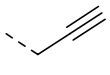
[0006] In a first aspect is an array that includes a support, a cross-linked epoxy polyhedral oligomeric silsesquioxane (POSS) resin film on a surface of the support, and a patterned hydrophobic polymer layer on the cross-linked epoxy POSS resin film, wherein the patterned hydrophobic polymer layer defines exposed discrete areas of the cross-linked epoxy POSS resin film, and a polymer coating is attached to the exposed discrete areas.

[0007] In some aspects are methods of forming arrays of this first aspect, which comprise forming a patterned hydrophobic polymer layer on a cross-linked epoxy POSS resin film on a support surface, thereby exposing discrete areas of the cross-linked epoxy POSS resin film. This method may further comprise applying a polymer coating to form an attached coating portion on the exposed discrete areas and an unattached coating portion on the patterned hydrophobic layer; and washing the unattached coating portion off of the patterned hydrophobic layer. The method may further comprise forming the cross-linked epoxy POSS resin film on the support surface, the forming involving: mixing an epoxy silane and at least one epoxy POSS monomeric unit in the presence of a photoacid generator and optionally a sensitizer to form a resin precursor; depositing the resin precursor on the support surface; and curing the resin precursor to form the cross-linked epoxy POSS resin film.

[0008] In a second aspect, an array includes a support, a modified epoxy POSS resin film on a surface of the support, and a patterned hydrophobic polymer layer on the modified epoxy POSS resin film, where the patterned hydrophobic polymer layer defines exposed discrete areas of the cross-linked epoxy POSS resin film. In some instances, the modified epoxy POSS resin film includes a polymer growth initiation site, and the patterned hydrophobic polymer layer defines exposed discrete areas of the modified epoxy POSS resin film. A polymer brush is attached to the polymer growth initiation site in the exposed discrete areas. In some respects, the array comprises a support, a modified epoxy polyhedral oligomeric silsesquioxane (POSS) resin film on a surface of the support, the modified epoxy POSS resin film including a polymer growth initiation site, a patterned hydrophobic polymer layer on the modified epoxy POSS resin film, the patterned hydrophobic polymer layer defining exposed discrete areas of the modified epoxy POSS resin film, and a polymer brush attached to the polymer growth initiation site in the exposed discrete areas.

[0009] Methods for producing arrays of the second aspect as described herein comprise forming a patterned hydrophobic polymer layer on a modified epoxy polyhedral oligomeric

[00049] As used herein, "alkynyl" refers to a straight or branched hydrocarbon chain containing one or more triple bonds (e.g., ). The alkynyl group may have 2 to 20 carbon atoms. The alkynyl group may be designated, for example, as "C2-4 alkynyl," which indicates that there are two to four carbon atoms in the alkynyl chain.

[00050] An “amino” functional group refers to an $-NR_aR_b$ group, where R_a and R_b are each independently selected from hydrogen (e.g., ), C1-6 alkyl, C2-6 alkenyl, C2-6 alkynyl, C3-7 carbocyclyl, C6-10 aryl, 5-10 membered heteroaryl, and 5-10 membered heterocyclyl, as defined herein.

[00051] As used herein, "aryl" refers to an aromatic ring or ring system (i.e., two or more fused rings that share two adjacent carbon atoms) containing only carbon in the ring backbone. When the aryl is a ring system, every ring in the system is aromatic. The aryl group may have 6 to 18 carbon atoms, which may be designated as C6-18. Examples of aryl groups include phenyl, naphthyl, azulenyl, and anthracenyl.

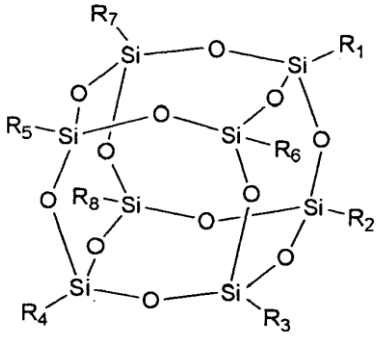
[00052] As used herein, the term “attached” refers to the state of two things being joined, fastened, adhered, connected or bound to each other. For example, a nucleic acid can be attached to a polymer coating by a covalent or non-covalent bond. A covalent bond is characterized by the sharing of pairs of electrons between atoms. A non-covalent bond is a chemical bond that does not involve the sharing of pairs of electrons and can include, for example, hydrogen bonds, ionic bonds, van der Waals forces, hydrophilic interactions and hydrophobic interactions.

