

CORE-SHELL NANOPARTICLES AND THEIR USE IN ELECTROCHEMICAL CELLS

RELATED APPLICATION

This application claims priority under applicable laws and regulations to Singapore application No. 10201710771Q filed on December 22nd, 2017, the content of which is
5 incorporated herein by reference in its entirety for all purposes.

TECHNICAL FIELD

The technical field generally relates to electrode materials comprising core-shell nanoparticles (NPs), their methods of synthesis and use in lithium-sulfur (Li-S) electrochemical cells.

10 BACKGROUND

A lithium-sulfur (Li-S) battery generally comprises a lithium metal anode, a cathode comprising elemental sulfur (S_8) and an electrolyte. Lithium-sulfur batteries are within the most promising candidates for satisfying emerging market demands. Indeed, Li-S batteries offer a theoretical capacity and an energy density of $1,675 \text{ mA h g}^{-1}$ and $2,500$
15 kW kg^{-1} respectively, through their multielectron redox reaction illustrated by the equation $16\text{Li} + S_8 \rightarrow 8 \text{Li}_2\text{S}$. Moreover, sulfur has a very high natural and synthetic abundance. The synthetic abundance is attributed to the fact that sulfur is a by-product of petroleum refining.

However, the practical applications of lithium-sulfur batteries are hindered
20 predominantly by the sulfur particles' poor electronic conductivity, the dissolution of intermediate polysulfides (Li_2S_x , where $3 < x \leq 8$) into the electrolyte, and the large volumetric expansion ($\sim 80\%$) upon lithiation, which result in a capacity fading and a low Coulombic efficiency. Once dissolved, Li_2S_x species are involved in a phenomenon called "shuttle effect" which destabilizes the lithium surface. This phenomenon also
25 plays a key role in reducing the battery stability and its low coulombic efficiency.

Extensive efforts have been devoted to improving the electronic conductivity of sulfur particles and to reduce the Li_2S_x "shuttle effect" in order to improve long-term cycling

performances of Li-S batteries. One of the proposed strategies is to encapsulate sulfur particles in porous conductive materials such as carbon, graphene oxide and/or a conductive polymer. However, none of these has been found optimal to prevent Li_2S_x dissolution. Structured metal oxides, metal nitrides, metal carbides and chalcogenides have also been extensively studied as host materials due to their strong chemical interactions with dissolved Li_2S_x . Indeed, they were found to significantly improved the cell's lifetime. However, these materials are known for their low electronic conductivity and therefore impeded the electron transport pathway, resulting in low sulfur utilization and poor cycling stability. Considerable efforts have also been made to tackle the third challenge (i.e. the volumetric expansion upon lithiation). One of the proposed strategies is the encapsulation of sulfur particles in composites with core-shell morphology. Using this approach significantly improved cycling stability and efficiency were obtained, but there is still room for improvement.

There is thus a need alternative and complementary technological approaches for improving the long-term cycling performance of Li-S batteries.

SUMMARY

According to one aspect, the present application relates to core-shell nanoparticles comprising a porous metal oxide core of formula M_yO_x , wherein M defines at least one transition metal, y is an integer selected from 1 to 4, and x is an integer selected from 1 to 8, x and y being selected to achieve electroneutrality; elemental sulfur (S_8) as an electrochemically active material, the elemental sulfur being incorporated into the pores of the metal oxide core; and an outer shell surrounding the core, the outer shell comprising TiO_2 . In one embodiment, M is Mn, Fe, Co, Ni, Zn or a combination thereof, y is an integer from 1 to 3; and x is an integer from 1 to 7. In a preferred embodiment, M is Mn, preferably M_yO_x is MnO . In a further embodiment, the M:Ti molar ratio is of about 10:1 to about 0.5:1, or about 4:1 to about 0.7:1, preferably about 3:1 to about 0.7:1 and most preferably about 2:1 to about 0.8:1.

According to another aspect, there is provided a nanocomposite material comprising the core-shell nanoparticles as defined herein and a first conductive nanomaterial. In one

embodiment, the core-shell nanoparticles are supported on the first conductive material, for instance, the latter being a nanocarbon nano-wire, nano-sheet, nano-belt, or a combination thereof.

According to another aspect, there is provided a method for producing core-shell nanoparticles or a nanocomposite material as herein defined, the method comprising:

5 nanoparticles or a nanocomposite material as herein defined, the method comprising: (a) contacting $M_y(\text{CO}_3)_x$ nanoparticles with TiO_2 or a TiO_2 precursor to form TiO_2 coated $M_y(\text{CO}_3)_x$ nanoparticles ($M_y(\text{CO}_3)_x/\text{TiO}_2$); (b) thermally treating the $M_y(\text{CO}_3)_x/\text{TiO}_2$ nanoparticles from step (a) at elevated temperature under inert gas to form core-shell $M_y\text{O}_x/\text{TiO}_2$ nanoparticles; (c) optionally thermally treating the core-shell $M_y\text{O}_x/\text{TiO}_2$ nanoparticles with a first conductive nanomaterial under inert gas at elevated temperature, optionally in the presence of hydrogen gas, to form a nanocomposite material; (d) optionally partly removing $M_y\text{O}_x$ after step (b) or (c) by treatment with an acid; (e) milling the obtained nanoparticles or nanocomposite material of step (b), (c) or (d) with elemental sulfur (S_8) to produce a mixture; and (f) heating the mixture obtained

10 nanoparticles with a first conductive nanomaterial under inert gas at elevated temperature, optionally in the presence of hydrogen gas, to form a nanocomposite material; (d) optionally partly removing $M_y\text{O}_x$ after step (b) or (c) by treatment with an acid; (e) milling the obtained nanoparticles or nanocomposite material of step (b), (c) or (d) with elemental sulfur (S_8) to produce a mixture; and (f) heating the mixture obtained

15 in step (f) at elevated temperature under inert gas to cause the sulfur to melt-diffuse into the into the pores of the nanoparticles and/or nanocomposite material.

According to yet a further aspect, there is provided a method for producing nanoparticles or a nanocomposite material as herein defined, the method comprising:

20 nanoparticles or a nanocomposite material as herein defined, the method comprising: (a) synthesizing MnCO_3 nanoparticles by a microemulsion-mediated solvothermal reaction; (b) reacting the MnCO_3 nanoparticles from step (a) in a polar solvent with a TiO_2 precursor, preferably an organotitanium compound, to produce $\text{MnCO}_3/\text{TiO}_2$ nanoparticles; (c) thermally treating the $\text{MnCO}_3/\text{TiO}_2$ nanoparticles at elevated temperature under inert gas to produce core-shell MnO/TiO_2 nanoparticles; (d) optionally thermally treating the core-shell MnO/TiO_2 nanoparticles with a first

25 conductive nanomaterial under inert gas at elevated temperature, optionally in the presence of hydrogen gas, to form a nanocomposite material; (e) optionally partly removing MnO after step (c) or (d) by treatment with an acid; (f) milling the nanoparticles or nanocomposite obtained in step (c), (d) or (e) with elemental sulfur to produce a mixture; and (g) heating the mixture obtained in step (f) at elevated

30 temperature under inert gas to cause the sulfur to melt-diffuse into the nanocomposite.

According to another aspect, the present technology also contemplates the core-shell nanoparticles or nanocomposite material obtained by a method as herein defined.

According to a further aspect, the present application relates to an electrode material comprising the core-shell nanoparticles or nanocomposite material as defined herein.

