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(54) Title: METHOD OF PREPARING NANOPARTICLE COMPOSITION AND NANOPARTICLE COMPOSITION FORMED THEREBY

(57) Abstract: A method of preparing a nanoparticle composition comprises forming a nanoparticle aerosol in a low pressure reactor, wherein the aerosol comprises MX-functional nanoparticles in a gas, with M being an independently selected from silicon, germanium and tin and X is a functional group independently selected from H and a halogen atom. The method further comprises collecting the MX-functional nanoparticles of the aerosol in a capture fluid, wherein the capture fluid is in communication with the low pressure reactor, and wherein the capture fluid comprises a compound including a functional group Y reactive with the functional group X of the MX-functional nanoparticles. Finally, the method comprises reacting the compound and the MX-functional nanoparticles to prepare the nanoparticle composition comprising nanoparticles.



METHOD OF PREPARING NANOPARTICLE COMPOSITION AND NANOPARTICLE COMPOSITION FORMED THEREBY

FIELD OF THE INVENTION

[0001] The invention generally relates to a method of preparing a nanoparticle composition and, more specifically, to a method of preparing a nanoparticle composition in a low pressure reactor.

DESCRIPTION OF THE RELATED ART

[0002] Nanoparticles are known in the art and can be prepared via various processes. For example, nanoparticles are often defined as particles having at least one dimension of less than 100 nanometers and are produced either from a bulk material, which is initially larger than a nanoparticle, or from particles smaller than the nanoparticles, such as ions and/or atoms. Nanoparticles are particularly unique in that they may have significantly different properties than the bulk material or the smaller particles from which the nanoparticles are derived. For example, a bulk material that acts as an insulator or semiconductor can be, when in nanoparticle form, electrically conductive.

[0003] Nanoparticles may also be produced via a plasma process. For example, nanoparticles may be produced in a plasma reactor from a precursor gas. In certain plasma processes, the nanoparticles produced in the plasma reactor are captured or collected in a fluid. However, once the nanoparticles are collected in the fluid, the resulting solution is unstable due to agglomeration of the nanoparticles. Typically, the instability of the solution (i.e., the agglomeration of the nanoparticles) is visually apparent as the solution is hazy and/or the nanoparticles undesirably settle.

SUMMARY OF THE INVENTION

[0004] The invention provides a method of preparing a nanoparticle composition. The method comprises forming a nanoparticle aerosol in a low pressure reactor, wherein the aerosol comprises MX-functional nanoparticles in a gas, with M being an independently selected Group IV element and X is a functional group independently selected from H and a halogen atom. The method further comprises collecting the MX-functional nanoparticles of the aerosol in a capture fluid, wherein the capture fluid is in communication with the low pressure reactor, and wherein the capture fluid comprises a compound including a functional group Y reactive with the

functional group X of the MX-functional nanoparticles. Finally, the method comprises reacting the compound and the MX-functional nanoparticles to prepare the nanoparticle composition comprising nanoparticles.

[0005] The invention also provides a nanoparticle composition formed in accordance with the method.

[0006] The inventive method prepares a nanoparticle composition having excellent physical properties, including clarity and stability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Other advantages and aspects of this invention may be described in the following detailed description when considered in connection with the accompanying drawings wherein:

[0008] Figure 1 illustrates one embodiment of a low pressure high frequency pulsed plasma reactor for producing nanoparticles;

[0009] Figure 2 illustrates an embodiment of a system including a low pressure pulsed plasma reactor to produce nanoparticles and a diffusion pump to collect the nanoparticles; and

[0010] Figure 3 illustrates a schematic view of one embodiment of a diffusion pump for collecting nanoparticles produced via a reactor.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The invention provides a method of preparing a nanoparticle composition. The method of the invention is particularly suitable for preparing a nanoparticle composition including nanoparticles produced via a plasma process, as described in greater detail below.

[0012] The method comprises forming a nanoparticle aerosol in a low pressure reactor, wherein the aerosol comprises MX-functional nanoparticles in a gas, with M being an independently selected Group IV element and X being a functional group independently selected from H and a halogen atom. As used herein, the group designations of the periodic table are generally from the CAS or old IUPAC nomenclature, although Group IV elements are referred to as Group 14 elements under the modern IUPAC system, as readily understood in the art. The method further comprises collecting the MX-functional nanoparticles of the aerosol in a capture fluid, wherein the capture fluid is in communication with the low pressure reactor. The method of the instant invention may be utilized in conjunction with various plasma

reactor systems utilizing different low pressure reactors. Specifically, the method of the instant invention may be utilized in any plasma reactor system which forms a nanoparticle aerosol, as described above, and which ultimately captures or collects MX-functional nanoparticles in a capture fluid.

[0013] Regardless of the particular plasma system and process utilized to produce the nanoparticles, the plasma system generally relies on a precursor gas. The precursor gas is generally selected based on the desired composition of the nanoparticles. For example, as introduced above, the nanoparticle aerosol comprises MX-functional nanoparticles, where M is an independently selected Group IV element.

[0014] To this end, the precursor gas utilized generally comprises M, i.e., the precursor gas generally comprises at least one of silicon, germanium and tin. For example, when the MX-functional nanoparticles comprise SiX-functional nanoparticles, the precursor gas generally comprises silicon. In this embodiment, the precursor gas may be selected from silanes, disilanes, halogen-substituted silanes, halogen-substituted disilanes, C₁-C₄ alkyl silanes, C₁-C₄ alkyl disilanes, and mixtures thereof. In one form of the present disclosure, the precursor gas may comprise silane which comprises from about 0.1 to about 2% of the total gas mixture. However, the gas mixture may also comprise other percentages of silane. The precursor gas may additionally or alternatively comprise SiCl₄, HSiCl₃, and H₂SiCl₂. Alternatively, when the MX-functional nanoparticles comprise GeH-functional nanoparticles, the precursor gas generally comprises germanium. In this embodiment, the precursor gas may be selected from germane, digermanes, halogen-substituted germanes, halogen-substituted digermanes, C₁-C₄ alkyl germanes, C₁-C₄ alkyl digermanes, and mixtures thereof.

[0015] Organometallic precursor molecules may also be used in or as the precursor gas. These molecules include a Group IV metal and organic groups. Organometallic Group IV precursors include, but are not limited to organosilicon, organogermanium and organotin compounds. Some examples of Group IV precursors include, but are not limited to, alkylgermaniums, alkylsilanes, alkylstannanes, chlorosilanes, chlorogermaniums, chlorostannanes, aromatic silanes, aromatic germaniums and aromatic stannanes. Other examples of silicon precursors include, but are not limited to, disilane (Si₂H₆), silicon tetrachloride (SiCl₄), trichlorosilane (HSiCl₃) and dichlorosilane (H₂SiCl₂). Still other suitable precursor molecules for use in forming

crystalline silicon nanoparticles include alkyl and aromatic silanes, such as dimethylsilane ($\text{H}_3\text{C-SiH}_2\text{-CH}_3$), tetraethyl silane ($(\text{CH}_3\text{CH}_2)_4\text{Si}$) and diphenylsilane ($\text{Ph-SiH}_2\text{-Ph}$). Particular examples of germanium precursor molecules that may be used to form crystalline Ge nanoparticles include, but are not limited to, tetraethyl germane ($(\text{CH}_3\text{CH}_2)_4\text{Ge}$) and diphenylgermane ($\text{Ph-GeH}_2\text{-Ph}$).

[0016] In another form of the present disclosure, the nanoparticles may undergo an additional doping step. For example, the nanoparticles may undergo gas phase doping in the plasma, where a second precursor gas is dissociated and is incorporated in the nanoparticles as they are nucleated. The nanoparticles may also undergo doping in the gas phase downstream of the production of the nanoparticles, but before the nanoparticles are captured in the liquid. Furthermore, doped nanoparticles may also be produced in the capture fluid where the dopant is preloaded into the capture fluid and interacts with the nanoparticles after they are captured. Doped nanoparticles can be formed by contact with organosilicon gases or liquids, including, but not limited to trimethylsilane, disilane, and trisilane. Gas phase dopants may include, but are not limited to, BCl_3 , B_2H_6 , PH_3 , GeH_4 , or GeCl_4 .

[0017] The precursor gas may be mixed with other gases, such as inert gases, to form a gas mixture or reactant gas mixture. Examples of inert gases that may be included in the gas mixture include argon, xenon, neon, or a mixture of inert gases. When present in the gas mixture, the inert gas may comprise from about 1% to about 99% of the total volume of the gas mixture. The precursor gas may have from about 0.1% to about 50% of the total volume of the gas mixture. However, it is also contemplated that the precursor gas may comprise other volume percentages such as from about 1% to about 50% of the total volume of the gas mixture.

[0018] In one form of the present disclosure, the reactant gas mixture also comprises a second precursor gas which itself can comprise from about 0.1 to about 49.9 volume % of the reactant gas mixture. The second precursor gas may comprise BCl_3 , B_2H_6 , PH_3 , GeH_4 , or GeCl_4 . The second precursor gas may also comprise other gases that contain carbon, germanium, boron, phosphorous, or nitrogen. The combination of the first precursor gas and the second precursor gas together may make up from about 0.1 to about 50% of the total volume of the reactant gas mixture.

[0019] In another form of the present disclosure, the reactant gas mixture further comprises hydrogen gas. Hydrogen gas can be present in an amount of from about 1%

to about 50%, alternatively 1% to 25%, alternatively 1% to 10%, of the total volume of the reactant gas mixture. However, it is also contemplated that the reactant gas mixture may comprise other percentages of hydrogen gas.

[0020] In one form of the present disclosure, the nanoparticles may comprise silicon alloys. Silicon alloys that may be formed include, but are not limited to, silicon carbide, silicon germanium, silicon boron, silicon phosphorous, and silicon nitride. The silicon alloys may be formed by mixing at least one first precursor gas with the second precursor gas or using a precursor gas that contains the different elements. However, other methods of forming alloyed nanoparticles are also contemplated.

