and homogeneous suspension, demonstrating the hydrophobic nature of the graphite particles, imparted by the hydrophobic PtBMA polymer brushes. 1.625 mL
- 25 methanesulfonic acid was then added to the stirred suspension of graphite with PtBMA polymer brushes to initiate the removal of the *tert*-butyl protecting group. Within 5 minutes the inventors observed that the smooth suspension of graphite particles in DCM started to form loose aggregates and larger particulates. This is well in line with expected behavior, since removal of the *tert*-butyl group leads to formation of PMAA. The carboxylic acid
- 30 functional group of this polymer brush is known to form strong hydrogen bonds and dimers with other carboxylic acids, leading to interaction between individual graphite-PMAA particles, resulting in aggregation. Combined with the hydrophilic nature of the carboxylic acid functional group and the hydrophobic DCM solvent, the formation of particulates and aggregates demonstrates well the fast and efficient conversion of PtBMA polymer brushes to
- 35 PMAA polymer brushes, with the concurrent switch in solubility and hydrophilicity. The Graphite-PMAA was recovered by partitioning the suspension into two centrifuge bottles and centrifuging for 5 minutes at 3900 RPM. The resulting supernatant was discarded and the Graphite-PMAA was resuspended in MeOH, by adding 200 mL MeOH to each centrifuge bottle,

and placing the bottles on a shakerboard for 10 minutes and sonicating for 10 minutes. If necessary, the bottles were shaken further by hand to ensure good suspension of Graphite-PMAA. After being resuspended, the suspension was centrifuged again for 5 minutes at 3900 RPM, and the supernatant was discarded. This rinsing process was repeated three times, and
5 the material was air dried under ambient conditions, yielding the Graphite-PMAA material.

Binding of lithium ions to PMAA polymer brushes on graphite particles.

To bind lithium ions to the PMAA polymer brushes, generating poly(lithium methacrylate) polymer brushes, the following procedure was carried out.

10

DI water (1250 mL) was purged with argon for 45 minutes while stirring at 250 RPM. Graphite-PMAA (114.2 g) was then added, and the suspension was stirred for 60 minutes at 800 RPM. The suspension was then sonicated for 10 minutes and stirred for an addition 10 minutes at 800 RPM. Lithium hydroxide monohydrate (LiOH, 5240 mg) was then added, and the
15 suspension was stirred for 60 minutes.

To recover the graphite particles with poly(lithium methacrylate) (PMAA-Li) polymer brushes, the suspension was partitioned into two centrifuge bottles and centrifuged for 5 minutes at 3900 RPM. The supernatant was decanted and 300 mL DI water was added to each centrifuge
20 bottle. The graphite particles with PMAA-Li polymer brushes (Graphite-PMAA-Li) were then resuspended by shaking on a shakerboard (120 RPM, 10 min), and sonicating for 10 minutes, before centrifuging again. These steps were repeated twice and the graphite powder with PMAA-Li polymer brushes was left to air dry under ambient conditions.

25 Data to support the formation of surface polymers on graphite particles

The elemental composition of the graphite particle surface was determined after each reaction by X-ray photoelectron spectroscopy (XPS), and the chemical functional groups present in the different materials were documented using ATR IR spectroscopy.

30 Table 19 shows the elemental composition for each step, as determined by XPS measurements.

Table 19. Elemental composition of the surface of graphite particles after different processing steps as determined by XPS analysis.

Material	C 1s [At%]	O 1s [At%]	Cl 2p [At%]	S 2p [At%]	Li 1s [At%]
Graphite-I	97.1	1.8	1.1	-	-
Graphite-PtBMA	86.4	13.6	-	-	-
Graphite-PMAA	82.8 ± 0.5	17.2 ± 0.5	-	-	-
Graphite-PMAA-Li	70.6 ± 1.5	18.6 ± 0.3	-	1.3 ± 0.1	9.4 ± 1.7

- 5 After the attachment of polymerization initiators (CBD) to yield initiator functionalized graphite, Graphite-I, a 1.1 At% chlorine component is detected, well in line with the presence of a chlorine atom in the polymerization initiator molecule, which takes the form of benzyl chloride after being covalently attached to the graphite surface. The low concentration of chlorine conforms well with the formation of a thin layer of initiators at the surface of the
10 graphite particles, since the polymerization initiator contains a chloride atom.