- 5 According to yet another aspect, the present application relates to a positive electrode comprising the electrode material as defined herein on a current collector.

According to another aspect, the present application relates to an electrochemical cell comprising the positive electrode as defined herein, a negative electrode and an electrolyte.

- 10 According to another aspect, the present application relates to a lithium sulfur battery comprising at least one electrochemical cell as defined herein.

According to another aspect, the present application relates to a lithium sulfur battery comprising the core-shell nanoparticles or nanocomposite material as defined herein.

- 15 According to a further aspect, the present application relates to the use of the core-shell nanoparticle as defined herein in a lithium sulfur battery.

According to yet a further aspect, the present technology also contemplates the use of a lithium sulfur battery as herein defined in mobile devices, for example mobile phones, cameras, tablets or laptops, in electric or hybrid vehicles, or for the storage of renewable energy.

20 **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 presents transmission electron microscopy (TEM) images of the MnCO_3 nanocubes as described in Example 1(a) at (A) low magnification and (B) high magnification.

- 25 Figure 2 displays the characterization of $\text{MnCO}_3/\text{TiO}_2$ core-shell nanocubes as described in Example 1(b) by: (A) TEM image; (B, C) high resolution TEM (HRTEM) images; (D) high-angle annular dark-field scanning transmission electron microscopy

(HAADF-STEM) image; (E) Ti and Mn map of the nanocube boxed in (D); (F) Ti map of the nanocube boxed in (D); (G) Mn map of the nanocube boxed in (D); and (H) O map of the nanocube boxed in (D).

Figure 3 presents the characterization of the nanocomposites: (A) powder XRD pattern of $\text{MnCO}_3/\text{TiO}_2$, MnO/TiO_2 , $\text{MnO}/\text{TiO}_2/\text{RGO}$, $\text{MnO}/\text{TiO}_2\text{-S}$, $\text{MnO}/\text{TiO}_2/\text{RGO-S}$ and $\text{MnO}/\text{TiO}_2/\text{RGO-acid-S}$ (each indicated); (B) N_2 adsorption/desorption isotherms of MnO/TiO_2 , $\text{MnO}/\text{TiO}_2/\text{RGO}$ and $\text{MnO}/\text{TiO}_2/\text{RGO-acid}$; and (C) thermogravimetric analysis (TGA) curves of $\text{MnO}/\text{TiO}_2\text{-S}$ and $\text{MnO}/\text{TiO}_2/\text{RGO-S}$.

Figure 4 displays the characterization of the MnO/TiO_2 core-shell nanocubes as described in Example 1(c) by: (A) TEM image; (B) HRTEM image; (C) HAADF-STEM image; (D) Ti and Mn map of the nanocube boxed in (C); (E) Ti map of the nanocube boxed in (C); (F) Mn map of the nanocube boxed in (C); and (G) O map of the nanocubes boxed in (C).

Figure 5 shows the linear energy-dispersive X-ray (EDX) profile of $\text{MnO}/\text{TiO}_2/\text{RGO}$ as described in Example 2.

Figure 6 presents the characterization of the $\text{MnO}/\text{TiO}_2/\text{RGO}$ nanocomposites as described in Example 2 by: (A) TEM image; (B, C) HRTEM images; (D) HAADF-STEM image; (E) C map of the nanocube boxed in (D); (F) Ti map of the nanocube boxed in (D); and (G) Mn map of the nanocube boxed in (D).

Figure 7 displays the characterization of the $\text{MnO}/\text{TiO}_2/\text{RGO-S}$ nanocomposite material as described in Example 3 by: (A) TEM image; (B) HRTEM image; (C) HAADF-STEM images; (D) Ti map of the nanocomposite in (C); (E) Mn map of the nanocomposite in (C); (F) S map of the nanocomposite in (C); and (G) O map of the nanocomposite material in (C).

Figure 8 shows the characterization of the $\text{MnO}/\text{TiO}_2\text{-S}$ nanocomposite material as described in Example 3 by: (A) TEM image; (B) HRTEM image; (C) HAADF-STEM images; (D) Ti and Mn map of the nanocomposite in (C); (E) Ti map of the

nanocomposite in (C); (F) Mn map of the nanocomposite in (C); and (G) O map of the nanocomposite material in (C).

Figure 9 displays the EDX profile of MnO/TiO₂/RGO-acid as described in Example 4.

Figure 10 presents the characterization of MnO/TiO₂/RGO-acid nanocomposites as described in Example 4 by: (A) low magnification TEM image; (B) high magnification TEM image; (C) HAADF-STEM image; (D) Ti map of nanocomposite in (C); (E) Mn map of nanocomposite in (C); and (F) O map of the nanocomposite material in (C).

Figure 11 displays the characterization of the MnO/TiO₂/RGO-acid-S nanocomposite material as described in Example 4 by: (A) TEM image; (B) HRTEM image; (C) HAADF-STEM image; (D) Ti map of nanocomposite in (C); (E) Mn map of nanocomposite in (C); (F) S map of nanocomposite in (C); and (G) O map of the nanocomposite material in (C).

Figure 12 demonstrates the electrochemical properties of nanocomposite materials and sulfur nanocrystals as cathode materials for Li-S battery: (A) CV profiles of MnO/TiO₂/RGO-acid-S recorded at a scan rate of 0.05 mV/S; (B) and (C) respectively initial charging and discharging curves at a 0.1 C rate and cycling performance recorded at a 0.2 C rate of MnO/TiO₂/RGO-acid-S, MnO/TiO₂/RGO-S, MnO/TiO₂-S nanocomposite material and sulfur nanocrystals at room temperature; and (D) electrochemical impedance curves of MnO/TiO₂/RGO-acid-S, MnO/TiO₂/RGO-S and MnO/TiO₂-S nanocomposites.

Figure 13 displays the CV profiles of MnO/TiO₂/RGO-S and MnO/TiO₂-S recorded at a scan rate of 0.05 mVs⁻¹ over a potential range of 1.5 to 2.8 (V vs. Li/Li⁺).

DETAILED DESCRIPTION

The following detailed description and examples are illustrative and should not be interpreted as further limiting the scope of the invention.

All technical and scientific terms and expressions used herein have the same definitions as those commonly understood by the person skilled in the art relating to the present

technology. The definition of some terms and expressions provided below take precedence over their common meaning given in the literature.

The expressions "nanocomposite material" and "nanocomposite" used herein refer to a material made from at least two constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components.

The term "nano" as used herein refers to an object having a nanoscale size (e.g., not more than 100 or not more than 500 nm) at least in one direction.

Unless mentioned otherwise, all ratios mentioned in the present application are weight ratios.

When an interval of values is mentioned in the present application, the lower and upper limits of the interval are, unless otherwise indicated, always included in the definition.

The term "approximately" or the equivalent term "about" as used herein means approximately in the region of, and around. When the term "approximately" or "about" is used in relation to a numerical value, it modifies it, for example, above and below by a variation of 10% in relation to the nominal value. This term may also take into account, for example, the experimental error of a measuring apparatus or rounding.

This application relates to core-shell nanoparticles (NPs) for use in the manufacture of electrochemical cells, particularly in lithium-sulfur (Li-S) electrochemical cells; and their methods of synthesis.

The present application thus proposes core-shell NPs which may be used in composite electrodes to improve the cyclability and to prevent electrochemical cells degradation.