[0021] As set forth above, X of the MX-functional nanoparticles comprises a functional group independently elected from H and a halogen atom. The precursor gas (or gasses in the reactant gas mixture) is generally selected based on the desired functional group of the MX-functional nanoparticles. For example, when X is H, the reactant gas mixture generally comprises hydrogen gas or a lesser concentration of halogenated species (e.g. SiCl_4 , HSiCl_3 , BCl_3 , GeCl_4 , etc.). In contrast, when X is the halogen atom, the precursor gas (or reactant gas mixture) comprises halogenated species (e.g. SiCl_4 , HSiCl_3 , BCl_3 , GeCl_4 , etc.). Any of these chlorinated species may comprise halogen atoms other than chlorine, e.g. bromine, fluorine, or iodine. For example, SiBr_4 may be utilized in combination with or in lieu of SiCl_4 contingent on the desired functional group X. Further, in embodiments where the functional group X is a halogen atom, the reactant gas mixture may further comprise a halogen gas. For example, in embodiments where the functional group X is Cl, chlorine gas (Cl_2) may be utilized in the reactant gas mixture, either as a separate feed or along with the precursor gas. The relative amount of the halogen gas, if utilized, may be optimized on a variety of factors, such as the precursor gas selected, etc. For example, lesser amounts of the halogen gas may be required to prepare halogen-functional nanoparticles when the precursor gas comprises halogenated species. In certain embodiments, the halogen gas may be utilized in an amount of from greater than 0 to about 25%, alternatively from 1% to 25%, alternatively from 1% to 10%, of the total volume of the reactant gas mixture.

[0022] Specific embodiments of plasma reactor systems particularly suitable for the instant method are described below. It is to be appreciated that the specific embodiments described below are merely exemplary and any low pressure reactor

suitable for producing MX-functional nanoparticles and suitable for capture or collection of the MX-functional nanoparticles in the capture fluid may be utilized in the instant method.

[0023] Referring to Figure 1, a plasma reactor system is shown at 20. In this embodiment, the plasma reactor system 20 comprises a plasma generating chamber 22 having a reactant gas inlet 29 and an outlet 30 having an aperture or orifice 31 therein. A particle collection chamber 26 is in communication with the plasma generating chamber 22. The particle collection chamber 26 contains a capture fluid 27 in a container 32. The container 32 may be adapted to be agitated (not shown). For example, the container 32 may be positioned on a rotatable support (not shown) or may include a stirring mechanism. Preferably the capture fluid is a liquid at the temperatures of operation of the system. The plasma reactor system 5 also includes a vacuum source 28 in communication with the particle collection chamber 26 and plasma generating chamber 22.

[0024] The plasma generating chamber 22 comprises an electrode configuration 24 that is attached to a variable frequency RF amplifier 21. The plasma generating chamber 22 also comprises a second electrode configuration 25. The second electrode configuration 25 is either ground, DC biased, or operated in a push-pull manner relative to the electrode configuration 24. The electrodes 24, 25 are used to couple the high frequency (HF) or very high frequency (VHF) power to the reactant gas mixture to ignite and sustain a glow discharge of plasma within the area identified as 23. The first reactive precursor gas (or gases) is then dissociated in the plasma to provide charged atoms which nucleate to form MX-functional nanoparticles. However, other discharge tube configurations are contemplated, and may be used in carrying out the method disclosed herein.

[0025] In the embodiment of Figure 1, the MX-functional nanoparticles are collected in the particle collection chamber 26 in the capture fluid. To control the diameter of the MX-functional nanoparticles which are formed, the distance between the aperture 31 in the outlet 30 of the plasma generating chamber 22 and the surface of the capture fluid ranges between about 5 to about 50 aperture diameters. It has been found that positioning the surface of the capture fluid too close to the outlet of the plasma generating chamber may result in undesirable interactions of plasma with the capture fluid. Conversely, positioning the surface of the capture fluid too far from the aperture

reduces particle collection efficiency. As collection distance is a function of the aperture diameter of the outlet and the pressure drop between the plasma generating chamber and the collection chamber, based on the operating condition described herein, an acceptable collection distance is from about 1 to about 20, alternatively from about 5 to about 10, cm. Said differently, an acceptable collection distance is from about 5 to about 50 aperture diameters.

[0026] The plasma generating chamber 22 also comprises a power supply. The power is supplied via a variable frequency radio frequency power amplifier 21 that is triggered by an arbitrary function generator to establish high frequency pulsed plasma in area 23. Preferably, the radiofrequency power is capacitively coupled into the plasma using a ring electrode, parallel plates, or an anode/cathode setup in the gas. Alternatively, the radiofrequency power may be inductively coupled mode into the plasma using an rf coil setup around the discharge tube.

[0027] The plasma generating chamber 11 may also comprise a dielectric discharge tube. Preferably, a reactant gas mixture enters the dielectric discharge tube where the plasma is generated. MX-functional nanoparticles which form from the reactant gas mixture start to nucleate as the first reactive precursor gas molecules are dissociated in the plasma.

[0028] The vacuum source 28 may comprise a vacuum pump. Alternatively, the vacuum source 28 may comprise a mechanical, turbo molecular, or cryogenic pump.

[0029] In one embodiment, the electrodes 24, 25 for a plasma source inside the plasma generating chamber 22 comprise a flow-through showerhead design in which a VHF radio frequency biased upstream porous electrode plate 24 is separated from a down stream porous electrode plate 25, with the pores of the plates aligned with one another. The pores may be circular, rectangular, or any other desirable shape. Alternatively, the plasma generating chamber 22 may enclose an electrode 24 that is coupled to the VHF radio frequency power source and has a pointed tip that has a variable distance between the tip and a grounded ring inside the chamber 22.

[0030] In one embodiment, the HF or VHF radio frequency power source operates in a frequency range of about 10 to about 500 MHz. In an alternative embodiment, the pointed tip 13 can be positioned at a variable distance from a VHF radio frequency powered ring 14 operated in a push-pull mode (180° out of phase). In yet another alternative embodiment, the electrodes 24, 25 include an inductive coil coupled to the

VHF radio frequency power source so that radio frequency power is delivered to the reactant gas mixture by an electric field formed by the inductive coil. Portions of the plasma generating chamber 22 can be evacuated to a vacuum level ranging between about 1×10^{-7} to about 500 Torr. However, other electrode coupling configurations are also contemplated for use with the method disclosed herein.

[0031] In the illustrated embodiment of Figure 1, the plasma in area 23 is initiated with a high frequency plasma via an RF power amplifier such as, for example, an AR Worldwide Model KAA2040, or an Electronics and Innovation Model 3200L, or an EM Power RF Systems, Inc. Model BBS2E3KUT. The amplifier can be driven (or pulsed) by an arbitrary function generator (e.g., a Tektronix AFG3252 function generator) that is capable of producing up to 200 watts of power from 0.15 to 150 MHz. In several embodiments, the arbitrary function may be able to drive the power amplifier with pulse trains, amplitude modulation, frequency modulation, or different waveforms. The power coupling between the amplifier and the reactant gas mixture typically increases as the frequency of the rf power increases. The ability to drive the power at a higher frequency may allow more efficient coupling between the power supply and discharge. At frequencies below 30 MHz, only 2 - 15% of the power is delivered to the discharge. This has the effect of producing high reflected power in the rf circuit that leads to increased heating and limited lifetime of the power supply. In contrast, higher frequencies allow more power to be delivered to the discharge, thereby reducing the amount of reflected power in the rf circuit.

[0032] In one embodiment, the power and frequency of the plasma system is preselected to create an optimal operating space for the formation of the MX-functional nanoparticles. Preferably, tuning both the power and frequency creates an appropriate ion and electron energy distribution in the discharge to help dissociate the molecules of the reactive precursor gas and nucleate the MX-functional nanoparticles.

[0033] The plasma reactor system 20 illustrated in Figure 1 may be pulsed to enable an operator to directly manage the resident time for particle nucleation, and thereby control the particle size distribution and agglomeration kinetics in the plasma. The pulsing function of the system 20 allows for controlled tuning of the particle resident time in the plasma, which affects the size of the MX-functional nanoparticles. By decreasing the "on" time of the plasma, the nucleating particles have less time to agglomerate, and therefore the size of the MX-functional nanoparticles may be

reduced on average (i.e., the nanoparticle distribution may be shifted to smaller diameter particle sizes).

[0034] Advantageously, the operation of the plasma reactor system 20 at higher frequency ranges and pulsing the plasma provides the same conditions as in conventional constricted/filament discharge techniques that use a plasma instability to produce the high ion energies/densities, but with the additional advantage that users can control operating conditions to select and produce MX-functional nanoparticles having various sizes, which impacts their characteristic physical properties, e.g. photoluminescence..

[0035] For a pulse injection, the synthesis of the MX-functional nanoparticles can be done with a pulsed energy source, such as a pulsed very high frequency RF plasma, a high frequency RF plasma, or a pulsed laser for pyrolysis. Preferably, the VHF radiofrequency is pulsed at a frequency ranging from about 1 to about 50 kHz.

[0036] Another method to transfer the MX-functional nanoparticles to the capture fluid is to pulse the input of the reactant gas mixture while the plasma is ignited. For example, one could ignite the plasma in which a first reactive precursor gas is present to synthesize the MX-functional nanoparticles, with at least one other gas present to sustain the discharge, such as an inert gas. The synthesis of the MX-functional nanoparticles is stopped when the flow of first reactive precursor gas is stopped with a mass flow controller. The synthesis of the MX-functional nanoparticles continues when the flow of the first reactive precursor gas is started again. This produces a pulsed stream of MX-functional nanoparticles. This technique can be used to increase the concentration of MX-functional nanoparticles in the capture fluid if the flux of MX-functional nanoparticles impinging on the capture fluid is greater than the absorption rate of the MX-functional nanoparticles into the capture fluid.

[0037] In another embodiment, the nucleated MX-functional nanoparticles are transferred from the plasma generating chamber 22 to particle collection chamber 26 containing capture fluid via the aperture or orifice 31 which creates a pressure differential. It is contemplated that the pressure differential between the plasma generating chamber 22 and the particle collection chamber 26 can be controlled through a variety of ways. In one configuration, the discharge tube inside diameter of the plasma generating chamber 22 is much less than the inside diameter of the particle collection chamber 26, thus creating a pressure drop. In another configuration, a

grounded physical aperture or orifice may be placed between the discharge tube and the collection chamber 26 that forces the plasma to reside partially inside the orifice, based on the Debye length of the plasma and the size of the chamber 22. Another configuration comprises using a varying electrostatic orifice in which a positive concentric charge is developed that forces the negatively charged plasma through the aperture 31.