- Formation of PtBMA polymer brushes lead to a higher amount of oxygen (13.6 At%), well in line with oxygen being present in the polymer repeating unit (3 O atoms and 8 C atoms). C is observed in a ratio higher than the implied 8 C-atoms to 3 O-atoms based on the polymer
15 composition,—due to the presence of background signal from the graphite substrate contributing to the amount of measured C. The theoretical C:O-ratio for PtBMA is 8:3, leading to a theoretical ratio of 27.3 At% O and 72.7 At% C.

- When the *tert*-butyl group is removed to yield Graphite-PMAA, the amount of oxygen
20 increases to 17.2 At%, well in line with fewer carbon atoms in the polymer brush, which now has the composition of 4 C atoms to 2 O atoms in its repeating unit, leading to an expected theoretical composition of 66.6 At% C and 33.3 At% O. Again, the contribution of the graphite substrate to the concentration of C is the explanation for the higher than expected C content.

- 25 Finally, subjecting the Graphite-PMAA to LiOH yields Graphite-PMAA-Li, indicated by a presence of 9.4 At% Lithium. Since the reaction between a carboxylic acid and LiOH is expected to lead to formation of lithium carboxylate, the ratio of oxygen to lithium is expected to be 2:1, with the experimental data indicating a $18.6:9.4 = 1.98$, which aligns very well with the theoretical composition of poly(lithium methacrylate) with 2 oxygens per Li atom.

- 30 The chemical structures of the surface polymers on graphite were further confirmed by ATR IR measurements, presented in Figure 24. Spectrum 1 in Figure 24, which pertains to Graphite-I, is largely featureless, well in line with a very thin layer of polymerization initiators

being below the detection limit of the instrument. Spectrum 2 in Figure 24, pertaining to Graphite-PtBMA, exhibits a strong peak at 1716 cm^{-1} (Peak A in Figure 24) which is due to the stretching of the ester carbonyl of the PtBMA surface polymer. Furthermore, the sharp peak at 1366 cm^{-1} (Peak D) indicates presence of the *tert*-butyl group and is assigned to the symmetric CH_3 bending vibration of the *tert*-butyl group. The remaining peaks from 1000 cm^{-1} to 1500 cm^{-1} are a combination of C-H bending vibrations, C-O stretching vibrations, and C-C skeletal vibrations, all in line with the presence of the PtBMA surface polymer.

Upon exposing Graphite-PtBMA to methanesulfonic acid in DCM, leading to Graphite-PMAA, visible changes are observed in the pertaining IR spectrum, Spectrum 3 in Figure 24. Namely, the sharp peak at 1366 cm^{-1} is gone, in line with the removal of the *tert*-butyl group. Furthermore, the position of the peak due to the C=O stretching vibration has shifted to 1689 cm^{-1} (Peak C), indicating presence of a carboxylic acid. The C=O stretching peak has also broadened, caused by hydrogen bonding between the formed carboxylic acid functional groups of the PMAA polymer brush.

Finally, for graphite-PMAA-Li, the main change is the formation of the lithium carboxylate, which is indicated in Spectrum 4 in Figure 24 by the shift of the C=O stretching peak from 1689 cm^{-1} to 1542 cm^{-1} (Peak C), well in line with the formation of a metal carboxylate functional group, due to the reaction of the carboxylic acid functional group of PMAA surface polymer with the LiOH, leading to formation of the PMAA-Li polymer brush.

Example 13: Attachment of polymerization initiators to Cu.

This example describes a procedure for cleaning and attachment of polymerization initiators on copper samples suitable for battery electrodes.

Prior to attachment of polymerization initiators, the samples are cleaned as follows:

In a reaction container, H_2SO_4 (1 mL) is added to DI water (99 mL). 6 Cu samples ($20\times 20\times 7\text{ mm}$) are flushed in iPrOH, dried and placed in a reaction container. The H_2SO_4 solution is poured into the reaction container and the system is left for 5 min. The samples are removed from the solution and flushed in DI water, then placed in a container with DI water and sonicated for 5 minutes. Next, the samples were flushed in iPrOH and transferred to a container with iPrOH and sonicated for 5 minutes. Finally, the samples were flushed with an Ar gas to dry.

The method of attachment of polymerization initiators is as follows:

The substrates were placed in a rack and placed in a vacuum oven with 16 vials of $100\text{ }\mu\text{L}$ CPTMS at approximately $45\text{ }^\circ\text{C}$ for 150 minutes. The gauge pressure was lowered to -0.96 bar , whereby the CPTMS evaporated, and the substrates were left for 150 minutes. Thereafter, the substrates were removed and placed in an oven at approximately $80\text{ }^\circ\text{C}$ for

15 minutes to anneal the silane layer. After annealing, the substrates were stored in ambient conditions and left for 24 hours.