The present application, for example relates to core-shell NPs comprising a porous nanocrystalline metal oxide (of formula M_yO_x) core which incorporates elemental sulfur (S_8) as an electrochemically active material and an amorphous TiO_2 outer shell. For example, core-shell NPs exhibit cubic or cubic-like morphology (e.g. rhombohedral). In one embodiment, the core-shell NPs may be deposited on a conductive nanomaterial,

for instance, reduced graphene oxide (RGO) to form RGO-supported M_yO_x/TiO_2 core-shell ($M_yO_x/TiO_2/RGO-S$) nanocomposites which can be used in cathode materials of electrochemical cells with advantageous capabilities.

5 The uniqueness of these materials lies at least in (i) the amorphous TiO_2 shell, which absorbs the volume expansion upon lithiation, and alleviates the Li_2S_x dissolution, and (ii) the porous nanocrystalline M_yO_x core, e.g. mesoporous, which provides strong chemical interactions with the lithium Li_2S_x ions. The $M_yO_x/TiO_2/RGO-S$ nanocomposites with different M:Ti molar ratios demonstrated good capacity, coulombic efficiency and cycling stability.

10 The present application, for example also relates to the synthesis of core-shell NPs defined herein via a wet chemical method. For instance, the process includes the preparation of monodispersed $M_y(CO_3)_x$ nanoparticles, for example, via a microemulsion-mediated solvothermal synthesis. These $M_y(CO_3)_x$ nanoparticles are then coated with a thin amorphous TiO_2 layer using a wet chemical step by reacting the
15 nanoparticles with a titanium oxide precursor, such as an organotitanium compound, in the presence of water. The $M_y(CO_3)_x/TiO_2$ nanoparticles are then thermally treated, e.g. annealed, to afford M_yO_x/TiO_2 core-shell nanoparticles. Without wishing to be bound by theory, one could believe that the elimination of CO_2 during this last process step would contribute to the formation of a porous, e.g. mesoporous, core structure. The present
20 description therefore also further relates to M_yO_x/TiO_2 core-shell nanoparticles, wherein the core M_yO_x is porous (or mesoporous) and crystalline and the shell comprises TiO_2 in amorphous form.

In another example, these core-shell NPs are used as intermediate to encapsulate elemental sulfur (S_8), the S_8 being incorporated in the core-shell NPs using a melt
25 diffusion method. The synthesis of nanoparticles with several M:Ti molar ratio is also demonstrated in the present application as well as its effect on the performance of electrochemical cells.

The core-shell NPs as described herein have a porous core which allows for the incorporation of elemental sulfur (S_8). NPs can exhibit improved sulfur absorption

capabilities which is highly dependent upon porosity and pore size distribution. In one embodiment, the number and/or size of pores can be increased by the partial removal of M through acidic treatment, thereby reducing the M:Ti molar ratio and leading to improved sulfur absorption capabilities. The NPs can also be annealed with conductive nanomaterials beforehand and the elemental sulfur may then be diffused therein as well. The resulting nanocomposite materials can be used as high-capacity cathode materials for lithium sulfur batteries.

The porous M_yO_x core reduces or prevents leakage of soluble polysulfide ions during battery operation from the core-shell NPs by adsorbing them in the M_yO_x core. The NPs also show a tolerance for volume expansion under operation conditions of the lithium batteries.

The present application proposes core-shell nanoparticles comprising

- a porous metal oxide core of formula M_yO_x ;
- elemental sulfur (S_8) as an electrochemically active material, the elemental sulfur being incorporated into the pores of the porous metal oxide core; and
- an outer shell surrounding the core, the outer shell comprising TiO_2 .

M defines at least one transition metal, y is an integer selected from 1 to 4 and x is an integer selected from 1 to 8, x and y being selected to achieve electroneutrality.

In one example, M is Mn, Fe, Co, Ni, Zn, or a combination thereof; y is an integer selected from 1 to 3; and x is an integer selected within the range of from 1 to 7.

Non-limiting examples of metal oxide cores of formula M_yO_x include manganese(II) oxide (MnO), manganese oxide (Mn_2O_4), manganese(II,III) oxide (Mn_3O_4), manganese(III) oxide (Mn_2O_3), manganese dioxide (MnO_2), manganese(VI) oxide (MnO_3), manganese(VII) oxide (Mn_2O_7), iron(II) oxide (FeO), iron(III) oxide (Fe_2O_3), iron(II,III) oxide (Fe_3O_4), cobalt(II) oxide (CoO), cobalt(III) oxide (Co_2O_3), cobalt(II,III) oxide (Co_3O_4), nickel(II) oxide (NiO), nickel(III) oxide (Ni_2O_3) and the like. For example, M is Mn, e.g. M_yO_x is MnO .

In one embodiment, the TiO_2 shell is in amorphous form, the metal oxide comprised in the core is in a crystalline form and the NPs have a cube-like morphology. In another example, the elemental sulfur comprises sulfur nanocrystals.

For example, the core-shell NPs as defined herein, have a M:Ti molar ratio of about 10:1 to about 0.5:1, preferably about 4:1 to about 0.7:1, preferably about 3:1 to about 0.7:1 and most preferably about 2:1 to about 0.8:1.

In another example, the core-shell NPs as defined herein, have an average size in the range of from about 10 to about 500 nm, preferably from about 75 to about 200 nm and an average shell thickness in the range of from about 1 to about 50 nm, preferably from about 5 to about 20 nm. The metal oxide core of the present nanoparticles has a porous morphology, for instance, a mesoporous morphology (i.e. pores having an average size below 50 nm). The specific surface area of the core-shell NPs before sulfur insertion, as measured by Brunauer–Emmett–Teller (B.E.T.), is between about 20 and about 150 m^2/g , or between about 30 and about 100 m^2/g , or between about 30 and about 60 m^2/g .

In another embodiment, a nanocomposite material is also contemplated, where the nanocomposite material comprises the core-shell NPs as described herein together with a first conductive agent. For instance, the nanocomposite material comprising the core-shell NPs as defined herein, wherein the nanoparticles are thermally treated with, e.g. annealed to, the first conductive nanomaterial. For instance, the NPs are supported on the first conductive material. Such nanocomposites have been shown to provide high capacity and cycling stability in electrochemical cells.

In one embodiment, the first conductive nanomaterial is a conductive nanocarbon nano-wire, nano-sheet, nano-belt, or a combination thereof. The first conductive nanomaterial is selected for its ability to improve the electrical conductivity of the NPs. For example, the first conductive nanomaterial is a reduced graphene oxide (RGO) nanosheet or a graphene nanosheet having a lateral size of about 50 to about 500 nm, preferably of about 100 to about 200 nm wherein the first conductive nanomaterial to NPs (excluding sulfur) weight ratio is about 1:1 to about 1:10, preferably about 1:2 to about 1:4. In

another embodiment, the nanocomposite material has specific surface area measured by Brunauer–Emmett–Teller (B.E.T.) of about 50 m²/g to about 150 m²/g, or about 50 m²/g to about 100 m²/g, preferably about 80 to about 100 m²/g, before addition of sulfur to the material. In another embodiment, the weight ratio of sulfur to the nanocomposite material before sulfur insertion is about 10:1 to about 1:2, preferably about 3:1 to about 1:1.