[0038] As first introduced above, in the embodiment of Figure 1, upon the dissociation of the first reactive precursor gas in the plasma generation chamber 22, MX-functional nanoparticles form and are entrained in the gas phase. The distance between the nanoparticle synthesis location and the surface of capture fluid must be short enough so that no unwanted functionalization occurs while the MX-functional nanoparticles are entrained. If the MX-functional nanoparticles interact within the gas phase, agglomerations of numerous individual small MX-functional nanoparticles will form and be captured in the capture fluid. If too much interaction takes place within the gas phase, the MX-functional nanoparticles may sinter together and form MX-functional nanoparticles having larger average diameters. The collection distance is defined as the distance from the outlet of the plasma generating chamber to the surface of the capture fluid. The capture fluid is described in detail below following the description of an alternative embodiment of a plasma reactor system.

[0039] Additional aspects relating to this particular embodiment in which the MX-functional nanoparticles are produced via this plasma process are described in International (PCT) Publication No. WO 2011/109299 (PCT/US2011/026491), which is incorporated by reference herein in its entirety.

[0040] Referring to Figure 2, an alternative embodiment of a plasma reactor system is shown at 50. In this embodiment, the MX-functional nanoparticles are prepared in a system having a reactor and a diffusion pump in fluid communication with the reactor for collecting the MX-functional nanoparticles of the aerosol. For example, MX-functional nanoparticles of various size distributions and properties can be prepared by introducing a nanoparticle aerosol produced in a reactor (e.g. a low-pressure plasma reactor) into a diffusion pump in fluid communication with the reactor, capturing the MX-functional nanoparticles of the aerosol in a condensate from the capture fluid, and collecting the captured MX-functional nanoparticles in a reservoir. In the embodiment of Figure 2, the capture fluid may alternatively be referred to as a

diffusion pump fluid, although the capture fluid and diffusion pump fluid are generally referred to herein as “the capture fluid” and are described collectively below.

[0041] Example reactors are described in WO 2010/027959 and WO 2011/109229, with each of which being incorporated herein in its respective entirety. Such reactors can be, but are not limited to, low pressure high frequency pulsed plasma reactors. For example, Figure 2 illustrates the plasma reactor of the embodiment of Figure 1, but includes the diffusion pump in fluid communication with the reactor. To this end, description relative to this particular plasma reactor is not repeated herein with respect to the embodiment of Figure 2.

[0042] In the embodiment of Figure 2, the plasma reactor system 50 includes a diffusion pump 120. As such, the MX-functional nanoparticles can be collected by the diffusion pump 120. A particle collection chamber 26 may be in fluid communication with the plasma generating chamber 22. The diffusion pump 120 may be in fluid communication with the particle collection chamber 26 and the plasma generating chamber 22. In other forms of the present disclosure, the system 50 may not include the particle collection chamber 26. For example, the outlet 30 may be coupled to an inlet 103 of the diffusion pump 120, or the diffusion pump 120 may be in substantially direct fluid communication with the plasma generating chamber 22.

[0043] Figure 3 is a cross-sectional schematic of an example diffusion pump 120 suitable for the system 50 of the embodiment of Figure 2. The diffusion pump 120 can include a chamber 101 having an inlet 103 and an outlet 105. The inlet 103 may have a diameter of about 2 to about 55 inches, and the outlet may have a diameter of about 0.5 to about 8 inches. The inlet 103 of the chamber 101 is in fluid communication with the outlet 30 of the reactor 20. The diffusion pump 120 may have, for example, a pumping speed of about 65 to about 65,000 liters/second or greater than about 65,000 liters/second.

[0044] The diffusion pump 120 includes a reservoir 107 in fluid communication with the chamber 101. The reservoir 107 supports or contains the capture fluid. The reservoir may have a volume of about 30 cc to about 15 liters. The volume of the capture fluid in the diffusion pump may be about 30 cc to about 15 liters.

[0045] The diffusion pump 120 can further include a heater 109 for vaporizing the capture fluid in the reservoir 107 to a vapor. The heater 109 heats up the capture fluid

and vaporizes the capture fluid to form a vapor (e.g., liquid to gas phase transformation). For example, the capture fluid may be heated to about 100 to about 400 °C or about 180 to about 250 °C.

[0046] A jet assembly 111 can be in fluid communication with the reservoir 107 comprising a nozzle 113 for discharging the vaporized capture fluid into the chamber 101. The vaporized capture fluid flows and rises up through the jet assembly 111 and emitted out the nozzles 113. The flow of the vaporized capture fluid is illustrated in Figure 3 with arrows. The vaporized capture fluid condenses and flows back to the reservoir 107. For example, the nozzle 113 can discharge the vaporized capture fluid against a wall of the chamber 101. The walls of the chamber 101 may be cooled with a cooling system 113 such as a water cooled system. The cooled walls of the chamber 101 can cause the vaporized capture fluid to condense. The condensed capture fluid can then flow along and down the walls of the chamber 101 and back to the reservoir 107. The capture fluid can be continuously cycled through diffusion pump 120. The flow of the capture fluid causes gas that enters the inlet 103 to diffuse from the inlet 103 to the outlet 105 of the chamber 101. A vacuum source 33 may be in fluid communication with the outlet 105 of the chamber 101 to assist removal of the gas from the outlet 105.

[0047] As the gas flows through the chamber 101, MX-functional nanoparticles in the gas can be absorbed by the capture fluid, thereby collecting the MX-functional nanoparticles from the gas. For example, a surface of the MX-functional nanoparticles may be wetted by the vaporized and/or condensed capture fluid. Furthermore, the agitating of cycled capture fluid may further improve absorption rate of the MX-functional nanoparticles compared to a static fluid. The pressure within the chamber 101 may be less than about 1 mTorr.

[0048] The capture fluid with the MX-functional nanoparticles can then be removed from the diffusion pump 120. For example, the capture fluid with the MX-functional nanoparticles may be continuously removed and replaced with capture fluid that substantially does not have MX-functional nanoparticles.

[0049] Advantageously, the diffusion pump 120 can be used not only for collecting MX-functional nanoparticles but also evacuating the reactor 20 (and collection chamber 26). For example, the operating pressure in the reactor 20 can be a low pressure, e.g. less than atmospheric pressure, less than 760 Torr, or between about 1

and about 760 Torr. The collection chamber 26 can, for example, range from about 1 to about 5 millitorr. Other operating pressures are also contemplated.

[0050] The system 50 may also include a vacuum pump or vacuum source 33 in fluid communication with the outlet 105 of the diffusion pump 120. The vacuum source 33 can be selected in order for the diffusion pump 120 to operate properly. In one form of the present disclosure, the vacuum source 33 comprises a vacuum pump (e.g., auxiliary pump). The vacuum source 33 may comprise a mechanical, turbo molecular, or cryogenic pump. However, other vacuum sources are also contemplated.

[0051] One method of producing MX-functional nanoparticles with the system 50 of Figure 2 can include forming a nanoparticle aerosol in the reactor 20. The nanoparticle aerosol can comprise MX-functional nanoparticles in a gas, and the method further includes introducing the nanoparticle aerosol into the diffusion pump 120 from the reactor 5. In this embodiment, the method also may include heating the capture fluid in a reservoir 107 to form a vapor, sending the vapor through a jet assembly 111, emitting the vapor through a nozzle 113 into a chamber 101 of the diffusion pump 120, condensing the vapor to form a condensate, and flowing the condensate back to the reservoir 107. Furthermore, the method can further include capturing the MX-functional nanoparticles of the aerosol in the condensate, which comprises the capture fluid, and collecting the captured MX-functional nanoparticles in the reservoir 107. The step of capturing the MX-functional nanoparticles of the aerosol in the condensation, which comprises the capture fluid, may be identical to the step of collecting the MX-functional nanoparticles of the aerosol in the capture fluid. The method can further include removing the gas from the diffusion pump with a vacuum pump. In the embodiment described above and illustrated in Figure 1, the MX-functional nanoparticles are collected directly in the capture fluid. However, in the embodiment described immediately above and illustrated in Figures 2 and 3, the capture fluid is vaporized and condensed in the diffusion pump, and the MX-functional nanoparticles are ultimately capture or collected in the capture fluid (once condensed).

[0052] Additional aspects relating to this particular embodiment in which the MX-functional nanoparticles are produced via this plasma process are described in U.S. Appln. Ser. No. 61/655,635, which is incorporated by reference herein in its entirety.

[0053] Independent of the particular low pressure reactor utilized to prepare the nanoparticle aerosol, the MX-functional nanoparticles are collected in the capture fluid (or diffusion pump fluid, which may also serve as the capture fluid). The capture fluid comprises a compound including a functional group Y reactive with the functional group X of the MX-functional nanoparticles. The capture fluid generally comprises compound at the time the MX-functional nanoparticles are collected in the capture fluid. It is has been found that even adding the compound to the capture fluid after collecting the MX-functional nanoparticles does not provide the same clarity and stability to the nanoparticle composition, although such utilization of the compound after collection of the MX-functional nanoparticles still provides benefits as compared to conventional collection methods.

[0054] The selection of the compound and the functional group Y of the compound is based on the functional group X of the MX-functional nanoparticles. For example, certain functional groups are reactive with hydrogen but not halogen atoms, whereas other functional groups are reactive with halogen atoms but not hydrogen. The compound is typically organic, i.e., the compound generally comprises carbon atoms.

[0055] In certain embodiments, the functional group X of the MX-functional nanoparticles is H, in which case the MX-functional nanoparticles may be referred to as MX-functional nanoparticles. In these embodiments, the compound typically comprises an unsaturated organic compound, and the functional group Y of the unsaturated compound is an aliphatic carbon-carbon multiple bond. These embodiments, i.e., those involving MX-functional nanoparticles where the compound comprises the unsaturated organic compound, are described immediately below.

[0056] The aliphatic carbon-carbon multiple bond may be a double bond ($C=C$) or a triple bond ($C\equiv C$). Further, the unsaturated organic compound may have more than one carbon-carbon multiple bond, with each carbon-carbon multiple bond being independently selected from a double bond and a triple bond. The aliphatic carbon-carbon multiple bond may be within a backbone of the unsaturated organic compound, pendent from the unsaturated organic compound, or at a terminal location of the unsaturated organic compound. For example, the unsaturated organic compound may be linear, branched, or partly branched, and the aliphatic carbon-carbon multiple bond may be located at any location of the unsaturated organic compound. Typically, the unsaturated organic compound is aliphatic, although the

unsaturated organic compound may have a cyclic and/or aromatic portion, so long as the carbon-carbon multiple bond is located in an aliphatic portion of the unsaturated organic compound, i.e., the carbon-carbon multiple bond of the unsaturated organic compound is not present in, for example, an aryl group. In certain embodiments, the aliphatic carbon-carbon multiple bond is present at a terminal location of the unsaturated organic compound, i.e., the alpha carbon of the unsaturated organic compound is part of the carbon-carbon multiple bond. This embodiment generally reduces steric hindrance of the aliphatic carbon-carbon multiple bond for reasons described below.