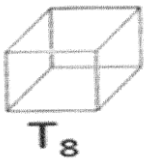
[00053] An “azide” or “azido” functional group refers to $-N_3$ (e.g., ).

[00054] As used herein, "carbocyclyl" means a ring or ring system containing carbon atoms in the ring backbone. When the carbocyclyl is a ring system, two or more rings may be joined together in a fused, bridged or spiro-connected fashion. Carbocyclyls may have any degree of saturation, provided that at least one ring in a ring system is not aromatic. Thus, carbocyclyls include cycloalkyls, cycloalkenyls, and cycloalkynyls. The carbocyclyl group may have 3 to 20 carbon atoms (i.e., C3-20).

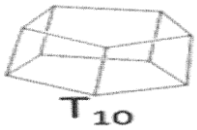
[00055] As used herein, “curing” means treatment of a polymer or resin precursor to promote polymerization and cross-linking. With respect to the POSS resin film described herein, curing refers to polymerization and cross-linking of the POSS resin precursors and/or components. Curing may be accomplished under a variety of conditions, such as exposure to actinic radiation, such as visible light radiation or ultraviolet (UV) radiation, or radiation of a wavelength between

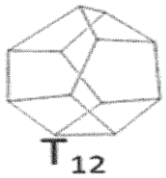
[00077] As used herein, the terms "polymer coating" and "polymer brush" are intended to mean a semi-rigid polymeric material that is permeable to liquids and gases and that is tethered to the substrate/support. The polymer coating and polymer brush may be a hydrogel that can swell when liquid is taken up and can contract when liquid is removed by drying. The polymer coating may be deposited, and the polymer brush may be grown from a polymer growth initiation site.

[00078] As used herein, the term "polyhedral oligomeric silsesquioxane" (POSS) refers to a chemical composition that is a hybrid intermediate ($RSiO_{1.5}$) between that of silica (SiO_2) and silicone (R_2SiO). The composition is an organosilicon compound with the chemical formula $[RSiO_{3/2}]_n$, where the R groups can be the same or different. The composition may comprise one or more different cage or core structures as monomeric units. In some instances, the structure comprises a polyoctahedral cage or core structure. For example, the polyhedral structure may be a T_8 structure, such as: 

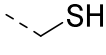
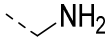
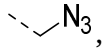
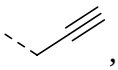
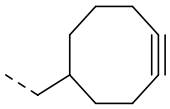
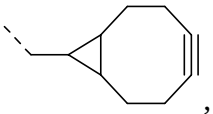
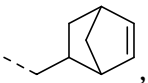
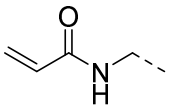
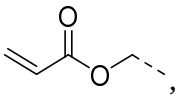
and represented by: 

. This monomeric unit typically has eight arms of functional groups R_1 through R_8.

[00079] The monomeric unit may have a cage structure with 10 silicon atoms and 10 R groups, referred to as T_{10}, such as: 

, or may have a cage structure with 12 silicon atoms and 12 R groups, referred to as T_{12}, such as: 

. The POSS material may comprise T_6, T_{14}, or T_{16} cage structures. The average cage content can be adjusted during the synthesis, and/or controlled by purification methods, and a distribution of cage sizes of the monomeric

to 20, , , , , , , , , and , and wherein --- represents an alkylsilane (e.g., by reaction of the hydroxyl groups with a trialkoxyalkylsilane), a poly(ethylene glycol)-silane (e.g., by reaction of the hydroxyl groups with a trialkoxysilane poly(ethylene glycol)), or an alkyl halide-silane (e.g., by reaction of the hydroxyl groups with an alkyl halide), or a polyethylene glycol chain, or any other silane that can form a tripodal connection with the hydroxyl group(s), or another group that can form a C-C-O- connection at the hydroxyl group(s). These functional groups, or any other functional groups that can withstand the processing that is performed during the formation of the patterned hydrophobic coating layer 16, may be used. The process conditions may also be adjusted to utilize a desirable functional group. While several examples of functional groups have been provided, it is to be understood that other hydrophilic or hydrophobic functional groups that can be covalently bonded to, or entrapped by the epoxy POSS resin film 14, and that introduces a desirable functionality to the epoxy POSS resin film 14 may be used. Still further, derivatives of the various functional groups FG and/or substituted variations of the functional groups FG may be used. In other examples, the polymer coating can be coated and cured to the cross-linked epoxy POSS resin film directly after plasma ashing, without a separate silanization or functionalization step.