Water contact angle (WCA) was measured to demonstrate the successful attachment of polymerization initiators (Table 20). The WCA increases significantly from the blank, pre-cleaned Cu substrate to the Cu with polymerization initiators attached, corresponding to the immobilization of a hydrophobic molecule.

Table 20. Water contact angle measurements for before and after CPTMS treatment.

	WCA, Blank (after cleaning) (°)	WCA, CPTMS (°)
Cu	33	96

Claims

1. A composite particle comprising a silicon core decorated with at least:
 - a first moiety comprising a first anchoring component covalently bonded to the silicon
 - 5 core, and a polymerization initiating group; and
 - a second moiety comprising a second anchoring component covalently bonded to the silicon core, and a functional group.
2. The composite particle of claim 1, wherein composite particle has an average diameter
 10 ($D_{[4,3]}$) from about 10 nm to about 500 nm, as measured by dynamic light scattering.
3. The composite particle of any preceding claim, wherein the first and second anchoring components are selected from $-C^*(R^{A1})(R^{A2})CH(R^{A3})-$, $-C^*HCH-$, or $-C^*MeCH-$,
 - wherein
 - 15 C^* represents the carbon covalently bonded to a silicon of the Si-particle; and
 - R^{A1} , R^{A2} , R^{A3} are each independently selected from H or Me.
4. The composite particle of any preceding claim, wherein the polymerization initiating group comprises a radical stabilising group and a leaving group.
 20
5. The composite particle of claim 3, wherein the polymerization initiating group is:

Rad-LG

wherein Rad is covalently bonded to the remainder of the first moiety and selected from $-(C_6(R^{Rad2})_4)C^*(R^{Rad1})_2-$, $-(C_{10}(R^{Rad2})_6)C^*(R^{Rad1})_2-$, $-C^*(R^{Rad3})_2$, $-OC(O)C^*(R^{Rad1})_2$,

- 25 or $-NR^{Rad1}C(O)C^*(R^{Rad1})_2$,
 - wherein C^* represents the carbon attached to LG;
 - each R^{Rad1} independently denotes H or methyl;
 - each R^{Rad2} independently denotes H or R^{Rad3} ;
 - R^{Rad3} denotes methyl; and
 - 30 LG is selected from Cl, Br or I.
6. The composite particle of any of the preceding claims, wherein the functional group denotes H, $-C_6H_5$, $-C_6F_5$, $-C(O)O-R^{FG3}$, or CN, wherein
 - R^{FG3} denotes CH_3 or *tert*-butyl.
 - 35
7. The composite particle of any of the preceding claims, wherein the relative surface stoichiometry of first moiety is at least 0.5%.

8. The composite particle of any of the preceding claims, wherein the silicon core comprises crystalline silicon.

9. The composite particle of any of the preceding claims, wherein the silicon core is an aggregate of particles, said aggregate

having an outermost surface and a plurality of internal surfaces, and comprising external composite particles and optionally internal particles, wherein

the optional internal particles comprise
a silicon core;
the external composite particles comprise
a silicon core; and

an external surface region, the external surface region comprising an area decorated with the first and second moieties covalently bonded to the silicon core of the external composite particles through the first and second anchoring components; wherein
said decorated area of the external surface region of the external composite particles forms the outermost surface of the aggregate, and
wherein none of the surface of the optional internal particles forms part of the outermost surface of the aggregate.

20

10. A method of forming a composite particle comprises the steps of

a. providing

i. silicon particles,

ii. a first moiety precursor comprising a first anchorable component and a polymerization initiating group, and

iii. a second moiety precursor comprising a second anchorable component and a functional group;

b. decorating the silicon particle by reacting the first anchorable component of the first moiety precursor to form a first anchoring component of a first moiety and

c. reacting the second anchorable component of the second moiety precursor to form a second anchoring component of a second moiety,
wherein the first anchoring component and the second anchoring component are covalently bonded to the silicon particle.

11. The method of claim 10, wherein step a.i. comprises, prior to reaction with the first and second moiety precursors, exposing the silicon particles to HF so as to form Si-H moieties on at least part of the surface of the silicon particles.