[0057] In certain embodiments, the unsaturated organic compound may comprise or consist of carbon and hydrogen atoms. Alternatively, the unsaturated organic compound may be substituted or unsubstituted. By “substituted,” it is meant that one or more hydrogen atoms of the unsaturated organic compound may be replaced with atoms other than hydrogen (e.g. a halogen atom, such as chlorine, fluorine, bromine, etc.), or one or more carbon atoms within the chain of the unsaturated organic compound may be replaced with an atom other than carbon, i.e., the unsaturated organic compound may include one or more heteroatoms within the chain, such as oxygen, sulfur, nitrogen, etc.

[0058] Generally, the unsaturated organic compound includes at least 5, alternatively at least 10, alternatively at least 15, alternatively at least 20, alternatively at least 25, carbon atoms in its chain. However, as described above, at least one carbon atom of the chain of the unsaturated organic compound may be substituted by an atom other than carbon, e.g. O. To this end, the values set forth above relative to the carbon atoms of the chain of the unsaturated compound also include any heteroatoms of the chain of the unsaturated compound.

[0059] For example, in various embodiments, the unsaturated organic compound may comprise an ester having the carbon-carbon multiple bond. In this embodiment, at least one carbon atom of the chain of the unsaturated organic compound is replaced by an oxygen atom so as to form an ether linkage with a carbonyl group adjacent thereto. In this embodiment, the unsaturated organic compound is typically a $\geq C_{10}$ ester. Specific examples of such esters suitable for the purposes of the unsaturated organic compound include, but are not limited to, allyl dodecanoate, dodecyl 3-butenate, propyl 10-undecenoate, 10-undecenyl acetate, and dodecyl (meth)acrylate.

[0060] In other embodiments, the functional group X of the MX-functional nanoparticles is the independently selected halogen atom. In these embodiments, the functional group X is independently selected from fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). Typically, X is Cl. In these embodiments, the functional group Y of the compound of the capture fluid is reactive with the functional group X of the MX-functional nanoparticles, i.e., the functional group Y is reactive with a halogen atom.

[0061] In embodiments where the functional group X of the MX-functional nanoparticles is the independently selected halogen atom, specific examples of the compound include, but are not limited to, an alcohol compound such as methanol, ethanol, 1-propanol, 2-propanol, *n*-butanol, *sec*-butanol, *iso*-butanol, *tert*-butanol, *n*-hexanol, *n*-octanol, *n*-decanol; a thiol compound such as methanethiol, ethanethiol, 1-propanethiol, 2-propanethiol, *n*-butanethiol, *sec*-butanethiol, *iso*-butanethiol, *tert*-butanethiol, *n*-hexanethiol, *n*-octanethiol, *n*-decanethiol; an amine compound such as methylamine, dimethylamine, ethylamine, diethylamine, phenylamine, diphenylamine; a carboxylic acid compound such as acetic acid, propanoic acid, butanoic acid, hexanoic acid, octanoic acid, decanoic acid, benzoic acid; a sulphide compound such as hydrogen sulfide; an amide compound such as acetamide, propanamide, butanamide, hexanamide, octanamide, decanamide, benzamide; a phosphine compound such as methylphosphine, dimethylphosphine, ethylphosphine, diethylphosphine, phenylphosphine, diphenylphosphine; a metal halide compound such as lithium fluoride, lithium chloride, lithium bromide, sodium fluoride, sodium chloride, sodium bromide, potassium fluoride, potassium chloride, potassium bromide; a terminal alkyne compound such as acetylene, propyne, but-1-yne, hex-1-yne, oct-1-yne, phenylacetylene; an organometallic compound, an alkali metal amide compound such as lithium amide, lithium methylamide, lithium dimethylamide, diisopropylamide; a metal thiolate compound such as lithium methanethiolate, sodium methanethiolate, potassium methanethiolate, lithium ethanethiolate, sodium ethanethiolate, potassium ethanethiolate, lithium phenylthiolate, sodium phenylthiolate, potassium phenylthiolate; and combinations thereof. Specific examples of organometallic compounds include, but are not limited to, metal alkoxide compounds such as lithium methoxide, sodium methoxide, potassium methoxide, lithium ethoxide, sodium ethoxide, potassium ethoxide, lithium phenoxide, sodium

phenoxide, potassium phenoxide; Grignard reagents such as methyl magnesium chloride, methyl magnesium bromide, ethyl magnesium chloride, ethyl magnesium bromide, phenyl magnesium chloride, phenyl magnesium bromide; organozinc reagents such as dimethyl zinc, diethyl zinc, diphenyl zinc, methylzinc chloride, methylzinc bromide, ethylzinc chloride, ethylzinc bromide, phenylzinc chloride, phenylzinc bromide; Gilman reagents such as lithium dimethylcuprate lithium diethylcuprate, lithium diphenylcuprate; organosodium reagents such as methylsodium, ethylsodium, phenylsodium; organopotassium reagents such as methylpotassium, ethylpotassium, phenylpotassium; organocalcium reagents such as methylcalcium iodide, diphenylcalcium, dibenzylcalcium; organolithium reagents such as methyllithium, ethyllithium, phenyllithium; and combinations thereof.

[0062] Each of these compounds includes a functional group Y that is reactive with a halogen atom. As in embodiments where the compound comprises the unsaturated organic compound, the functional group Y may be located at any location within the compound, but is typically terminal, e.g. bonded to an alpha carbon of the compound. Some of the compounds set forth above may be complexes including ligands. There are no specific limitations with respect to the compound so long as the compound is reactive with the functional group X of the MX-functional nanoparticles.

[0063] If desired, the compound may have additional functionality (i.e., functionality other than and in addition to the functional group Y). For example, in certain embodiments, the compound further comprises at least one functional group Z in addition to the functional group Y, with the functional group Z being convertible to a hydrophilic functional group. The functional group Z may, in certain embodiments, be selected from some of the functional groups set forth above suitable for the functional group Y, although in such embodiments, the functional group Z is separate from and in addition to the functional group Y in the compound.

[0064] Specific examples of hydrophilic functional groups include carboxylic acid functional groups, alcohol functional groups, hydroxy functional groups, azide functional groups, silyl ether functional groups, ether functional groups, phosphonate functional groups, sulfonate functional groups, thiol functional groups, amine functional groups, and combinations thereof. The amine functional group may be primary, secondary, tertiary, or cyclic. Such hydrophilic functional groups may be

bonded directly to the chain of the compound, e.g. to a carbon atom of the chain, or may be bonded via a heteroatom or bivalent linking group.

[0065] In certain embodiments, the compound may include the hydrophilic functional group, such as any of the hydrophilic functional groups set forth above. Alternatively, the compound may include the at least one functional group Z convertible to a hydrophilic functional group such that the unsaturated organic compound does not include a hydrophilic functional group until the at least one functional group is converted thereto.

[0066] Specific examples of the at least one functional group Z convertible to a hydrophilic functional group include, but are not limited to: ester functional groups (RCO_2R^1), including those of oxo acids, such as esters of carboxylic acid, sulfuric acid, phosphoric acid, nitric acid, and boric acid; acid halide functional groups (RCOX); amide functional groups (RCONH_2); nitrile functional groups (RCN); epoxide functional groups; silyl ether functional groups; ethylenically unsaturated groups in addition to the aliphatic carbon-carbon multiple bond; oxazoline functional groups ($\text{RC}_3\text{H}_5\text{NO}$); and anhydride functional groups, where R represents the compound, R^1 is a hydrocarbyl group, and X is a halogen atom. The esters of oxo acids may be derived from the condensation of any alcohol with the particular oxo acid. For example, the alcohol may be aliphatic or aromatic. The at least one functional group Z may be a substituent of the compound or a moiety within the compound. For example, when the compound includes an ester functional group, the ester functional group is generally a moiety within the compound, as opposed to a substituent bonded thereto.

[0067] The at least one functional group Z of the compound is generally selected based on the functional group X of the MX-functional nanoparticles as well as the functional group Y of the compound. For example, when X is H, reacting X and Y results in Si-C bonds. In contrast, when X is the independently selected halogen atom, reacting X with Y may result in SiC bonds, Si-O-C bonds, and/or Si-N-C bonds. Because Si-O-C bonds, and/or Si-N-C bonds may hydrolyze, further reaction to form the hydrophilic functional group is generally not carried out in an aqueous medium. In these embodiments, the compound may further comprise a butoxycarbonyl group.

[0068] The capture fluid may comprise compounds, components, or fluids in addition to the c compound. For example, conventional components utilized in conventional

capture fluids may be utilized in addition to the unsaturated organic compound in the capture fluid of the instant method. For example, conventional components of conventional capture fluids include silicone fluids, such as polydimethylsiloxane, phenylmethyl-dimethyl cyclosiloxane, tetramethyltetraphenyltrisiloxane, and/or pentaphenyltrimethyltrisiloxane; hydrocarbons; phenyl ethers; fluorinated polyphenyl ethers; and ionic fluids. The capture fluid may have a dynamic viscosity of about 0.001 to about 1 Pa·s, about 0.005 to about 0.5 Pa·s, or about 0.01 to about 0.1 Pa·s at 23 ± 3 °C. Furthermore, the fluid may have a vapor pressure of less than about 1×10^{-4} Torr. In some embodiments, the capture fluid is at a temperature ranging from about -20 °C to about 150 °C and a pressure ranging from about 1 to about 5 millitorr (about 0.133 Pa to about 0.665 Pa). In some embodiments, the capture fluid has a vapor pressure less than the pressure in the particle collection chamber.

[0069] The capture fluid generally comprises the compound in an amount sufficient to provide a molar ratio of the functional group Y to MX bonds in the MX-functional nanoparticles of at least 1:1, alternatively at least 1.2:1, alternatively at least 1.4:1. Molar ratios much higher than 1.4:1 may advantageously be utilized.

