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Diacetylene Phospholipid-Mediated Synthesis of Germania Nanotubules and Nanoparticles

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A very facile synthesis of nanometer-sized germania-coated nanotubules and germania crystals has been investigated through hydrolysis of germanium tetraalkoxide (TEOG) and subsequent condensation of germania in aqueous synthetic diacetylene phospholipid [1,2-bis(tricosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine ($DC_{8,9}$-PC)] solutions. In the presence of the $DC_{8,9}$-PC, TEOG rapidly hydrolyzes in aqueous ethanol solution, leading to solvated germinate species at lower germania concentrations yielding germania/lipid composite nanotubules and the onset of nanometer-sized germania crystals at room temperature with increasing germania content. Phospholipid and germania concentration both influence crystallite size and morphology (i.e., polyhedral, cubic). Germania molecules hydrolyzed on the surface of lipid bilayer bring up to the secondary tubular structure by the self-assembling driving force of the lipid molecules. The fact that the germania crystal morphology formed at higher TEOG concentrations shows no signs of nanoparticle aggregative assembly in the absence of $DC_{8,9}$-PC suggests that the crystal growth should take place by addition of dissolved species like weakly acidic $DC_{8,9}$-PC rather than nanoparticles.

Introduction

Studied extensively in early of 1960s,[1,2] germania has been revisited recently, often in conjunction with its silica analogue, owing to its enhancement of materials properties ranging from catalytic reactivity[3] to optical and electronic properties.[4] The preparation of silica, which typically employs nonaqueous or aqueous sol–gel routes and occurs at relatively low temperatures,[5] generally results in poor control over the structure and processing of the product. Biological organisms, in contrast, are able to uptake, store, and process soluble silicon (in an as yet unknown form) and mold it with great sophistication into ornate hierarchical patterned biosilicas.[6] Specifically, the copolymerization of silica and germania in biogenic systems has been observed,[7] evidence exists for the importance of germanium in biosilicification,[8] and it is recognized that similar biomineralization mechanisms may govern synthesis of complex germania structures as well.[9] Recently, Tsapatsis et al. showed that hydrolysis of tetraethylorthosilicate (TEOS)[10] and tetraethylorthogermanate (TEOG)[11] in aqueous lysine solutions lead to the formation of fairly monodisperse silica and germania nanoparticles.

Phospholipids self-organize to form a spherical, bilayer aggregate known as a liposome in solution due to their amphiphilic structure. Synthetic phospholipids such as 1,2-bis(tricosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine ($DC_{8,9}$-PC) with diacetylenes in the acyl chains were found to self-assemble into hollow, cylindrical structures, known as tubules, induced by chiral interactions, when the lipids are cooled into the gel phase.[6,12] It forms tubules typically tens of micrometers in length and about 500 nm in external diameter.[6,13–18] Lipid nanotubules formed from $DC_{8,9}$-PC have been extensively investigated,[1,12]

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and studies on silica and metallic coatings and surface decoration with gold nanoparticles or polypyrrole threads have been carried out.[12,19–21] Interested in investigating how the chemistry of germania compares to that of silica and spurred by an interest in exploring bioinspired germania crystallization and nanoparticle formation, we report here on the condensation of germania in aqueous mixtures at mild conditions in the presence of $DC_{8,9}$-PC as a template.

Experimental Section

Preparation of $DC_{8,9}$-PC/Germania Tubular Composite and Germania Nanocrystals. To prepare $DC_{8,9}$-PC/germania nanotubules, sol–gel reactions of TEOG (99.95%, Aldrich) were started by introducing various amounts of TEOG [5 μL (22.6 nmol)–30 μL (135.6 nmol)] in the homogeneous mixture consisting of 10 mg (10.8 μmol) of $DC_{8,9}$-PC (Avanti), 3.5 mL of anhydrous ethanol (Aldrich), and 1.5 mL of purified water (Millipore Elix, 10 MΩ cm) at 50 °C under vigorous stirring. The resulting mixtures were subjected to slow cooling (1 °C/10 min) to room temperature without stirring. All microscopic characterizations were carried out without further purification of the resulting turbid mixture containing composite tubules. Germania nanocrystals with different morphology were obtained by similar sol–gel reactions with increased amount of TEOG [50 μL (0.226 μmol)–120 μL (0.542 μmol)]. Similar sol–gel reaction using 100 μL (0.452 μmol) of TEOG keeping other conditions the same under ultrasonic conditions using JAC Ultrasonic 1505 (Kodo; 40 kHz) was also carried out to decrease the size of germania crystals. Alternatively the TEOG condensation was started by slowly introducing 1.5 mL of water (10 μL/min) by using a syringe pump (Harvard PHD 22/2000) into the homogeneous reaction mixture consisting of $DC_{8,9}$-PC (10 mg), 3.5 mL of absolute ethanol, and 20 μL (90.4 nmol) of TEOG at room temperature.