The core-shell NPs may be made through different methods. One method for the preparation of the present core-shell nanoparticles includes the steps of preparing core-shell M_yO_x/TiO₂ nanoparticles, wherein the M_yO_x core is porous (e.g. mesoporous) and the TiO₂ shell is amorphous; mixing the M_yO_x/TiO₂ nanoparticles with elemental sulfur; and heating at a temperature allowing the sulfur to melt and diffuse into the pores of the core. One method for preparing core-shell nanoparticles or nanocomposite materials as herein defined involves:

- (a) contacting M_y(CO₃)_x nanoparticles with TiO₂ or a TiO₂ precursor to form TiO₂ coated M_y(CO₃)_x nanoparticles (i.e. M_y(CO₃)_x/TiO₂);
- (b) thermally treating (e.g. annealing) the M_y(CO₃)_x/TiO₂ nanoparticles from step (a) at elevated temperature under inert gas to form core-shell M_yO_x/TiO₂ nanoparticles;
- (c) optionally thermally treating (e.g. annealing) the core-shell nanoparticles with a first conductive nanomaterial under inert gas at elevated temperature, optionally in the presence of hydrogen gas, to form a nanocomposite material;
- (d) optionally partly removing M_yO_x after step (b) or (c) by treatment with an acid;
- (e) milling the obtained nanoparticles or nanocomposite material with elemental sulfur (S₈) to produce a mixture; and
- (f) heating the obtained mixture obtained in step (e) at elevated temperature under inert gas to cause the sulfur to melt-diffuse into the pores of the nanoparticles and/or nanocomposite material.

The above process may further include step (c) or step (d) or both of steps (c) and (d) in any order. When step (c) is present, then the product obtained is a nanocomposite material.

For example, the acid of step (d) is a mineral acid, preferably H_2SO_4 or HCl , preferably used in a concentration of 0.1 to 5 M. In another example, the thermal treatment steps (b) and (c) when present, are performed each independently at a temperature of about 200 to about 500 °C, preferably about 300 to about 400 °C and the heating step (f) is performed at a temperature of about 140 to about 180 °C for about 5 to about 48 hours.

Another method for producing the nanoparticles or nanocomposite material herein described, e.g. $\text{MnO}/\text{TiO}_2\text{-S}$, $\text{MnO}/\text{TiO}_2\text{-acid-S}$, $\text{MnO}/\text{TiO}_2/\text{RGO-S}$, or $\text{MnO}/\text{TiO}_2/\text{RGO-acid-S}$, involves:

- (a) synthesizing of MnCO_3 nanoparticles by a microemulsion-mediated solvothermal reaction;
- (b) reacting the MnCO_3 nanoparticles from step (a) in a polar solvent with a TiO_2 precursor, preferably an organotitanium compound, to produce $\text{MnCO}_3/\text{TiO}_2$ nanoparticles;
- (c) thermally treating (e.g. annealing) the $\text{MnCO}_3/\text{TiO}_2$ nanoparticles at elevated temperature under inert gas to produce core-shell MnO/TiO_2 nanoparticles;
- (d) optionally thermally treating (e.g. annealing) the MnO/TiO_2 core-shell nanoparticles with a first conductive nanomaterial under inert gas at elevated temperature, optionally in the presence of hydrogen gas, to form a nanocomposite material;
- (e) optionally partly removing MnO after step (c) or (d) by treatment with an acid;
- (f) milling the nanoparticles or nanocomposite obtained in step (c), (d) or (e) with elemental sulfur to produce a mixture; and
- (g) heating the mixture obtained in step (f) at elevated temperature under inert gas to cause the sulfur to melt-diffuse into the nanocomposite.

The above process may further include step (d) or step (e) or both of steps (d) and (e) in any order. When step (d) is present, then the product obtained is a nanocomposite material.

For example, the acid of step (e) is a mineral acid, preferably H_2SO_4 or HCl , preferably used in a concentration of 0.1 to 5 M. In another example, the thermal treatment steps (c) and (d) when present are performed each independently at a temperature of about 200 to about 500 °C, preferably about 300 to about 400 °C and the heating step (f) is performed at a temperature of about 140 to about 180 °C for about 5 to about 48 hours.

Non-limiting examples of titanium oxide precursors include one or more organotitanium compounds selected from titanium tetraisopropoxide, titanium tetra-n-butoxide, titanium tetrakis(2-ethylhexyloxy), titanium tetrastearoyloxy, titanium acetylacetonate, titanium ethyl acetoacetate, salicylaldehyde ethyleneimine titanate, diacetone alkoxy titanium, octylene glycoxy titanium, triethanolamine titanate, titanium lactate, monocyclopentadienyltitanium trihalides, dicyclopentadienyltitanium dihalides, cyclopentadienyltitanium trimethoxide, cyclopentadienyltitanium triethoxide and cyclopentadienyltitanium tripropoxide. For example, the organotitanium compound is titanium tetra-n-butoxide (Ti(IV) butoxide).

Electrochemical cells and batteries comprising the nanocomposite as defined herein are also contemplated. For example, at least one element of the electrochemical cells comprises the nanocomposite as defined herein. Such element may be an electrode material, and more preferably the positive electrode material. The electrode material may further comprise a second conductive material, a binder and/or optional additives. For example, the electrode material may be mixed as a slurry with the second conductive material, the binder, a solvent and optionally one or more additives.

Non-limiting examples of the second conductive material may include a carbon source such as carbon black, carbon KetjenTM, acetylene black, graphite, graphene, carbon fibers (such as carbon nanofibers or VGCF formed in the gas phase), and carbon nanotubes, or a combination of at least two of these. For example, the second

conductive material is a combination of Ketjen™ black carbon (e.g. ECP600JD) and vapor grown carbon fibers (VGCF).

Non-limiting examples of binders include a linear, branched and/or crosslinked polymeric binder of the polyether type and may be based on poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) or a mixture of the two (or an EO/PO copolymer), which optionally comprises crosslinkable units; a fluorinated polymer such as polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE); or a water-soluble binder such as SBR (styrene-butadiene rubber), NBR (acrylonitrile-butadiene rubber), HNBR (hydrogenated NBR), CHR (epichlorohydrin rubber) acrylate), optionally comprising CMC (carboxymethylcellulose). For example, the binder is PVDF.

According to one example, the positive electrode material can be applied to a current collector (e.g., aluminum, copper) to form the positive electrode. Alternatively, the positive electrode can be self-supporting. For example, the current collector is aluminum.

The present application also proposes an electrochemical cell comprising the positive electrode as defined herein, a negative electrode and an electrolyte.

For more certainty, the electrochemically active material of the negative electrode may be selected from any known material compatible with the use of the present positive electrode material, such as alkali metal films, e.g. metallic lithium film or an alloy thereof. For example, the negative electrode is a metallic lithium film.

The electrolyte is selected for its compatibility with the various elements of the electrochemical cell. Any type of electrolyte is contemplated including, for example, liquid, gel or solid electrolytes.

Compatible electrolytes generally comprise at least one lithium salt such as lithium hexafluorophosphate (LiPF_6), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), 2-trifluoromethyl-4-dicyanoimidazolate (LiTDI), lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA), lithium bis(pentafluoroethylsulfonyl)imide (LiBETI), lithium tetrafluoroborate (LiBF_4), lithium bis(oxalato)borate (LiBOB), lithium

nitrate (LiNO_3), lithium chloride (LiCl), lithium bromide (LiBr), lithium fluoride (LiF), and compositions comprising them dissolved in a non-aqueous (organic) solvent or a solvating polymer.