[0070] In various embodiments, the capture fluid comprises the compound in an amount of from greater than 0 to 100, alternatively from greater than 0 to 50, alternatively from 1 to 40, alternatively from 2 to 30, alternatively from 5 to 15, percent by weight based on the total weight of the capture fluid. The balance of the capture fluid may comprise any of the conventional components or conventional capture fluids set forth above, although the balance of the capture fluid comprises hydrocarbons for miscibility with the compound. The capture fluid may comprise the compound, consist essentially of the compound, or consist of the compound.

[0071] The method further comprises reacting the MX-functional nanoparticles with the compound of the capture fluid to form the nanoparticle composition comprising nanoparticles.

[0072] The MX-functional nanoparticles and the compound may be reacted via known methods. When X is H, this reaction is generally referred to as an addition reaction. For example, in hydrosilylation, i.e., when the MH-functional nanoparticles comprise SiH-functional nanoparticles, the carbon-carbon multiple bond of the unsaturated organic compound undergoes an addition reaction with the SiH-functional nanoparticles. For SiH-functional

nanoparticles, this addition reaction is referred to as hydrosilylation; for GeH-functional nanoparticles, this addition reaction is referred to as hydrogermylation; for SnH-functional nanoparticles, this addition reaction is referred to as hydrostannylation. Alternatively, when X is the halogen atom, the reaction between the MX-functional nanoparticles and the compound is generally classified based on the selection of the compound.

[0073] In certain embodiments, particularly X is H and the compound comprises the unsaturated organic compound, reacting the MX-functional nanoparticles with the unsaturated organic compound comprises irradiating a suspension of the MH-functional nanoparticles in the capture fluid with UV radiation. For example, reacting the MH-functional nanoparticles with the unsaturated organic compound may be photoinitiated. When reacting the MH-functional nanoparticles and the unsaturated organic compound comprises irradiating the suspension of the MH-functional nanoparticles in the capture fluid with radiation, the radiation typically has a wavelength of from 10 to 400, alternatively 280 to 320, nm.

[0074] Alternatively or in addition to radiation, reacting the MX-functional nanoparticles with the compound may comprise heating a suspension of the MX-functional nanoparticles and the capture fluid to or at a first temperature for a first period of time. When heat is utilized to react the MX-functional nanoparticles with the compound, the first temperature is typically from 50 to 250 °C and the first period of time is from 5 to 500 minutes.

[0075] Alternatively still, the MX-functional nanoparticles may inherently react with the compound once the MX-functional nanoparticles are collected in the capture fluid such that no reaction condition (e.g. irradiation or heat) is utilized or applied. However, utilizing heat or irradiation generally improves the reaction between the MX-functional nanoparticles and the compound, which may improve physical properties of the nanoparticle composition, including photoluminescence and photoluminescent intensity.

[0076] If desired, a catalyst or photocatalyst may be utilized during the step of reacting the MX-functional nanoparticles with the compound. Such catalysts are well known in the art based on the desired reaction mechanism, e.g. when X is H, any catalysts suitable for hydrosilylation may be utilized, which are typically

based on precious metals, e.g. platinum. However, catalysts or photocatalysts are not required for the step of reacting the MX-functional nanoparticles with the compound.

[0077] After reacting the MX-functional nanoparticles and the compound of the capture fluid, nanoparticles result which have a substituent, which is typically organic and is formed from the compound. For example, the compound is generally bonded to the nanoparticles, e.g. as a ligand or substituent. These nanoparticles are generally no longer MX-functional, and thus these nanoparticles have increased stability in solution or suspension. A suspension comprising the nanoparticles in the capture fluid is generally referred to as the nanoparticle composition. The invention also provides the nanoparticle composition formed in accordance with the method.

[0078] When the compound of the capture fluid includes the at least one functional group Z convertible to a hydrophilic functional group, the method may further comprise the step of converting the functional group Z to a hydrophilic functional group. The functional group Z of the compound may be converted to a hydrophilic functional group before, during, and/or after reacting the MX-functional nanoparticles and the compound. Typically, the functional group Z of the compound is converted to a hydrophilic functional group after reacting the MX-functional nanoparticles and the compound.

[0079] The functional group Z of the compound may be converted to a hydrophilic functional group via known methods. In various embodiments, converting the functional group Z of the compound comprises hydrolyzing the functional group Z.

[0080] For example, the functional group Z of the compound may be converted to a hydrophilic functional group by acidic or basic treatment. In these embodiments, the acid or base utilized is generally selected such that the acid or base is miscible with the capture fluid. Further, the acid is typically selected such that it can be removed from the capture fluid, e.g. by vacuum or washing with solvent. To this end, the acid may be selected from trifluoroacetic acid, hydrofluoric acid, and combinations thereof. The acid may be utilized in various concentrations in an aqueous form.

[0081] In one specific embodiment, the MX-functional nanoparticles are collected in the capture fluid, and the MX-functional nanoparticles and the compound of the capture fluid are reacted. After reacting the MX-functional nanoparticles and the compound of the capture fluid, nanoparticles result which have a substituent formed

from the compound. If the compound further includes the functional group Z convertible to a hydrophilic functional group, the functional group Z is present in the substituent of the nanoparticles. To this end, if the compound further includes the functional group Z convertible to a hydrophilic functional group, the method may further comprise converting the functional group Z to a hydrophilic group. An aqueous acid may be disposed in the capture fluid to convert the functional group Z to a hydrophilic functional group, optionally at a reflux temperature of the capture fluid including the aqueous acid. After converting the functional group Z to a hydrophilic functional group, the substituent of the nanoparticles includes a hydrophilic functional group.

[0082] In various embodiments, the method further comprises separating the nanoparticles and the capture fluid to form separated nanoparticles. For example, the nanoparticles and the capture fluid may be separated by centrifuging and/or decanting. The separated nanoparticles may be further washed by suspension in a solvent, e.g. toluene, followed by repeated separation from the solvent by centrifuging and/or decanting. The separated nanoparticles may ultimately be dried, e.g. in vacuo, to form a dried solid. In this embodiment, the separated nanoparticles are free-standing and not in solution or suspension. These separated nanoparticles may be utilized in various end uses and applications due to the separation from the capture fluid.

[0083] Further, when the compound includes the functional group Z convertible to a hydrophilic functional group, and when the method further comprises converting the functional group to a hydrophilic functional group, the nanoparticles may advantageously be suspended in a polar solvent, which offers significant advantages. For example, in this embodiment, the method may further comprise suspending the separated nanoparticles in a polar solvent, such as an aqueous solution, optionally along with ions, e.g. from disassociated sodium bicarbonate. The polar solvent may be selected from water and a dipolar aprotic organic solvent.

[0084] MX-functional nanoparticles and nanoparticle compositions generally can be prepared by any of the methods described above. Contingent on the precursor gas and molecules utilized in the plasma process, nanoparticles of various composition may be produced. The description below refers to the nanoparticles generally, which is applicable to both the MX-functional nanoparticles, as well as the nanoparticles of the

nanoparticle composition formed by reacting the MX-functional nanoparticles and the compound.

[0085] The nanoparticles may exhibit a number of unique electronic, magnetic, catalytic, physical, optoelectronic and optical properties due to quantum confinement effects. For example, many semiconductor nanoparticles exhibit photoluminescence effects that are significantly greater than the photoluminescence effects of macroscopic materials having the same composition.

[0086] The nanoparticles may have a largest dimension or average largest dimension less than 50, less than 20, less than 10, or less than 5, nm. Furthermore, the largest dimension or average largest dimension of the nanoparticles may be between 1 and 50, between 2 and 50, between 2 and 20, between 2 and 10, or between about 2.2 and about 4.7, nm. The nanoparticles can be measured by a variety of methods, such as with a transmission electron microscope (TEM). For example, as understood in the art, particle size distributions are often calculated via TEM image analysis of hundreds of different nanoparticles. In various embodiments, the nanoparticles may comprise quantum dots, typically silicon quantum dots. Quantum dots have excitons confined in all three spatial dimensions and may comprise individual crystals, i.e., each quantum dot is a single crystal.

[0087] In various embodiments, the nanoparticles may be photoluminescent when excited by exposure to UV light. Depending on the average diameter of the nanoparticles, they may photoluminescence in any of the wavelengths in the visible spectrum and may visually appear to be red, orange, green, blue, violet, or any other color in the visible spectrum. For example, nanoparticles with an average diameter less than about 5 nm may produce visible photoluminescence, and nanoparticles with an average diameter less than about 10 nm may produce near infrared (IR) luminescence. In one form of the present disclosure, the photoluminescent silicon nanoparticles have a photoluminescent intensity of at least 1×10^6 at an excitation wavelength of about 365 nm. The photoluminescent intensity may be measured with a Fluorolog3 spectrofluorometer (commercially available from Horiba of Edison, NJ) with a 450 W Xe excitation source, excitation monochromator, sample holder, edge band filter (400 nm), emission monochromator, and a silicon detector photomultiplier tube. To measure photoluminescent intensity, the excitation and emission slit width are set to 2 nm and the integration time is set to 0.1s. In these or other embodiments,

the photoluminescent silicon nanoparticles may have a quantum efficiency of at least 4% at an excitation wavelength of about 395 nm as measured on an HR400 spectrophotometer (commercially available from Ocean Optics of Dunedin, Florida) via a 1000 micron optical fiber coupled to an integrating sphere and the spectrophotometer with an absorption of >10% of the incident photons. Quantum efficiency was calculated by placing a sample into the integrating sphere and exciting the sample via a 395 nm LED driven by an Ocean Optics LED driver. The system was calibrated with a known lamp source to measure absolute irradiance from the integrating sphere. The quantum efficiency was then calculated by the ratio of total photons emitted by the nanoparticles to the total photons absorbed by the nanoparticles. Further, in these or other embodiments, the nanoparticles may have a full width at half maximum emission of from 20 to 250 at an excitation wavelength of 270-500 nm.

[0088] Furthermore, both the photoluminescent intensity and luminescent quantum efficiency may continue to increase over time when the nanoparticles (optionally in the capture fluid) are exposed to air. In another form of the present disclosure, the maximum emission wavelength of the nanoparticles shift to shorter wavelengths over time when exposed to oxygen. The luminescent quantum efficiency of the directly captured silicon nanoparticle composition may be increased by about 200% to about 2500% upon exposure to oxygen. However, other increases in the luminescent quantum efficiency are also contemplated. The photoluminescent intensity may increase from 400 to 4500% depending on the time exposure to oxygen and the concentration of the nanoparticles in the fluid. However, other increases in the photoluminescent intensity are also contemplated. The wavelength emitted from the direct capture composition also experiences a blue shift of the emission spectrum. In one form of the present disclosure, the maximum emission wavelength shifts about 100 nm, based on about a 1 nm decrease in nanoparticle core size, depending on the time exposed to oxygen. However, other maximum emission wavelength shifts are also contemplated.