[000122] The method used to attach the functional group FG to the hydroxyl groups of the cross-linked epoxy POSS resin film 14 may vary depending upon the functional group FG that is being used. Examples of suitable methods include vapor deposition, the YES method, solution deposition methods, or other deposition methods.

[000123] With Route B, the cross-linked epoxy POSS resin film 14 is modified to form a functionalized cross-linked epoxy POSS resin film 14'. The patterned hydrophobic polymer layer 16 (including its interstitial regions 20 and depressions 18) may then be formed in the manner previously described on the functionalized cross-linked epoxy POSS resin film 14'. In this example, discrete portions of the functionalized cross-linked epoxy POSS resin film 14' are exposed at the depressions 18.

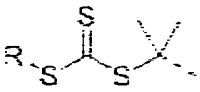
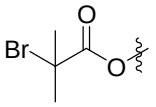
structure. Examples of the other functional group include any of the examples of the functional group FG.

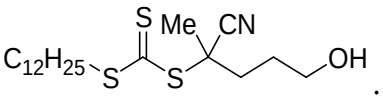
[000147] Resin precursors including the modified epoxy POSS monomeric unit(s) may include from about 50 mol% to about 90 mol% of the epoxy POSS monomeric unit(s) and from about 10 mol% to about 50 mol% of the modified epoxy POSS monomeric unit(s) (i.e., 100 mol% - X mol% of the epoxy POSS monomeric unit(s)). As such, the mass or molar ratio of epoxy POSS monomeric unit(s) to modified epoxy POSS monomeric unit(s) in some examples of the resin precursors ranges from about 1:1 to about 9:1. In these resin precursors, when two different (non-modified) epoxy POSS monomeric units are used in combination, any suitable mass or molar ratio of the two units may be selected. For example, a first epoxy POSS monomeric unit (e.g., epoxycyclohexylalkyl POSS) may be present in an amount (Y) ranging from about 10 mol% to about 90 mol% of the total amount of epoxy POSS monomeric units and a second epoxy POSS monomeric unit (e.g., glycidyl POSS) may make up the balance of the total epoxy POSS monomeric units (i.e., 100 mol% of epoxy POSS monomeric units - Y mol%). In other examples, any of the epoxy POSS monomeric units and any of the modified epoxy POSS monomeric units may be present in an amount ranging from about 10 mol% to about 90 mol%.

[000148] The use of the modified epoxy POSS monomeric unit to form the resin film introduces the functional group FG directly into the backbone of the resin film, and thus provides a site (other than the unreacted epoxy groups) for attachment of the polymeric coating 22 without having to perform further processes on the resin film as described in Route B.

[000149] FIGS. 2A through 2D together illustrate another example of the method disclosed herein, which forms another example of the array disclosed herein. FIG. 2C is an enlarged view of a depression of the array that is formed.

[000150] In the example method(s) shown in FIGS. 2A through 2D, a modified epoxy POSS resin film 14'' is formed, which includes a controlled radical polymerization (CRP) agent (shown schematically as 26 in FIG.2C) incorporated into the cross-linked matrix. The CRP agent 26 may be a reversible addition-fragmentation chain transfer (RAFT) agent or an atom transfer radical polymerization (ATRP) initiator. For the RAFT agents, the orientation of the thiocarbonyl group at the surface affects the polymerization. In one example, the RAFT agent is capable of covalently attaching to the surface of the modified epoxy POSS resin film 14'' via the