Compatible liquid electrolytes may further include a polar aprotic solvent such as ethylene carbonate (EC), diethyl carbonate (DEC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), γ -butyrolactone (γ -BL), vinyl carbonate (VC), dimethoxyethane (DME), 1,3-dioxolane (DOL) and mixtures thereof, and lithium salts as defined above. Other examples of compatible liquid electrolytes include molten salt (ionic liquid) electrolytes. Non-limiting examples of liquid electrolytes of molten salts include lithium salts such as LiCl , LiBr , LiF , and compositions comprising them, or organic salts. Non-limiting examples of molten salts liquid electrolytes can be found in US20020110739 A1. The liquid electrolyte may impregnate a separator such as a polymer separator (e.g., polypropylene, polyethylene, or a copolymer thereof). For example, the electrolyte is lithium bis(trifluoromethane)sulfonamide and lithium nitrate (2%) in a solvent mixture of 1,3-dioxolane and 1,2-dimethoxy ethane (1:1 v/v) impregnating a polyethylene-based separator.

Compatible gel electrolytes may include, for example, polymer precursors and lithium salts (such as LiTFSI , LiPF_6 , etc.), an aprotic polar solvent as defined above, a polymerization and/or crosslinking initiator when required. Examples of such gel electrolytes include, without limitation, the gel electrolytes disclosed in the PCT applications published under WO2009/111860 (Zaghib et al.) and WO2004/068610 (Zaghib et al.). A gel electrolyte may also impregnate a separator as defined above.

Solid polymer electrolytes can generally comprise a crosslinked or non-crosslinked polar solvating solid polymer or polymers and salts, for example, lithium salts such as LiTFSI , LiPF_6 , LiDCTA , LiBETI , LiFSI , LiBF_4 , LiBOB , etc. Polyether polymers such as polymers based on poly(ethylene oxide) (PEO) may be used, but several other lithium compatible polymers are also known to produce solid polymer electrolytes. Examples of such polymers include star-shaped or comb-like multi-branched polymers such as those disclosed in PCT application no. WO2003/063287 (Zaghib et al.).

According to another aspect, an electrochemical cell of the present application is included in a lithium battery. For example, the lithium battery is a lithium-sulfur battery.

The present application also proposes an electrochemical cell of the present application included in a high performance all-solid-state lithium-sulfur battery. For example, the
5 electrochemical cell comprises the positive electrode as defined herein, a negative electrode and a solid polymer electrolyte.

According to another aspect, the electrochemical cells of the present application are used in mobile devices, for example mobile phones, cameras, tablets or laptops, in electric or hybrid vehicles, or for the storage of renewable energy.

10

EXAMPLES

The following non-limiting examples are illustrative embodiments and should not be construed as further limiting the scope of the present invention. These examples will be better understood with reference to the accompanying figures.

The nanoparticles, nanocubes and nanocomposite materials described in the following
15 example were characterized by TEM, HRTEM and HAADF-STEM (FEI Tecnai G² F20 electron microscope). Samples for TEM studies were prepared by putting a droplet of the NPs solution on a copper grid coated with a thin carbon film, followed by evaporation in air at room temperature. The catalyst composition was determined *in situ* by an EDX attachment (Oxford Instruments X-Max 80TLE) to the microscope. XRD
20 patterns were recorded on a Rigaku D/Max-3B diffractometer using Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$). B.E.T. surface areas of the samples were calculated from nitrogen sorption at 77 K on a Micromeritics ASAP 2020 instrument. The TGA experiment was performed under flowing nitrogen on a TA Instruments Discovery TGA 55 (heating rate = 5°C/min).

Example 1 – Synthesis of core-shell MnO/TiO₂ NPs

25 (a) *Synthesis of monodispersed MnCO₃ precursor nanoparticles*

In one example, the core-shell MnO/TiO₂ NPs are MnO/TiO₂ NPs. The MnO/TiO₂ NPs uses monodispersed MnCO₃ NPs as a synthesis precursor. In the first step of the

synthesis, monodispersed MnCO_3 NPs were prepared as a self-template via a cationic surfactant-CTAB-microemulsion-mediated solvothermal method. To perform this synthesis, 2.0 g of cetyltrimethylammonium bromide (CTAB), 10 mmol of manganese(II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), 2.0 mL of water, 3.0 mL of 1-butanol and 60 mL of cyclohexane were added to a first container and mixed to form a first microemulsion. 8.0 g of CTAB, 19 mmol of potassium bicarbonate (KHCO_3), 1.0 mmol of ammonium bicarbonate (NH_4HCO_3), 2.0 mL of water, 3.0 mL of 1-butanol and 240 mL of cyclohexane were added to a second container and mixed to form a second microemulsion. Both water-in-oil microemulsions were obtained after magnetic stirring at room temperature for 1 hour. The feedstock from the first container was then introduced in the second container under continuous stirring. The resulting microemulsion was then stirred for 30 minutes.

A size-selective separation process was then performed on the resulting microemulsion to obtain highly monodispersed manganese (II) carbonate (MnCO_3) nanocubes. To do so, the resulting microemulsion was centrifuged at 8000 rpm for 5 minutes, the supernatant was removed, and the precipitate was dispersed in ethanol by ultrasonication to form a uniform suspension. The suspension was then centrifuged at 3000 rpm for 2 minutes; after these 2 minutes the milky supernatant suspension was saved, while the precipitate was discarded. The suspension was then centrifuged at 8000 rpm for 5 minutes and the precipitate was collected and re-dispersed in ethanol by ultrasonication to form a uniform MnCO_3 nanocubes suspension. The concentration of the MnCO_3 nanocubes suspension was determined by weighting dried MnCO_3 nanocubes from a fixed volume of said MnCO_3 nanocubes suspension and was determined to be about 0.1 M. The MnCO_3 precursor NPs were obtained by drying the MnCO_3 nanocubes suspension in an oven at 80 °C.

The MnCO_3 precursor NPs were then characterized using low and high magnification transmission electron microscopy (TEM) images. As can be appreciated from Figure 1 (A and B), the sample has a highly monodispersed cube-like morphology with a particle size of about 125 nm.

(b) *Preparation of the MnCO₃/TiO₂ core-shell nanoparticles*

The synthesis of the MnCO₃/TiO₂ core-shell nanomaterials was performed by dispersing 8 mL of the MnCO₃ NPs from (a) at a concentration of 0.2 M in ethanol in 125 mL of acetonitrile, 375 mL of ethanol and 5.4 mL of deionized water. The solution was stirred
5 vigorously for 30 minutes. Then, 1 mL of Ti(IV) tetra-n-butoxide (from Sigma-Aldrich) was added to the dispersion. The dispersion was allowed to react for 20 hours. The MnCO₃/TiO₂ core-shell NPs were collected by centrifugation, washed with ethanol and then dried.

The morphology of the MnCO₃/TiO₂ core-shell NPs was then characterized by TEM. As
10 can be seen in Figure 2 (A), the TEM images showed that the resulting material is highly monodispersed with a cube-like morphology. Figures 2 (B) and (C) are high resolution TEM (HRTEM) images and illustrate the core shell structure, where the core was shown to be porous and the shell had a thickness of about 9.5 nm. The formation of core-shell structure was confirmed by the elemental maps in Figures 2 (D) to (H) of
15 these NPs in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image. Powder X-ray diffraction (XRD) was then performed and the pattern in Figure 3 (A) indicated only crystalline peaks for rhombohedral MnCO₃ (JCPDS card No. 44-1472) and the TiO₂ phase was found to be amorphous.