[0089] It is to be understood that the appended claims are not limited to express and particular compounds, compositions, or methods described in the detailed description, which may vary between particular embodiments which fall within the scope of the appended claims. With respect to any Markush groups relied upon herein for

describing particular features or aspects of various embodiments, different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

[0090] Further, any ranges and subranges relied upon in describing various embodiments of the invention independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the invention, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range “of from 0.1 to 0.9” may be further delineated into a lower third, i.e., from 0.1 to 0.3, a middle third, i.e., from 0.4 to 0.6, and an upper third, i.e., from 0.7 to 0.9, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as “at least,” “greater than,” “less than,” “no more than,” and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of “at least 10” inherently includes a subrange of from at least 10 to 35, a subrange of from at least 10 to 25, a subrange of from 25 to 35, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range “of from 1 to 9” includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

[0091] The following examples are intended to illustrate the invention and are not to be viewed in any way as limiting to the scope of the invention.

EXAMPLES

[0092] MX-functional nanoparticles are prepared via a plasma process and subsequently reacted with a compound to prepare nanoparticle compositions in accordance with the invention.

[0093] Examples 1-4 and Comparative Examples 1-2:

[0094] In Examples 1-4 and Comparative Examples 1-2, the functional group X of the MX-functional nanoparticles is H. In these examples, the functional group Y of the compound is an aliphatic carbon-carbon multiple bond. The compound is referred to as an unsaturated organic compound.

[0095] Example 1:

[0096] Nanoparticles are prepared in accordance with the subject disclosure. In particular, nanoparticles are prepared via a plasma reactor system from a precursor gas comprising SiH_4 (2% vol. in Ar) at 16 sccm with additional Ar and H_2 in the precursor gas. The precursor gas is delivered to the reactor via mass flow controllers.

[0097] SiH-functional nanoparticles are produced for ten minutes via the method and collected directly in a capture fluid. The capture fluid comprises a 9:1 (w/w) mixture of an oil and an unsaturated organic compound having an aliphatic carbon-carbon multiple bond. The unsaturated organic compound is allyl dodecanoate. The oil comprises petroleum distillates and is commercially available under the tradename Diffoil-20 Ultra from the Kurt J. Lesker Company of Jefferson Hills, PA. The allyl dodecanoate is present in an amount sufficient to provide at least one mole of allyl functionality per mole of SiH in the SiH-functional nanoparticles.

[0098] A suspension comprising the capture fluid and the SiH-functional nanoparticles is removed from the plasma reactor system, placed into an ultrasonic water bath for about an hour, and exposed to radiation at a wavelength of 365 nm for determining photoluminescence. The nanoparticles of the suspension are visibly photoluminescent upon exposure to the radiation.

[0099] The suspension formed in Example 1 has significantly improved optical clarity as compared to the suspensions of Comparative Examples 1 and 2, described below. Further, the suspension formed in Example 1 had only minimal settling of the solid phase after a 24 hour period, which is significantly improved as compared to the settling of the suspensions of Comparative Examples 1 and 2.

[00100] Example 2:

[00101] The procedure from Example 1 is repeated, however, immediately upon capturing the SiH-functional nanoparticles in the capture fluid, a suspension comprising the capture fluid and the SiH-functional nanoparticles is removed from the plasma reactor system and subjected to irradiation (at 254 nm) to promote hydrosilylation of the unsaturated organic compound with the SiH-functional nanoparticles.

[00102] After irradiation, no haze could be visibly detected in the suspension and there was no settling of the solid phase (i.e., the nanoparticles) after a 24 hour period, which is significantly improved as compared to the settling of the suspensions of Comparative Examples 1 and 2, described below. Further, the suspension is exposed to radiation at a wavelength of 365 nm for determining photoluminescence. The photoluminescence is more visibly intense than that of the nanoparticles of Example 1, attributable to the irradiation.

[00103] Example 3:

[00104] Nanoparticles are prepared in accordance with the subject disclosure. In particular, nanoparticles are prepared via a plasma reactor system from a precursor gas comprising SiH₄ (2% vol. in Ar) at 16 sccm with additional Ar and H₂ in the precursor gas. The precursor gas is delivered to the reactor via mass flow controllers.

[00105] SiH-functional nanoparticles are produced for ten minutes via the method and collected directly in 10 g of a capture fluid. The capture fluid comprises a 9:1 (w/w) mixture of a hydrogenated oil and an unsaturated organic compound having an aliphatic carbon-carbon multiple bond. The unsaturated organic compound also comprises a functional group convertible to a hydrophilic functional group. In particular, the unsaturated compound comprises dodecyl methacrylate, which includes an ester moiety, i.e., the functional group convertible to a hydrophilic functional group. The hydrogenated oil comprises saturated polymerized ethylene and is commercially available under the tradename Permavis 10 from the Kurt J. Lesker Company of Jefferson Hills, PA.

[00106] A suspension comprising the capture fluid and the SiH-functional nanoparticles is removed from the plasma reactor system and placed into a sealed vial. The sealed vial is placed in an ultrasonic bath for about 1 hour. The suspension is removed from the sealed vial and placed into a capped quartz flask along with 20 mL of toluene. The capped quartz flask including the suspension is then irradiated with

254 nm UV radiation for about four hours with agitation every 20 minutes to photoinitiate hydrosilylation between the unsaturated organic compound and the SiH-functional nanoparticles.

[00107] The next day, 20 mL of H₂O, 2.25 g of trifluoroacetic acid, and 10 mL of THF are disposed in the flask and the contents of the flask are refluxed for about three hours. The aqueous acid converts the ester group of the unsaturated organic compound to a hydrophilic group. Namely, the aqueous acid converts the ester group of the unsaturated organic compound to a carboxyl group once the ester group hydrolyzes in the presence of the aqueous acid.

[00108] After refluxing for three hours, the contents of the flask are centrifuged to concentrate the nanoparticles into a packed solid. The remaining fluids are removed from the nanoparticles and the solid nanoparticles are washed by repeated suspension in toluene and subsequent centrifuging. The solid nanoparticles are dried *in vacuo* to form a dried solid. The dried solid is disposed in 5 mL of 0.1M sodium bicarbonate solution having a pH of 7 and placed in an ultrasonic bath for several hours to form an aqueous suspension. When subjected to UV irradiation, the nanoparticles of the aqueous suspension exhibit a bright yellow-orange photoluminescence.

[00109] The aqueous suspension formed in Example 3 has significantly improved optical clarity and resistance to settling as compared to the suspensions of Comparative Examples 1 and 2. Moreover, because the unsaturated organic compound utilized in Example 3 includes the functional group convertible to a hydrophilic group, the resulting nanoparticles of Example 3 can be disposed and suspended in polar solvents, such as water. This is not the case for nanoparticles that do not include a hydrophilic group.

[00110] Example 4:

[00111] The procedure of Example 3 is repeated. However, in Example 4, the unsaturated organic compound comprises dodecyl butenoate, whereas in Example 3, the unsaturated organic compound comprises dodecyl methacrylate. All other aspects, including relative amounts of the unsaturated organic compound, are identical between Examples 3 and 4. The nanoparticles produced and collected in Example 4 also exhibit a bright yellow-orange photoluminescence when subjected to UV irradiation. Similarly, the nanoparticles of Example 4 had excellent stability while suspended in polar solvents, such as water.

[00112] Comparative Example 1:

[00113] Nanoparticles are prepared in accordance with the procedure described in Example 1, but the capture fluid in Comparative Example 1 did not include the unsaturated organic compound. Instead, the capture fluid in Comparative Example 1 consists of the oil described in Example 1.

[00114] Immediately after collecting the SiH-functional nanoparticles in the capture fluid, the resulting solution is removed from the plasma reactor system. The solution is a hazy solution and, after about 1 hour, significant settling of the SiH-functional nanoparticles is observed. After about 24 hours standing at room temperature, the solids of the solution were completely settled and no longer suspended in the capture fluid. Finally, when subjected to UV irradiation at 365 nm, the SiH-functional nanoparticles did not exhibit any photoluminescence.

[00115] Comparative Example 2:

[00116] Nanoparticles are prepared in accordance with the procedure described in Example 1, but the capture fluid in Comparative Example 1 did not include the unsaturated organic compound at the time of collecting the SiH-functional nanoparticles. Instead, the capture fluid in Comparative Example 1 consists of the oil described in Example 1 at the time of collecting the SiH-functional nanoparticles in the capture fluid.

[00117] However, after capturing the SiH-functional nanoparticles in the capture fluid, an unsaturated organic compound is disposed in the capture fluid. The unsaturated organic compound is allyl dodecanoate, i.e., the same unsaturated organic compound of Example 1, and the unsaturated organic compound is utilized in the same amount in Comparative Example 2 as in Example 1. A suspension including the SiH-functional nanoparticles and the capture fluid is subjected to irradiation (at 254 nm) to promote hydrosilylation of the unsaturated organic compound with the SiH-functional nanoparticles.

[00118] Despite the unsaturated organic compound being present in the capture fluid immediately after collecting the SiH-functional nanoparticles, the resulting solution is a hazy solution. The solution is exposed to 365 nm UV irradiation, but no improvements relative to haze or photoluminescence were observed relative to Comparative Example 1.

[00119] Notably, the only difference between Comparative Example 2 and Example 1 is that the unsaturated organic compound is present in the capture fluid at the time of collecting the SiH-functional nanoparticles in Example 1, whereas the unsaturated organic compound is only present in the capture fluid after collecting the SiH-functional nanoparticles in Comparative Example 2. Surprisingly, despite this seemingly insignificant difference between Example 1 and Comparative Example 2, the suspension of Example 1 had significantly improved stability, clarity, shelf-life, and photoluminescence as compared to the suspension of Comparative Example 1. This is particularly surprisingly considering the SiH-functional nanoparticles and the unsaturated organic compound of Comparative Example 2 could still undergo photoinitiated hydrosilylation. Accordingly, Comparative Example 2 illustrates the impact of including the unsaturated organic compound in the capture fluid at the time of collecting the SiH (or MH)-functional nanoparticles.