12. The method of any of claims 10 to 11, wherein the first and the second moiety precursors are immobilised on the surface of a Si-particle in the same step.
13. The method of any of claims 10 to 12, wherein the ratio of first moiety precursors to second moiety precursors used to decorate the Si-particle is from 1:9 to 9:1.
14. The method of any of claims 10 to 13, wherein silicon core has an average diameter ($D_{[4,3]}$) from about 10 nm to about 500 nm, as measured using dynamic light scattering.
15. The method of any of claims 10 to 14, wherein the first moiety precursor comprises 4-vinyl benzyl chloride, and wherein the second moiety precursor comprises *tert*-butyl acrylate, styrene, pentafluorostyrene, or acrylonitrile.
16. A polymer brush composite particle comprising a silicon core decorated with at least
a first moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymeric moiety; and
a second moiety comprising a second anchoring component and one or more functional groups.
17. The polymer brush composite particle of 16, wherein the polymeric moiety is a linear polymeric chain with an average length of from about 2 repeat units to about 1000 repeat units.
18. A method of forming a polymer brush composite particle, said method comprising
a) providing a composite particle comprising a silicon core decorated with at least;
a first moiety comprising a first anchoring component covalently bonded to the silicon core, and a polymerization initiating group; and
a second moiety comprising a second anchoring component covalently bonded to the silicon core, and a functional group;
b) forming a polymerization reaction composition comprising one or more polymerization catalysts and one or more monomers; and
c) exposing the composite particle to the polymerization reaction composition.
19. The method of claim 18, wherein the polymer brushes are synthesised by SIP (Surface-Initiated Polymerization).
20. The method of claim 18 or claim 19, wherein the polymerization reaction composition is formed from

a polymerization composition comprising at least one dormant transition metal catalyst, an activation agent comprising an oxygen scavenger, and one or more monomers, wherein the one or more monomers may be provided as a part of the polymerization composition, a part of the activation agent, or as a discrete composition.

21. An anode comprising the composite particle of any of claims 1 to 9, 16 or 17.
22. A cell, for example a secondary lithium-ion cell, comprising the anode of claim 21.
23. A composite particle comprising a silicon-carbon composite core decorated with at least; a first moiety comprising a first anchoring component covalently bonded to the silicon-carbon composite core, and a polymerization initiating group; and a second moiety comprising a second anchoring component covalently bonded to the silicon-carbon composite core, and a functional group.
24. The composite particle of claim 23, where Si/C composite is prepared by mixing silicon microparticles and PVDC powder, milling them together to form a polymer-coated silicon nanoparticle, subsequently carbonizing to yield the Si/C composite, and optionally coating said Si/C composite with a graphitic carbon layer via CVD; crushing, milling, and etching metallurgical grade Si chips to produce porous silicon particles, coating them with carbon via emulsion-polymerization, carbonizing to obtain the Si/C composite, and optionally coating said Si/C composite with a graphitic carbon layer via CVD; or conducting magnesiothermic reduction of silica microparticles to create porous silicon, coating the etched product with polyvinylidene chloride (PVDC) via emulsion polymerization, drying the product, heating in a tube furnace to 900°C under argon atmosphere to yield the Si/C composite, and optionally coating said Si/C composite with a graphitic carbon layer via CVD; or loading silicon nanoparticles into a tube furnace and coating them with a graphitic carbon layer via CVD.
25. The composite particle of claim 23, wherein the composite particle has an average diameter ($D_{[4,3]}$) from about 3 μm to about 15 μm , as measured by dynamic light scattering.
26. The composite particle of any one of claims 23-25, wherein the first and second anchoring components are selected from $-\text{C}^*(\text{R}^{\text{A1}})(\text{R}^{\text{A2}})\text{CH}(\text{R}^{\text{A3}})-$, $-\text{C}^*\text{HCH}-$, or $-\text{C}^*\text{MeCH}-$, wherein

C* represents the carbon covalently bonded to a graphitic carbon layer on the silicon-carbon composite particle; and

R^{A1}, R^{A2}, R^{A3} are each independently selected from H or Me.

- 5 27. The composite particle of any one of claims 23-26, wherein the polymerization initiating group comprises a radical stabilizing group and a leaving group.

28. The composite particle of claim 25, wherein the polymerizing initiating group is:

Rad-LG

- 10 wherein Rad is covalently bonded to the remainder of the first moiety and selected from $-(C_6(R^{Rad2})_4)C^*(R^{Rad1})_2$, $-(C_{10}(R^{Rad2})_6)C^*(R^{Rad1})_2$, $-C^*(R^{Rad3})_2$, $-OC(O)C^*(R^{Rad2})_2$, or $-NR^{Rad1}C(O)C^*(R^{Rad1})_2$,

wherein C* represents the carbon attached to LG;

each R^{Rad1} independently denotes H or methyl;

- 15 each R^{Rad2} independently denotes H or R^{Rad3};

R^{Rad3} denotes methyl; and

LG is selected from Cl, Br or I.