(c) *Preparation of the MnO/TiO₂ nanoparticles*

20 This example illustrates the process for producing MnO/TiO₂ NPs. The MnO/TiO₂ NPs were obtained by annealing at a temperature of about 350 °C the MnCO₃/TiO₂ core-shell NPs as described in Example 1 (b) under an argon atmosphere for 4 hours.

The MnO/TiO₂ NPs were then characterized. The core-shell structure could be easily observed in Figure 4 from the contrast between Mn and Ti in TEM and HAADF-STEM
25 images. The shell thickness was about 9.8 nm. The core-shell structure was confirmed by the elemental maps of these NPs in HAADF-STEM image. In Figure 5, the linear energy-dispersive X-ray (EDX) profile of an individual core-shell nanoparticle confirmed a Ti:Mn molar ratio of 1:4. The XRD pattern (Figure 3 (A)) of the material was similar to that of MnO nanocubes (JCPDS 01-075-109) and no crystalline TiO₂ phase was

detected. The nitrogen adsorption-desorption isotherms of the as-prepared MnO/TiO₂ NPs (Figure 3 (B)) showed a type IV hysteresis loop, which is characteristic of a mesoporous material. The Brunauer-Emmett-Teller (B.E.T.) surface area was 46.8 m²/g. The porous core structure could be generated by the release of CO₂ gas during the decomposition of MnCO₃ upon calcination.

Example 2 – Production of nanocomposite material comprising a conductive nanomaterial

This example illustrates the addition of a conductive nanomaterial to MnO/TiO₂ NPs in order to increase its electronic conductivity. To do so, a uniform graphene oxide suspension was prepared by ultrasonically dispersing 100 mg of graphene oxide (GO) in 100 mL of deionized water with 100 mg of CTAB. 400 mg of as-prepared MnO/TiO₂ NPs from Example 1 were then added to the GO suspension under magnetic stirring. After thorough mixing, the water was removed by centrifugation, and the sample was dried at room temperature in a vacuum oven overnight. The dried powder was annealed under argon atmosphere containing H₂ (5%) at 350°C for 4 hours to form the MnO/TiO₂/RGO nanocomposite material.

The MnO/TiO₂/RGO nanocomposite material was then characterized. The TEM images suggested that the MnO/TiO₂ NPs were well-dispersed on the RGO nanosheets (Figure 6). The core-shell structure of MnO/TiO₂ NPs was preserved, as shown by the HAADF-STEM image of these particles. The crystalline nature of the core was confirmed by the high-resolution TEM (HRTEM) image and the corresponding fast Fourier-transform (FFT) pattern (Figure 6 (C)) of the area selected in Figure 6 (B). The 0.222 nm d-spacing marked in Figure 6 (C) corresponded to (200) lattice fringes of the cubic MnO with a unit cell of $a = b = c = 4.446 \text{ \AA}$. No phase change was observed when comparing the XRD patterns of MnO/TiO₂/RGO nanocomposite material and MnO/TiO₂ NPs (see Figure 3 (A)). The porous nature of the MnO/TiO₂/RGO nanocomposite material was illustrated by N₂ adsorption-desorption isotherms (Figure 3 (B)). The sample has a specific surface area measured by B.E.T. of 60.7 m²/g.

Example 3 – Elemental sulfur (S₈) incorporation by melt-diffusion

This example illustrates the incorporation of elemental sulfur (S₈) in the MnO/TiO₂ nanoparticles of Example 1 or the MnO/TiO₂/RGO nanocomposite material of Example 2 by melt-diffusion. An amount of 1 g of MnO/TiO₂ NPs and of MnO/TiO₂/RGO
5 nanocomposite were each milled with 2 g of sulfur nanocrystals. The mixtures were each sealed in a polytetrafluoroethylene (PTFE) or TeflonTM container under inert atmosphere in a glove box and heated at 160°C for 20 hours to incorporate the sulfur into the nanocomposite material by melt-diffusion to obtain MnO/TiO₂-S and MnO/TiO₂/RGO-S nanocomposite materials.

10 TEM images and elemental maps of HAADF-STEM image (Figure 7) of the MnO/TiO₂/RGO-S nanocomposite suggested that the MnO/TiO₂-S NPs were well-dispersed on RGO nanosheets and preserved their core-shell structure. The elemental maps of these NPs in HAADF-STEM image also confirmed that the sulfur nanocrystals were trapped in the MnO/TiO₂/RGO nanocomposite materials. The sample had an XRD
15 pattern (Figure 3 (A)) similar to that of sulfur nanocrystals (JCPDS card No. 01-083-1763). Thermal gravimetric analysis (TGA) indicated a similar loading of sulfur nanocrystals in MnO/TiO₂/RGO-S and MnO/TiO₂-S (about 66.7 wt% and 68.2 wt%, respectively) (Figure 3 (C)). TEM images, HRTEM images and elemental maps of HAADF-STEM image were also recorded for MnO/TiO₂-S nanocomposites (Figure 8).

20 Example 4 – Molar ratios of MnO and TiO₂.

MnO/TiO₂/RGO-S with different molar ratios of MnO to TiO₂ were also synthesized. The MnO/TiO₂/RGO nanocomposite was treated with acid to remove excess MnO (partial removal). To prepare MnO/TiO₂/RGO with different Ti:Mn ratios, the dried powder (500 mg) was dispersed in 100 mL of deionized water, and then treated with 10 mL of H₂SO₄
25 (1 M) to remove part of the MnO. After 1 hour of reaction, the nanocomposite was collected by centrifugation and dried in a vacuum oven to afford a nanocomposite referred to as MnO/TiO₂/RGO-acid.

The EDX profile of an individual MnO/TiO₂/RGO-acid core-shell NP confirmed that the Ti:Mn molar ratio was about 1:1 (Figure 9). As shown by the TEM and the HAADF-

STEM images (Figure 10), MnO/TiO₂ NPs in the MnO/TiO₂/RGO-acid sample preserved the cubic morphology, and the NPs were well-dispersed on the RGO nanosheets. The elemental maps of these particles in HAADF-STEM image also confirmed that the shell was comprised of TiO₂, and the core was comprised of MnO. The MnO/TiO₂/RGO-acid nanocomposite material had a B.E.T. specific surface area of 95.9 m²/g.

Sulfur nanocrystals were then incorporated by melt diffusion as described in Example 3. The resulting MnO/TiO₂/RGO-acid-S still retained the cubic morphology of MnO/TiO₂, and the NPs were well dispersed on the surface of RGO (Figure 11). The elemental maps of these particles in HAADF-STEM image also confirmed that the sulfur nanocrystals were trapped in the MnO/TiO₂/RGO-acid nanocomposite material. MnO/TiO₂/RGO-acid-S showed a XRD pattern similar to that of sulfur nanocrystals (Figure 3 (A)).

Example 5: Preparation of cells

(a) Cathodes

Cathode materials comprising nanocomposite materials were prepared in the weight ratios detailed in Table 1. The materials were prepared by mixing the nanocomposite material using a SamplePrep 8000M Mixer/Mill™ high-energy ball miller from Spex™ for 1 hour, Ketjen™ black carbon (ECP600JD), vapor grown carbon fibers (VGCF), and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The mixture was then rolled into thin sheets with a thickness of about 15μm, which were then punched and pressed onto round aluminum meshes.