[00120] Examples 5-6 and Comparative Examples 3-4:

[00121] In Examples 5-6 and Comparative Examples 3-4, the functional group X of the MX-functional nanoparticles is a halogen atom (specifically, Cl).

[00122] Example 5:

[00123] Nanoparticles are prepared in accordance with the subject disclosure. In particular, nanoparticles are prepared via a plasma reactor system from a precursor gas comprising SiH₄ (2% vol. in Ar) at 30 sccm with additional Ar and H₂ in the precursor gas. The precursor gas is utilized along with a feed of SiCl₄ to form a reactant gas mixture. The SiCl₄ is for imparting the MX-functional nanoparticles with the Cl functionality. The SiCl₄ is utilized at 10 sccm (2% vol. in Ar). The precursor gas is delivered to the reactor via mass flow controllers.

[00124] SiCl-functional nanoparticles are produced for ten minutes via the method and collected directly in a capture fluid. The capture fluid comprises a 9:1 (w/w) mixture of an oil and a compound having a functional group Y reactive with Cl of the SiCl-functional nanoparticles. The compound comprises dodecanol, and the functional group Y of the compound is an alcohol functional group. The oil comprises saturated polymerized ethylene and is commercially available under the tradename Permavis 10 from the Kurt J. Lesker Company of Jefferson Hills, PA.

[00125] A suspension comprising the capture fluid and the SiCl-functional nanoparticles is removed from the plasma reactor system. The suspension

immediately exhibited photoluminescence upon exposure to radiation at a wavelength of 365 nm. The photoluminescent efficiency increased overtime while being in a sealed container, i.e., while not being exposed to ambient conditions. The suspension is hazy.

[00126] Example 6:

[00127] Nanoparticles are prepared in accordance with the subject disclosure. In particular, nanoparticles are prepared via a plasma reactor system from a precursor gas comprising SiH_4 (2% vol. in Ar) at 80 sccm with additional Ar and H_2 in the precursor gas. The precursor gas is utilized along with a feed of Cl_2 to form a reactant gas mixture. The Cl_2 is for imparting the MX-functional nanoparticles with the Cl functionality. The Cl_2 is utilized at 2 sccm. The precursor gas is delivered to the reactor via mass flow controllers.

[00128] SiCl-functional nanoparticles are produced for ten minutes via the method and collected directly in a capture fluid. The capture fluid comprises a 9:1 (w/w) mixture of an oil and a compound having a functional group Y reactive with Cl of the SiCl-functional nanoparticles. The compound comprises dodecanol, and the functional group Y of the compound is an alcohol functional group. The oil comprises saturated polymerized ethylene and is commercially available under the tradename Permavis 10 from the Kurt J. Lesker Company of Jefferson Hills, PA.

[00129] A suspension comprising the capture fluid and the SiCl-functional nanoparticles is removed from the plasma reactor system. The suspension immediately exhibited photoluminescence upon exposure to radiation at a wavelength of 365 nm. The photoluminescent efficiency increased overtime while being in a sealed container, i.e., while not being exposed to ambient conditions. The suspension has increased clarity as compared to that of Example 5. It is believed that the nanoparticle synthesis of Example 6 increased the Cl functionality of the SiCl-functional nanoparticles as compared to the synthesis of Example 5.

[00130] Comparative Example 3:

[00131] The procedure from Example 5 is repeated, however, the capture fluid is free from the compound including the functional group Y. A suspension comprising the capture fluid and the SiCl-functional nanoparticles is removed from the plasma reactor system. The suspension is very hazy with some settling. The suspension does

not exhibit any photoluminescence upon exposure to radiation at a wavelength of 365 unless exposed to air for an extended period of time.

[00132] Comparative Example 4:

[00133] The procedure from Example 6 is repeated, however, the capture fluid is free from the compound including the functional group Y. A suspension comprising the capture fluid and the SiCl-functional nanoparticles is removed from the plasma reactor system. The suspension is very hazy with some settling. The suspension does not exhibit any photoluminescence upon exposure to radiation at a wavelength of 365 unless exposed to air for an extended period of time.

[00134] The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Obviously, many modifications and variations of the invention are possible in light of the above teachings. The invention may be practiced otherwise than as specifically described.

CLAIMS

What is claimed is:

1. A method of preparing a nanoparticle composition, said method comprising:
forming a nanoparticle aerosol in a low pressure reactor, wherein the aerosol comprises MX-functional nanoparticles in a gas, wherein M is an independently selected Group IV element and X is a functional group independently selected from H and a halogen atom;

collecting the MX-functional nanoparticles of the aerosol in a capture fluid, wherein the capture fluid is in communication with the low pressure reactor, and wherein the capture fluid comprises a compound including a functional group Y reactive with the functional group X of the MX-functional nanoparticles; and

reacting the compound and the MX-functional nanoparticles to prepare the nanoparticle composition comprising nanoparticles.

2. The method according to claim 1 wherein X is H and wherein Y is an aliphatic carbon-carbon multiple bond.

3. The method according to claim 1 wherein X is a halogen atom independently selected from F, Cl, Br, and I.

4. The method according to claim 3 wherein Y is a nucleophilic functional group reactive with the halogen atom X of the MX-functional nanoparticles.

5. The method according to claim 4 wherein the compound is selected from the group of an alcohol compound, a thiol compound, a cyanate compound, an amine compound, an azide compound, a nitrile compound, a carboxylic acid compound, a sulphide compound, an amide compound, a phosphine compound, a metal halide compound, a terminal alkyne compound, an organometallic compound, an alkali metal amide compound, a metal thiolate compound, and combinations thereof.

6. The method according to any one preceding claim wherein the compound is organic.

7. The method according to any one preceding claim wherein forming the nanoparticle aerosol comprises:

applying a preselected HF or VHF radio frequency having a continuous frequency of from about 10 to about 500 MHz and a coupled power of from about 5 to about 1000 W to a reactant gas mixture in a plasma reactor having a reactant gas inlet and an outlet having an aperture therein to generate a plasma for a time sufficient to form the nanoparticle aerosol comprising MX-functional nanoparticles in a gas, with the reactant gas mixture comprising from about 0.1 to about 50% by volume of a first precursor gas containing M, and at least one inert gas.

8. The method according to any one preceding claim further comprising:

introducing the nanoparticle aerosol into a diffusion pump from the low pressure reactor;

heating the capture fluid in a reservoir to form a vapor and sending the vapor through a jet assembly;

emitting the vapor through a nozzle into a chamber of the diffusion pump and condensing the vapor to form a condensate comprising the capture fluid;

flowing the condensate back to the reservoir; and

capturing the MX-functional nanoparticles of the aerosol in the condensate comprising the capture fluid.

9. The method according to any one preceding claim wherein the compound further comprises at least one functional group Z in addition to Y with Z being convertible to a hydrophilic functional group and wherein the method further comprises the step of converting the functional group Z to a hydrophilic functional group.

10. The method according to claim 9 wherein the at least one functional group Z convertible to a hydrophilic functional group is selected from an ester functional group, an acid halide functional group, an amide functional group, a nitrile functional group, a silyl ether functional group, an epoxide functional group, a disulfide

functional group, an ethylenically unsaturated group, an oxazoline functional group, an anhydride functional group, and combinations thereof.

11. The method according to any one of claims 1-8 wherein the compound further comprises a hydrophilic functional group different from Y and selected from a carboxylic acid functional group, an alcohol functional group, a hydroxy functional group, an azide functional group, a silyl ether functional group, an ether functional group, a phosphonate functional group, a sulfonate functional group, a thiol functional group, an amine functional group, an anhydride functional group, and combinations thereof.

12. The method according to any one of claims 1 and 3-8 wherein the compound further comprises a butoxycarbonyl group.

13. The method according to any one preceding claim further comprising separating the nanoparticles and the capture fluid to obtain separated nanoparticles.

14. The method according to claim 13 wherein the separated nanoparticles are a solid.

15. The method according to claims 13 or 14 further comprising suspending the separated nanoparticles in a polar solvent selected from water and a dipolar aprotic organic solvent.