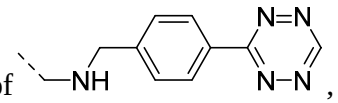
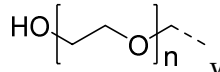
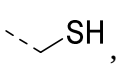
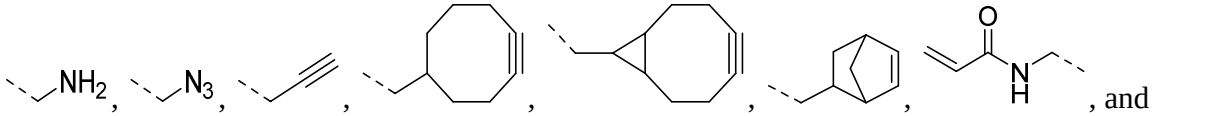
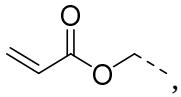
R_8 or R_{10} or R_{12} and having the CRP agent 26 as at least one of R_1 through R_8 or R_{10} or R_{12}. As such, in this example, the CRP agent 26 is incorporated directly into the POSS core or cage structure. As examples, any RAFT agent with the structure  and any ATRP initiator with the structure  may be used, e.g., 2-azidoethyl 2-bromoisobutyrate, 2-bromoisobutyric anhydride, bromoisobutyryl bromide, or poly(ethylene glycol) bis(2-bromoisobutyrate). For example, the RAFT agent may be:



Other suitable RAFT agents are dithiobenzoates, trithiocarbonates, and dithiocarbamates. The specific RAFT agents or ATRP initiators previously mentioned may also be used to modify the epoxy POSS core/cage.

[000159] In Route C, the resin precursor including the CRP-containing monomeric unit(s) may include from about 50 mol% to about 90 mol% of the epoxy POSS monomeric unit(s) and from about 10 mol% to about 50 mol% of the CRP-containing monomeric unit(s) (i.e., 100 mol% - X mol% of the epoxy POSS monomeric unit(s)). As such, the molar or mass ratio of epoxy POSS monomeric unit(s) to CRP-containing monomeric unit(s) in some examples of the resin precursors ranges from about 1:1 to about 9:1. As one example, the molar or mass ratio of total epoxy POSS monomeric units (e.g., epoxycyclohexylalkyl POSS and glycidyl POSS) to epoxy-functionalized CRP agent(s) ranges from about 1:1 to about 9:1. In these resin precursors, when two different (non-modified) epoxy POSS monomeric units are used in combination, any suitable mass or molar ratio of the two units may be selected. For example, a first epoxy POSS monomeric unit (e.g., epoxycyclohexylalkyl POSS) may be present in an amount (Y) ranging from about 10 mol% to about 90 mol% of the total amount of epoxy POSS monomeric units and a second epoxy POSS monomeric unit (e.g., glycidyl POSS) may make up the balance of the total epoxy POSS monomeric units (i.e., 100 mol% of epoxy POSS monomeric units - Y mol%). In other examples, any of the epoxy POSS monomeric units and any of the CRP-containing monomeric unit(s) may be present in an amount ranging from about 10 mol% to about 90 mol%.

an alkyne functional group that has been attached at the hydroxyl group of the cross-linked epoxy POSS resin film.

[000170] Examples of suitable functional groups for Route D are selected from the group consisting of ,  wherein n ranges from 1 to 20, , , and , and wherein --- represents a species that is capable of reacting with the –OH group of the cross-linked epoxy POSS resin film. Examples of --- include an alkylsilane (e.g., by reaction of the hydroxyl groups with a trialkoxyalkylsilane), a poly(ethylene glycol)-silane (e.g., by reaction of the hydroxyl groups with a trialkoxysilane poly(ethylene glycol)), or an alkyl halide-silane (e.g., by reaction of the hydroxyl groups with an alkyl halide), or a polyethylene glycol chain, or any other silane that can form a tripodal connection with the hydroxyl group(s), or another group that can form a C-C-O- connection at the hydroxyl group(s). Some specific examples include of the functional groups include silane PEG azide (Polysciences, Inc.), silane PEG alkyne (Polysciences, Inc.), 3-azidopropyltriethoxysilane (Gelest), or (Bicyclo[2.2.1]hept-5-en-2-yl)triethoxysilane. While several examples have been provided, it is to be understood that any functional group that can attach to the hydroxyl group(s) of the cross-linked epoxy POSS resin film and to the CRP agent 26 may be used.