Table 1. Cathode material weight concentration

Cathode	Nanocomposite material (wt%)	Carbon 1 (wt%)	Carbon 2 (wt%)	Binder (wt%)
C1	Sulfur nanocrystals (60 %)	C- Ketjen™ (15 %)	C- VGCF (15 %)	PVDF (10%)
C2	MnO/TiO ₂ -S (60 %)	C- Ketjen™ (15 %)	C- VGCF (15 %)	PVDF (10%)
C3	MnO/TiO ₂ /RGO-S (60 %)	C- Ketjen™ (15 %)	C- VGCF (15 %)	PVDF (10%)
C4	MnO/TiO ₂ /RGO-acid-S (60 %)	C- Ketjen™ (15 %)	C- VGCF (15 %)	PVDF (10%)

(b) Cells

The cells were assembled in standard CR2032 size coin cell casings (*i.e.* 20 mm diameter and 3.2 mm height), with the cathodes prepared in (a), a metallic lithium disk as the anode, 25 μm polyethylene-based separators impregnated lithium bis(trifluoromethane)sulfonamide and lithium nitrate (2%) in a solvent mixture of 1,3-dioxolane and 1,2-dimethoxy ethane (1:1 v/v) as the electrolyte. All cells were assembled in an argon-filled glove box.

Table 2. Cell configurations

Cell	Cathode
Cell 1	C1
Cell 2	C2
Cell 3	C3
Cell 4	C4

10 **Example 6: Electrochemical properties***(a) Cyclic voltammetry*

Cyclic voltammograms (CV) were recorded for the Li-S cells prepared in Example 5, *i.e.* comprising the composite materials described in Examples 3 and 4 as cathode active material. The CV were recorded with the electrochemical workstation (from Autolab) at a scanning rate of 0.05 mVs^{-1} in the range of 1.5 to 2.8 (V vs Li/Li⁺). As can be observed in Figure 12 (A) and Figure 13, the CV displayed two reduction peaks, one at 2.33 V and another at 2.02 V in Figure 12A, which corresponded to the reduction of elemental (S₈) into a long-chain polysulfide (Li₂S_x, $4 \leq x \leq 8$), and lower polysulfide species Li₂S₂ and Li₂S. A difference in reduction peaks between the first and fifth cycles may be observed and could be attributed to the partial decomposition of electrolyte at the high voltage, and the formation of a solid-electrolyte interface (SEI).

(b) Galvanostatic charge and discharge profile

The galvanostatic charge and discharge profiles were studied to test the performances of cells prepared in Example 5 comprising the composite materials as described herein.

The galvanostatic charge/discharge tests were performed using an Arbin Instruments testing system (Arbin BT-2000).

As shown in Figure 12 (B), a high initial charge capacity of 1562 mAh/g and a discharge capacity of 1451 mAh/g were obtained for Cell 4 comprising the MnO/TiO₂/RGO-acid-S, nanocomposite material, which were higher than those of Cell 3 comprising the MnO/TiO₂/RGO-S nanocomposite material (1145 mAh/g and 1045 mAh/g) and Cell 2 comprising the MnO/TiO₂-S nanocomposite material (948 mAh/g and 938 mAh/g), corresponding to a more active sulfur utilization. Although some capacity loss could not be avoided, reversible discharge capacities of about 986 mAh/g for Cell 4, about 712 mAh/g for Cell 3 and about 463 mAh/g for Cell 2 were retained after 100 cycles at 0.2 C with good coulombic efficiency (> 98%), respectively (see Figure 12 (C)), which was superior to that of the sulfur nanocrystal-containing Cell 1 (about 160 mAh/g and 83%). The superior electrochemical performance of Cell 3 could be attributed to its stable hollow architecture, which could have prevented the swelling problem associated with sulfur and polysulfide formation during the charge and discharge cycles. Furthermore, strong chemical adsorption between polysulfide and MnO could have further enhanced the sulfur stability of the Li-S battery. Cell 4 comprising a low Mn:Ti molar ratio (1:1) displayed better capacity than that with high Mn:Ti molar ratio (4:1). This could be attributed to more a porous MnO core which could have accommodated more sulfur crystal after acid treatment. This was confirmed by the much higher B.E.T. specific surface area for MnO/TiO₂/RGO-acid-S compared to that of MnO/TiO₂/RGO-S nanocomposite materials.

(c) Impedance

Electrochemical impedance spectroscopy (EIS) was performed on the cells comprising the nanocomposites (see Figure 12 (D)). The depressed semicircle in the high-to-medium frequency region of the Nyquist profiles corresponded to the charge-transfer resistance at the electrode/electrolyte interface: about 52.4 Ω for Cell 4, about 119.6 Ω for Cell 3, and about 169.8 Ω for Cell 2. The low transfer resistance of Cell 4 indicated the high rate capability and stability of this material. EIS were recorded by applying a sine wave with an amplitude of 10 mV over the frequency range of 100 kHz to 10 MHz.

Numerous modifications could be made to any of the embodiments described above without departing from the scope of the present invention. Any references, patents or scientific literature documents referred to in the present document are incorporated herein by reference in their entirety for all purposes.

CLAIMS

1. Core-shell nanoparticles comprising
 - a porous metal oxide core of formula M_yO_x , wherein M defines at least one transition metal, y is an integer selected from 1 to 4, and x is an integer selected from 1 to 8, x and y being selected to achieve electroneutrality;
 - elemental sulfur (S_8) as an electrochemically active material, the elemental sulfur being incorporated into the pores of the metal oxide core; and
 - an outer shell surrounding the core, the outer shell comprising TiO_2 .
2. The core-shell nanoparticles of claim 1, wherein M is Mn, Fe, Co, Ni, Zn or a combination thereof; y is an integer from 1 to 3; and x is an integer from 1 to 7.
3. The core-shell nanoparticles of claim 2, wherein M is Mn.
4. The core-shell nanoparticles of claim 3, wherein M_yO_x is MnO .
5. The core-shell nanoparticles of any one of claims 1 to 4, wherein the TiO_2 is in an amorphous form.
6. The core-shell nanoparticles of any one of claims 1 to 5, wherein the metal oxide comprised in the core is in a crystalline form.
7. The core-shell nanoparticles of any one of claims 1 to 6, wherein the nanoparticles have a cube-like morphology.
8. The core-shell nanoparticles of any one of claims 1 to 7, wherein the M:Ti molar ratio is about 10:1 to about 0.5:1, preferably about 4:1 to about 0.7:1, preferably about 3:1 to about 0.7:1 and most preferably about 2:1 to about 0.8:1.
9. The core-shell nanoparticles of any one of claims 1 to 8, wherein the average size of the core-shell nanoparticles is in the range from about 10 to about 500 nm, preferably about 75 to about 200 nm, and the average thickness of the shell of the core-

shell particle is in the range of about 1 to about 50 nm, preferably about 5 to about 20 nm.

10. The core-shell nanoparticles of any one of claims 1 to 9, wherein the elemental sulfur comprises sulfur nanocrystals.

5 11. A nanocomposite material comprising the core-shell nanoparticles as defined in any one of claims 1 to 10 and a first conductive nanomaterial.

12. The nanocomposite material of claim 11, wherein the core-shell nanoparticles are supported on the first conductive material.

10 13. The nanocomposite material of claim 11 or 12, wherein the first conductive nanomaterial is a conductive nanocarbon nano-wire, nano-sheet, nano-belt, or a combination thereof.