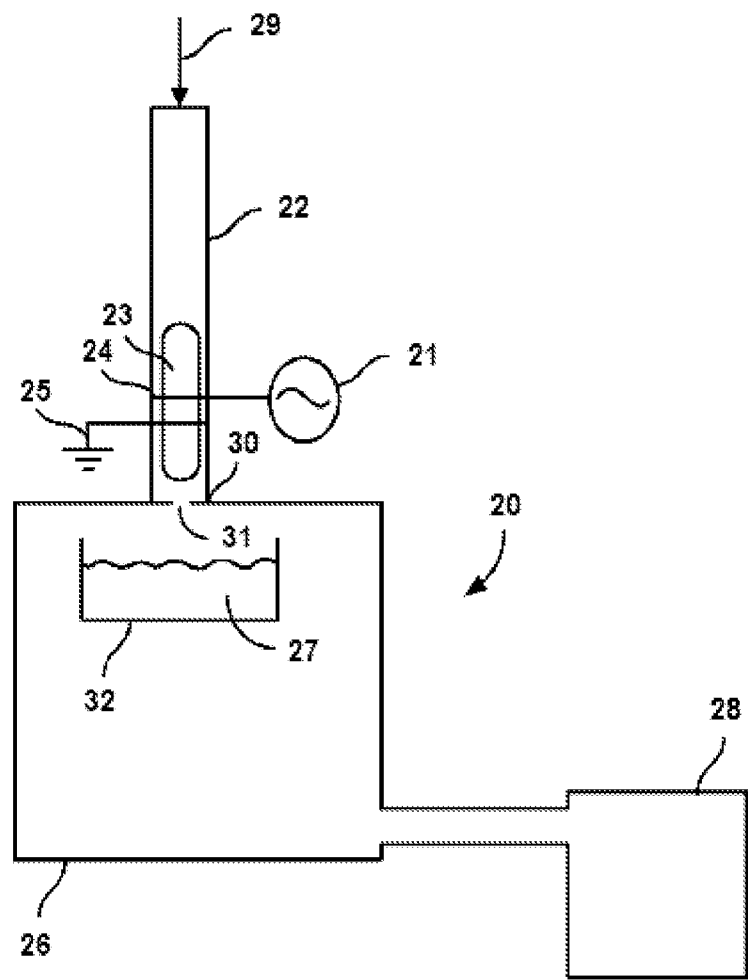


Figure 1

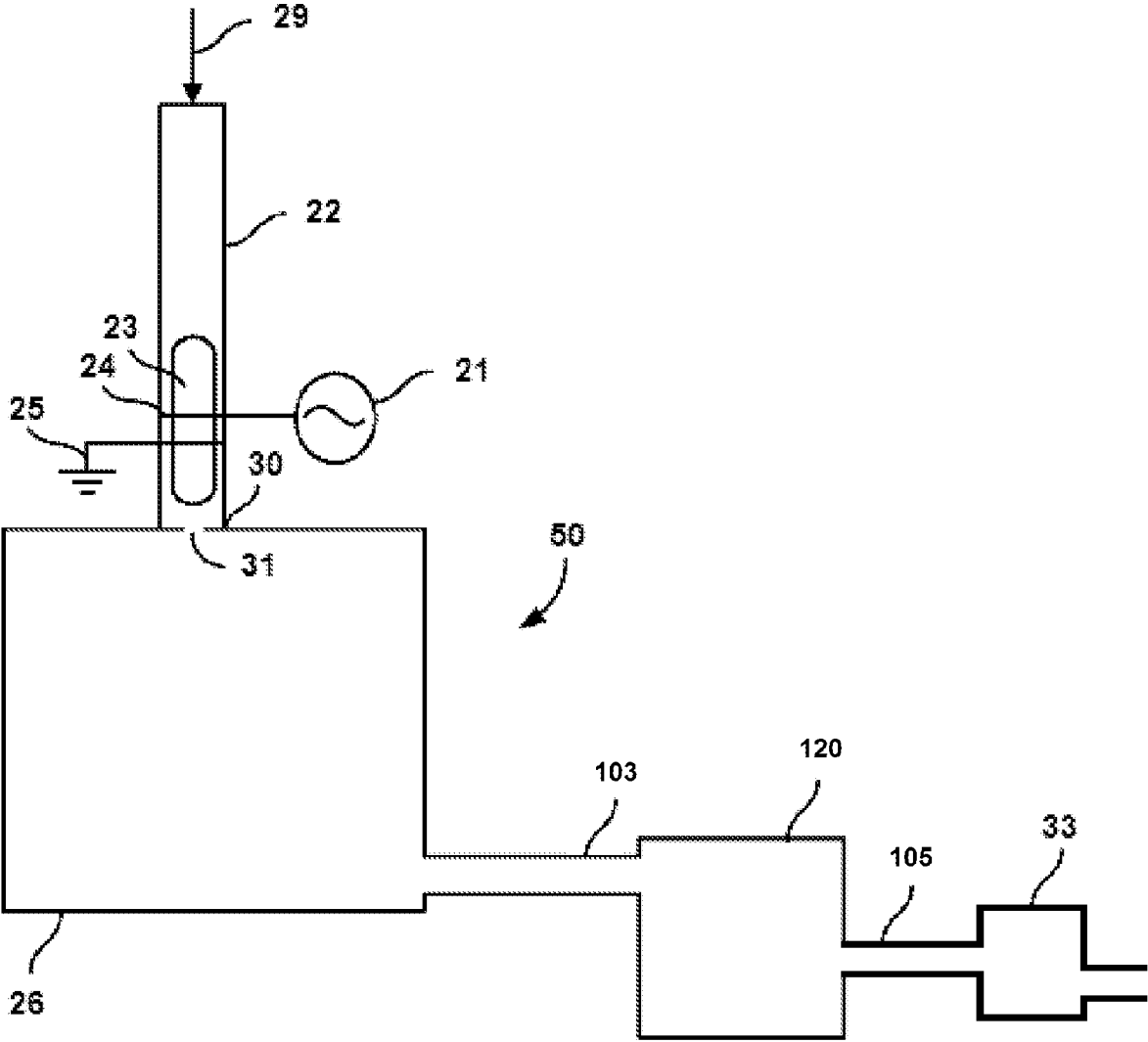


Figure 2

3/3

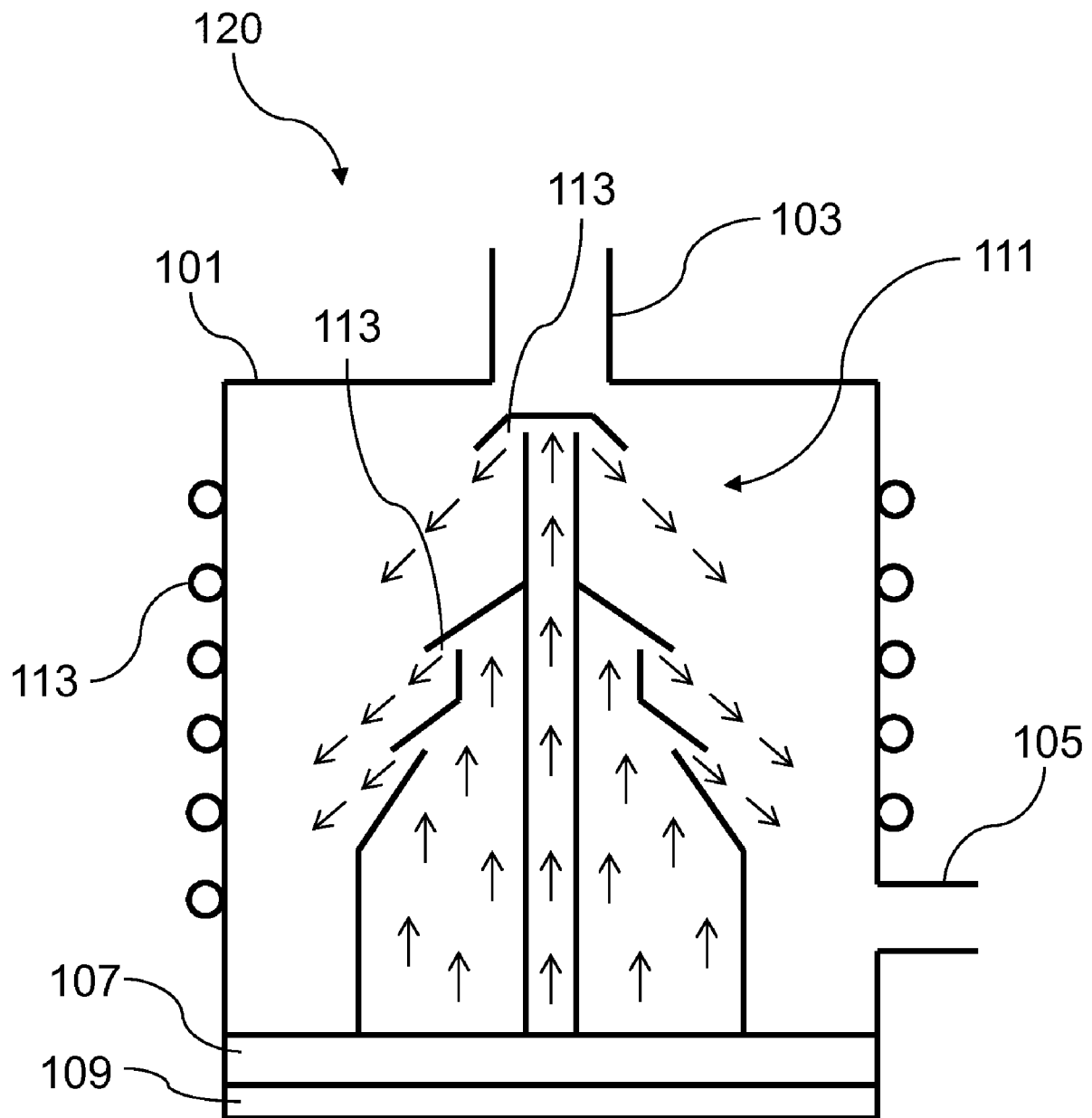


Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/040199

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B33/027 B01J2/04 C01B33/029 C01B33/03 C09K11/59
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B B01J C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/109299 A1 (DOW CORNING [US]; ANDERSON JEFFERY [US]; CASEY JAMES ALLEN [US]; SHAMA) 9 September 2011 (2011-09-09) the whole document	1,3-8, 13-15
Y	JING ZOU ET AL: "Functionalization of Silicon Nanoparticles via Silanization: Alkyl, Halide and Ester", JOURNAL OF CLUSTER SCIENCE, KLUWER ACADEMIC PUBLISHERS-PLENUM PUBLISHERS, NE, vol. 19, no. 2, 20 March 2008 (2008-03-20) , pages 341-355, XP019608275, ISSN: 1572-8862 abstract page 341 - page 344	2,9-12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 September 2014

Date of mailing of the international search report

11/09/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Mertins, Frédéric

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/040199

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GUPTA A ET AL: "Luminescent colloidal dispersion of silicon quantum dots from microwave plasma synthesis: exploring the photoluminescence behavior across the visible spectrum", ADVANCED FUNCTIONAL MATERIALS, WILEY - V C H VERLAG GMBH & CO. KGAA, DE, vol. 19, no. 5, 10 March 2009 (2009-03-10) , pages 696-703, XP001520273, ISSN: 1616-301X, DOI: 10.1002/ADFM.200801548 the whole document -----	2,9-12
Y	HUA F ET AL: "Organically Capped Silicon Nanoparticles with Blue Photoluminescence Prepared by Hydrosilylation Followed by Oxidation", LANGMUIR, AMERICAN CHEMICAL SOCIETY, NEW YORK, NY; US, no. 22, 30 March 2006 (2006-03-30), pages 4363-4370, XP002489361, ISSN: 0743-7463 [retrieved on 2006-03-30] the whole document -----	2,9-12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/040199

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-15(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-15(partially)

Present claim 1 relates to an extremely large number of possible methods. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the methods claimed, see the description on page 3, paragraph 14 and on pages 26-32, examples 1-6. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claim 1 (PCT Guidelines 9.19 and 9.23).

The search of claim 1 was restricted to those claimed methods which appear to be sufficiently supported and disclosed, namely the method of claim 1 with the following restrictions:

- i) the low pressure reactor is a plasma reactor
- ii) M is chosen from the group consisting of Si, Ge and Sn

A similar reasoning applies to the dependent claims 2-15 (Articles 5 and 6 PCT).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/040199

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011109299 A1	09-09-2011	CN 102781834 A	14-11-2012
		EP 2542502 A1	09-01-2013
		JP 2013521215 A	10-06-2013
		KR 20130014529 A	07-02-2013
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		US 2012326089 A1	27-12-2012
		WO 2011109299 A1	09-09-2011