[000171] The method used to attach the functional group to the hydroxyl groups of the cross-linked epoxy POSS resin film may vary depending upon the functional group that is being used. Examples of suitable methods include vapor deposition, the YES method, solution deposition methods (e.g., dunk coating), or other deposition methods.

[000172] Any of the CRP agents 26 previously described (e.g., 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid 3-azido-1-propanol ester, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanol, etc.) may then be attached to the functional group of the cross-linked epoxy POSS resin film. The method used to attach the CRP agents 26 to the functional group of the cross-linked epoxy POSS resin film may vary depending upon the

CRP agent 26 that is being used. Examples of suitable methods include solution deposition methods.

[000173] With Route D, the cross-linked epoxy POSS resin film is first modified to add the previously described functional group(s), and then the CRP agent 26 is attached to at least some of the functional groups to form an example of the modified epoxy POSS resin film 14'' (which includes a polymer growth initiation site).

[000174] Like Route D, Route E involves attaching the CRP agent 26 to the backbone of the cross-linked matrix after the resin film 14'' has been cured.

[000175] In Route E, the resin precursor is a mixture including the epoxy POSS monomeric unit(s) and a modified epoxy POSS monomeric unit. In this example of the modified epoxy POSS monomeric unit, at least one of R_1 through R_8 or R_{10} or R_{12} is an epoxy group (for incorporation into the epoxy POSS resin film 14'') and at least one of R_1 through R_8 or R_{10} or R_{12} is a non-epoxy functional group that can attach to the CRP agent 26 (e.g., the non-epoxy functional group may be selected from the group consisting of an azide, a thiol, a poly(ethylene glycol), a norbornene, and a tetrazine). This non-epoxy functional group will be integrated into an initially modified epoxy POSS resin film during curing.

[000176] Resin precursors for Route E may include from about 50 mol% to about 90 mol% of the epoxy POSS monomeric unit(s) and from about 10 mol% to about 50 mol% of the modified epoxy POSS monomeric unit(s) (i.e., 100 mol% - X mol% of the epoxy POSS monomeric unit(s)). As such, the molar or mass ratio of epoxy POSS monomeric unit(s) to modified epoxy POSS monomeric unit(s) in some examples of the resin precursors ranges from about 1:1 to about 9:1. In these resin precursors, when two different (non-modified) epoxy POSS monomeric units are used in combination, any suitable mass or molar ratio of the two units may be selected. For example, a first epoxy POSS monomeric unit (e.g., epoxycyclohexylalkyl POSS) may be present in an amount (Y) ranging from about 10 mol% to about 90 mol% of the total amount of epoxy POSS monomeric units and a second epoxy POSS monomeric unit (e.g., glycidyl POSS) may make up the balance of the total epoxy POSS monomeric units (i.e., 100 mol% of epoxy POSS monomeric units - Y mol%). In other examples, any of the epoxy POSS monomeric units and any of the modified monomeric unit(s) may be present in an amount ranging from about 10 mol% to about 90 mol%.

Claims

1. A method, comprising:

forming a patterned hydrophobic polymer layer on a cross-linked epoxy polyhedral oligomeric silsesquioxane (POSS) resin film on a support surface, thereby exposing discrete areas of the cross-linked epoxy POSS resin film;

applying a polymer coating to form an attached coating portion on the exposed discrete areas and an unattached coating portion on the patterned hydrophobic layer; and

washing the unattached coating portion off of the patterned hydrophobic layer.

2. The method as defined in claim 1, further comprising forming the cross-linked epoxy POSS resin film on the support surface, the forming involving:

mixing an epoxy silane and at least one epoxy POSS monomeric unit in the presence of a photoacid generator and optionally a sensitizer to form a resin precursor;

depositing the resin precursor on the support surface; and

curing the resin precursor to form the cross-linked epoxy POSS resin film.