29. The composite particle of any one of claims 23-28, wherein the functional group denotes
20 H, -C₆H₅, -C₆F₅, -C(O)O-R^{FG3}, or CN,
wherein R^{FG3} denotes CH₃ or *tert*-butyl.

30. The composite particle of any one of claims 23-29, wherein the relative surface stoichiometry of first moiety is at least 0.5%.

25

31. The composition particle of any one of claims 23-30, wherein the silicon-carbon composite core comprises a graphitic carbon layer on the surface.

32. A method of forming a composite particle comprises the steps of

30 a) providing

i. silicon-carbon composite particle,

ii. a first moiety precursor comprising a first anchorable component and a polymerization initiating group, and

iii. a second moiety precursor comprising a second anchorable component and a

35 functional group;

b) decorating the silicon-carbon composite particle by reacting the first anchorable component of the first moiety precursor to form a first anchoring component of a first moiety and reacting the second anchorable component of the second moiety precursor to form a

second anchoring component of a second moiety, wherein the first anchoring component and the second anchoring component are covalently bonded to the silicon-carbon composite particle.

- 5 33. The method of any of claim 32, wherein the first and the second moiety precursors are immobilized on the surface of silicon-carbon composite particle in the same step.

34. The method of any one of claims 32 and 33, wherein the ratio of first moiety precursors to second moiety precursors used to decorate the silicon-carbon composite particle is from
10 1:9 to 9:1.

35. The method of any one of claims 32-34, wherein silicon-carbon core has an average diameter ($D_{[4,3]50}$) from about 3 μm to about 15 μm , as measured using dynamic light scattering.

- 15 36. The method of any one of claims 32-35, wherein the first moiety precursor comprises 4-(chloromethyl)benzenediazonium tetrafluoroborate (CBD), and wherein the second moiety precursor comprises *tert*-butyl acrylate, styrene, pentafluorostyrene, or acrylonitrile.

- 20 37. A polymer brush composite particle comprising a silicon-carbon composite core decorated with at least

a first moiety comprising a first anchoring component covalently bonded to the silicon-carbon core, and a polymeric moiety; and

- 25 a second moiety comprising a second anchoring component and one or more functional groups.

38. The polymer brush composite particle of claim 37, wherein the polymeric moiety is a linear polymeric chain with an average length of from about 2 repeat units to about 1,000 repeat units.

- 30 39. A method of forming a polymer brush composite particle, said method comprising:
a) providing a composite particle comprising:

a silicon-carbon core decorated with at least;

- 35 a first moiety comprising a first anchoring component covalently bonded to the silicon-carbon core, and a polymerization initiating group; and

a second moiety comprising a second anchoring component covalently bonded to the silicon-carbon core, and a functional group.

- b) forming a polymerization reaction composition comprising one or more polymerization catalysts and one or more monomers; and
- c) exposing the composite particle to the polymerization reaction composition.

5 40. The method of claim 39, wherein the polymer brushes are synthesized by SIP (surface-initiated polymerization).

41. The method of any one of claims 39 or 40, wherein the polymerization reaction composition is formed from

- 10 a) a polymerization composition comprising at least one dormant transition metal catalyst,
- b) an activation agent comprising an oxygen scavenger, and
- c) one or more monomers, wherein the one or more monomers may be provided as a part of the polymerization composition, a part of the activation agent or as a discrete
- 15 composition.

42. An electrode is provided comprising a polymer brush layer adjacent to an electrically electrically conductive support comprising;
a first moiety featuring a first anchoring component covalently bonded to the electrically
20 conductive support, along with a polymerization initiating group; and
a second moiety comprising a second anchoring component covalently bonded to the electrically conductive support, along with one or more functional groups; and
an electroactive layer.

25 43. The electrode of claim 42, wherein the electroactive layer is;
a cathode comprising cathode active materials, such as lithium cobalt oxide (LiCoO_2 or LCO), lithium nickel manganese cobalt oxide (LiNiMnCoO_2 or NMC), lithium iron phosphate (LiFePO_4 or LFP), or lithium nickel cobalt aluminum oxide (LiNiCoAlO_2 or NCA) or
an anode comprising anode active materials, such as lithium metal or silicon anode.