14. The nanocomposite material of any one of claims 11 to 13, wherein the first conductive nanomaterial is a reduced graphene oxide nanosheet or a graphene nanosheet of a lateral size of about 50 to about 500 nm, preferably 100 to about 200
15 nm.

15. The nanocomposite material of any one of claims 11 to 14, wherein the weight ratio of the first conductive nanomaterial to the nanoparticles excluding sulfur is about 1:1 to about 1:10, preferably about 1:2 to about 1:4.

16. The nanocomposite material of any one of claims 11 to 15, wherein the weight
20 ratio of sulfur to the nanocomposite material excluding sulfur is about 10:1 to about 1:2, preferably about 3:1 to about 1:1.

17. A method for producing core-shell nanoparticles as defined in any one of claims 1 to 10 or a nanocomposite material as defined in any one of claims 11 to 16, the method comprising:

25 (a) contacting $M_y(\text{CO}_3)_x$ nanoparticles with TiO_2 or a TiO_2 precursor to form TiO_2 coated $M_y(\text{CO}_3)_x$ nanoparticles ($M_y(\text{CO}_3)_x/\text{TiO}_2$);

- (b) thermally treating the $M_y(\text{CO}_3)_x/\text{TiO}_2$ nanoparticles from step (a) at elevated temperature under inert gas to form core-shell $M_y\text{O}_x/\text{TiO}_2$ nanoparticles;
- (c) optionally thermally treating the core-shell $M_y\text{O}_x/\text{TiO}_2$ nanoparticles with a first conductive nanomaterial under inert gas at elevated temperature, optionally in the presence of hydrogen gas, to form a nanocomposite material;
- (d) optionally partly removing $M_y\text{O}_x$ after step (b) or (c) by treatment with an acid;
- (e) milling the obtained nanoparticles or nanocomposite material of step (b), (c) or (d) with elemental sulfur (S_8) to produce a mixture; and
- (f) heating the mixture obtained in step (e) at elevated temperature under inert gas to cause the sulfur to melt-diffuse into the pores of the nanoparticles and/or nanocomposite material.

18. A method for producing nanoparticles as defined in any one of claims 1 to 10 or a nanocomposite material as defined in any one of claims 11 to 16, comprising a porous MnO core and a TiO_2 outer shell, said MnO core comprising sulfur entrapped in said pores, the method comprising:

- (a) synthesizing MnCO_3 nanoparticles by a microemulsion-mediated solvothermal reaction;
- (b) reacting the MnCO_3 nanoparticles from step (a) in a polar solvent with a TiO_2 precursor, preferably an organotitanium compound, to produce $\text{MnCO}_3/\text{TiO}_2$ nanoparticles;
- (c) thermally treating the $\text{MnCO}_3/\text{TiO}_2$ nanoparticles at elevated temperature under inert gas to produce core-shell MnO/TiO_2 nanoparticles;
- (d) optionally thermally treating the core-shell MnO/TiO_2 nanoparticles with a first conductive nanomaterial under inert gas at elevated temperature, optionally in the presence of hydrogen gas, to form a nanocomposite material;
- (e) optionally partly removing MnO after step (c) or (d) by treatment with an acid;
- (f) milling the nanoparticles or nanocomposite obtained in step (c), (d) or (e) with elemental sulfur to produce a mixture; and

- (g) heating the mixture obtained in step (f) at elevated temperature under inert gas to cause the sulfur to melt-diffuse into the nanocomposite.
19. The method of claim 17 or 18, wherein the TiO_2 precursor is at least one organotitanium compound selected from the group consisting of titanium tetraisopropoxide, titanium tetra-n-butoxide, titanium tetrakis(2-ethylhexyloxi-
5 de), titanium tetrastearoyloxi-
de, titanium acetylacetonate, titanium ethyl acetoacetate, salicylaldehyde ethyleneimine titanate, diacetone alkoxy titanium, octylene glycoxy titanium, triethanolamine titanate, titanium lactate, monocyclopentadienyltitanium trihalides, dicyclopentadienyltitanium dihalides, cyclopentadienyltitanium trimethoxide,
10 cyclopentadienyltitanium triethoxide and cyclopentadienyltitanium tripropoxide.
20. The method of claim 19, wherein the organotitanium compound is titanium tetra-n-butoxide.
21. The method of any one of claims 17 to 20, wherein the nanoparticles or nanocomposite material before the milling step has specific surface area measured by
15 Brunauer–Emmett–Teller (B.E.T.) of about $40 \text{ m}^2/\text{g}$ to about $150 \text{ m}^2/\text{g}$, or of about $60 \text{ m}^2/\text{g}$ to about $120 \text{ m}^2/\text{g}$, preferably about 80 to about $100 \text{ m}^2/\text{g}$.
22. The method of any one of claims 17 to 21, wherein the acid is a mineral acid, preferably H_2SO_4 or HCl , preferably used in a concentration of 0.1 to 5 M.
23. The method of any one of claims 17 to 22, wherein each thermal treatment step
20 is independently performed at a temperature of about 200 to about 500°C , preferably about 300 to about 400°C .
24. The method of any one of claims 17 to 23, wherein the heating step is performed at a temperature of about 140°C to about 180°C for about 5 to about 48 hours.
25. Nanoparticles or a nanocomposite material obtained by the method of any one of
25 claims 17 to 24.
26. An electrode material comprising core-shell nanoparticles as defined in any one of claims 1 to 10 or a nanocomposite material as defined in any one of claims 11 to 16.

27. The electrode material of claim 26, further comprising a second conductive material, a binder and optionally one or more additives.
28. The electrode material of claim 27, wherein the second conductive material is selected from the group consisting of carbon black, carbon KetjenTM, acetylene black, graphite, graphene, carbon fibers (such as carbon nanofibers or VGCF), carbon nanotubes, and a combination of at least two of these.
29. The electrode material of claim 27 or 28, wherein the binder material is selected from the group consisting of a polymeric binder of the polyether type, a fluoropolymer, a water-soluble binder and a combination thereof.
30. The electrode material of claim 29, wherein the polyether type polymer binder is a linear, branched and/or crosslinked polymer based on polyethylene oxide (PEO), poly(propylene oxide) (PPO) or a mixture of the two (or an EO/PO copolymer), and optionally comprises crosslinkable units.
31. The electrode material of claim 29, wherein the fluoropolymer binder is PVDF (polyvinylidene fluoride) or PTFE (polytetrafluoroethylene).
32. The electrode material of claim 29, wherein the water-soluble binder is SBR (styrene-butadiene rubber), NBR (acrylonitrile-butadiene rubber), HNBR (hydrogenated NBR), or CHR (epichlorohydrin rubber) acrylate), optionally comprising CMC (carboxymethylcellulose).
33. A positive electrode comprising the electrode material as defined in any one of claims 26 to 32 on a current collector.
34. An electrochemical cell comprising the positive electrode as defined in claim 33, a negative electrode and an electrolyte.
35. The electrochemical cell of claim 34, wherein the negative electrode is a metallic lithium film.

36. A lithium sulfur battery comprising at least one electrochemical cell as defined in claim 34 or 35.

37. A lithium sulfur battery comprising the core-shell nanoparticles as defined in any one of claims 1 to 10 or a nanocomposite material as defined in any one of claims 11 to
5 16.

38. Use of a lithium sulfur battery as defined in claim 36 or 37, in mobile devices, for example mobile phones, cameras, tablets or laptops, in electric or hybrid vehicles, or for the storage of renewable energy.