3. The method as defined in claim 2, wherein the mixing and depositing occur at the same time.

4. The method as defined in claim 2, wherein the epoxy silane is an epoxy silane bound to the support surface.

5. The method as defined in claim 1, further comprising forming the cross-linked epoxy POSS resin film on the support surface, the forming involving:

mixing an epoxy silane, epoxycyclohexylalkyl POSS, and glycidyl POSS in the presence of a photoacid generator and optionally a sensitizer to form a resin precursor;

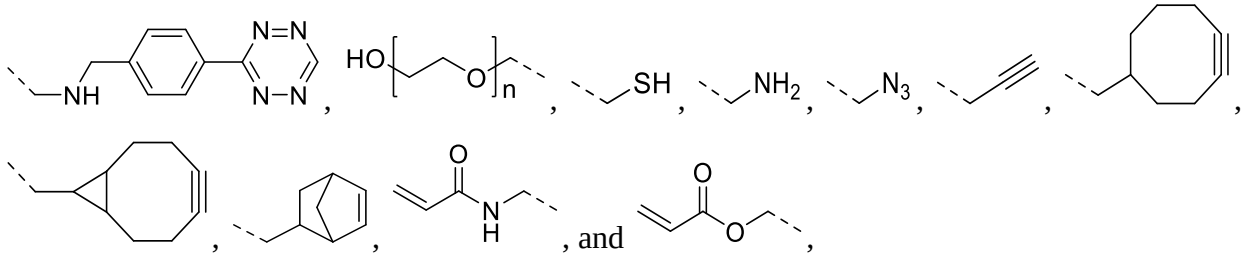
depositing the resin precursor on the support surface; and

curing the resin precursor to form the cross-linked epoxy POSS resin film.

6. The method as defined in claim 1, wherein prior to forming the patterned hydrophobic polymer layer, the method further comprises:

exposing the cross-linked epoxy POSS resin film to plasma ashing or a chemical treatment to introduce -OH groups to the cross-linked epoxy POSS resin film; and

attaching functional groups to at least some of the -OH groups, the functional groups being selected from the group consisting of:



wherein n ranges from 1 to 20, and

wherein --- represents an alkylsilane, a poly(ethylene glycol)-silane, an alkyl, or a polyethylene glycol chain.

7. The method as defined in claim 1, further comprising forming the cross-linked epoxy POSS resin film on the support surface, the forming involving:

mixing, in the presence of a photoacid generator and optionally a sensitizer, an epoxy silane, epoxycyclohexylalkyl POSS, glycidyl POSS, and a POSS core including at least one epoxy functional group and a non-epoxy functional group to form a resin precursor;

depositing the resin precursor on the support surface; and

curing the resin precursor to form the cross-linked epoxy POSS resin film.

8. The method as defined in claim 1, wherein washing involves sonication in water.

9. The method as defined in claim 1, wherein forming the patterned hydrophobic polymer layer involves:

i) depositing a hydrophobic polymer on the cross-linked epoxy POSS resin film; and patterning the deposited hydrophobic polymer using at least one of nanoimprint lithography and photolithography; or

ii) depositing the hydrophobic polymer in a pattern on the cross-linked epoxy POSS resin film using at least one of inkjet printing and microcontact printing.

10. The method as defined in claim 1, further comprising grafting an amplification primer to the attached coating portion.

11. A method, comprising:

forming a cross-linked epoxy POSS resin film on a support surface, where the forming involves mixing a support-bound epoxy silane with one or more epoxy-functionalized POSS reagents in the presence of a photoacid generator and optionally a sensitizer to form a support-bound resin precursor;

curing the resin precursor to form a support-bound cross-linked epoxy POSS resin film; and

forming a hydrophobic polymer layer on the cross-linked, support-bound epoxy POSS resin film, wherein the hydrophobic polymer layer is patterned to expose the cross-linked, support-bound epoxy POSS resin film in discrete areas or wells while remaining on the cross-linked, support-bound epoxy POSS resin film in interstitial areas of the cross-linked, support-bound epoxy POSS resin film between the discrete areas or wells.

12. The method as defined in claim 11, wherein the one or more epoxy-functionalized POSS reagents comprise an epoxycyclohexylalkyl POSS and a glycidyl POSS.

13. The method as defined in claim 11, further comprising reacting the support surface with an epoxy silane to form the support-bound epoxy silane.