30 44. The electrode of claim 42 or 43, wherein the first and second anchoring components are selected from $\text{Si}^+(\text{R}^{\text{A1}})(\text{R}^{\text{A2}})(\text{R}^{\text{A3}})$, wherein
 Si^+ represents silicon covalently bonded to a partially oxidized surface of the electrically conductive support; and
35 R^{A1} , R^{A2} , R^{A3} are each independently selected from alkoxy groups, such as methoxy, ethoxy, *iso*-propoxy, and butoxy.

45. The electrode of any one of claims 42 to 43, wherein the polymerization initiating group comprises a radical stabilizing group and a leaving group.

46. The electrode of any one of claims 42-45, wherein the polymerizing initiating group is:

Rad-LG, wherein

Rad is covalently bonded to the remainder of the first moiety and selected from $-(C_6(R^{Rad2})_4)C^*(R^{Rad1})_2$, $-(C_{10}(R^{Rad2})_6)C^*(R^{Rad1})_2$, $-C^*(R^{Rad3})_2$, $-OC(O)C^*(R^{Rad2})_2$, or $-NR^{Rad1}C(O)C^*(R^{Rad1})_2$, wherein

C* represents the carbon attached to LG;
each R^{Rad1} independently denotes H or methyl;
each R^{Rad2} independently denotes H or R^{Rad3} ;
 R^{Rad3} denotes methyl; and
LG is selected from Cl, Br or I.

47. The electrode of any one of claims 42-46, wherein the functional group denotes H, $-C_6H_5$, $-C_6F_5$, $-C(O)O-R^{FG3}$, or CN, wherein R^{FG3} denotes CH_3 or *tert*-butyl.

48. The electrode of any one of claims 42-47, wherein the relative surface stoichiometry of the first moiety is at least 0.5%.

49. A method of forming a polymer brush decorated electrically conductive support comprising:

providing:

- i. an electrically conductive support,
- ii. a first moiety precursor comprising a first anchorable component and a polymerization initiating group, and
- iii. a second moiety precursor comprising a second anchorable component and a functional group;

decorating the electrically conductive support by reacting the first anchorable component of the first moiety precursor to form a first anchoring component of a first moiety and reacting the second anchorable component of the second moiety precursor to form a second anchoring component of a second moiety, wherein the first anchoring component and the second anchoring component are covalently bonded to the electrically conductive support.

50. The method of claim 49, wherein the first and the second moiety precursors are immobilized on the surface of the electrically conductive support simultaneously.

51. The method of any of claims 50 or 51, wherein the ratio of first moiety precursors to second moiety precursors used to decorate the electrically conductive support is from 1:9 to 9:1.

5

52. The method of any one of claims 50-51, wherein the first moiety precursor comprises p-chloromethyl)phenyltrimethoxy silane (CPTMS) and 3-trimethoxysilylpropyl 2-bromo-2-methyl-propionate (BPTMS); and wherein the second moiety precursor comprises 4-aminopropyltrimethoxysilane (APTMS).

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53. A polymer brush decorated electrically conductive support comprising an electrically conductive support decorated with at least:

a first moiety comprising a first anchoring component covalently bonded to the electrically conductive support, and a polymeric moiety; and a second moiety comprising a second anchoring component and one or more functional groups, the one or more functional groups including α -bromoisobutyryl bromide (BiBB).

15

54. The polymer brush decorated electrically conductive support of claim 53, wherein the polymeric moiety is a linear polymeric chain with an average length of from about 2 repeat units to about 1,000 repeat units.

20

55. A method of forming a polymer brush decorated electrically conductive support, said method comprising:

providing an electrically conductive support comprising:

25 a first moiety comprising a first anchoring component covalently bonded to the electrically conductive support, and a polymerization initiating group; and

a second moiety comprising a second anchoring component covalently bonded to the electrically conductive support, and a functional group.

forming a polymerization reaction composition comprising one or more polymerization catalysts and one or more monomers; and

30

exposing the decorated electrically conductive support to the polymerization reaction composition.

56. The method of claim 55, wherein the polymer brushes are synthesized by SIP (surface-initiated polymerization).

35

57. The method of claim 54 or claim 55, wherein the polymerization reaction composition is formed from:

a polymerization composition comprising at least one dormant transition metal catalyst, an activation agent comprising an oxygen scavenger, and one or more monomers, wherein the one or more monomers may be provided as a part of the polymerization composition, a part of the activation agent or as a discrete composition.