Characterization. TEM grids (Formvar-coated or carbon coated) were treated by oxygen plasma (from a Harrick plasma cleaner/sterilizer) for 20 s to render their surface hydrophilic. Ten microliters of the resulting gel or GeO_2 nanoparticles dispersed in water were mixed on the surface of a plastic Petri dish to form a small bead. A TEM grid was then floated on the top of the bead with the hydrophilic face contacting the solution. The TEM grid was carefully removed with a pair of tweezers, wicked with a filter paper to remove excess liquid, and then dried in air for 1 min. The same samples prepared for TEM were utilized for SEM. For energy-filtering transmission electron microscopy (EF-TEM), unstained specimens were examined with a Zeiss LEO 912 Omega, at an accelerating voltage of 120 kV. General TEM was also done with a Philips EM400T TEM, at an accelerating voltage of 80 kV. SEM images were obtained by using a Leica 440 SEM at 30 kV. Crystalline germania precipitates were isolated by dissolving the sols in chloroform, withdrawing the supernatant, and drying the samples at room temperature under vacuum. Raman spectra were obtained using a triple-grating micro-Raman spectrometer (T64000 Jobin Yvon) in a confocal configuration. The samples were excited by the 514.5 nm line of an Ar^+ laser. XRD measurement at room temperature was carried out by using Cu Kα radiation with a normal $\theta-2\theta$ scan in a Siemens D-500 spectrometer. Infrared spectra and thermogravimetric analysis of the dried hybrid tubules were recorded on a Bruker FT-IR spectrophotometer between 4000 and 400 cm^{-1} and on a TA Instruments Q500 under nitrogen atmosphere over the range 20 to 600 °C at a heating rate of 10 °C, respectively.

Results and Discussion

To investigate the sol–gel reaction of TEOG in the presence of $DC_{8,9}$-PC template, two protocols have been employed, including (i) coassembly of $DC_{8,9}$-PC in an aqueous dispersion in the presence of TEOG solution and (ii) crystallization of TEOG solution in aqueous dispersions of preformed $DC_{8,9}$-PC tubule aggregates. The first one-pot method was more facile and yielded more regenarable results. Employing this protocol, different amounts of TEOG [5 μL (22.6 nmol)–30 μL (135.6 nmol)] were mixed with 10 mg of $DC_{8,9}$-PC (10.8 μmol) dissolved in 5 mL of 70% ethanol solution at 50 °C, and the clear mixtures were subjected to slow cooling (1 °C/10 min) to room temperature. Synergistic coassembly of germania–lipid helical coils has been achieved by hydrolysis and condensation of TEOG in the presence of $DC_{8,9}$-PC. This method differs strikingly from the general sol–gel transcription method developed in that hydrolysis and condensation of TEOG are specifically associated and coupled with self-assembly of the lipid molecule.

Transmission electron microscopy (TEM) studies revealed that the morphology of hybrid $DC_{8,9}$-PC/germania tubules is sensitive to the amount of TEOG (Figure 1). At a low TEOG amount ($[DC_{8,9}\text{-PC}]/[TEOG] = 477$ (Figure 1a) and 239 (Figure 1b)), most of the tubules were open-ended helical tubules with uniform diameters (~500 nm), lengths, and wall thicknesses of > 10 μm and 50–150 nm, respectively. These hybrid tubules consisted of smooth external and internal surfaces and multiple bilayers, which, along with the general absence of colloidal germania precipitation, suggested that TEOG hydrolysis and condensation occurred in combination with self-assembly of the lipid molecules. It is interesting to note that the condensation reaction at the similar concentration of TEOS ($[DC_{8,9}\text{-PC}]/[TEOS] \sim 300$) is incomplete even after the much longer time of reaction, yielding no hybrid tubules obtained in TEOG condensation reactions. In general, acid or base solution catalysts play an indispensable role in initiating and accelerating the hydrolysis of silica precursors and the subsequent sol–gel condensation.[5] As a result, a sol–gel reaction with TEOS is unlikely to occur in the aqueous dispersion in the absence of active solution catalysts such as H^+, OH^-, or benzylamine. In the present experiment, we added no definitive solution catalysts and nucleation seeds to the aqueous ethanol solution. Thus the diacetylenic phospholipid $DC_{8,9}$-PC self-assembles in the solution to form a well-defined tubular structure that acts as a template. The TEOG hydrolyzes successfully in the absence of any catalysts to produce negatively charged germania anions which interact with the lipid's cationic headgroups. A strong affinity between biological cell surfaces and

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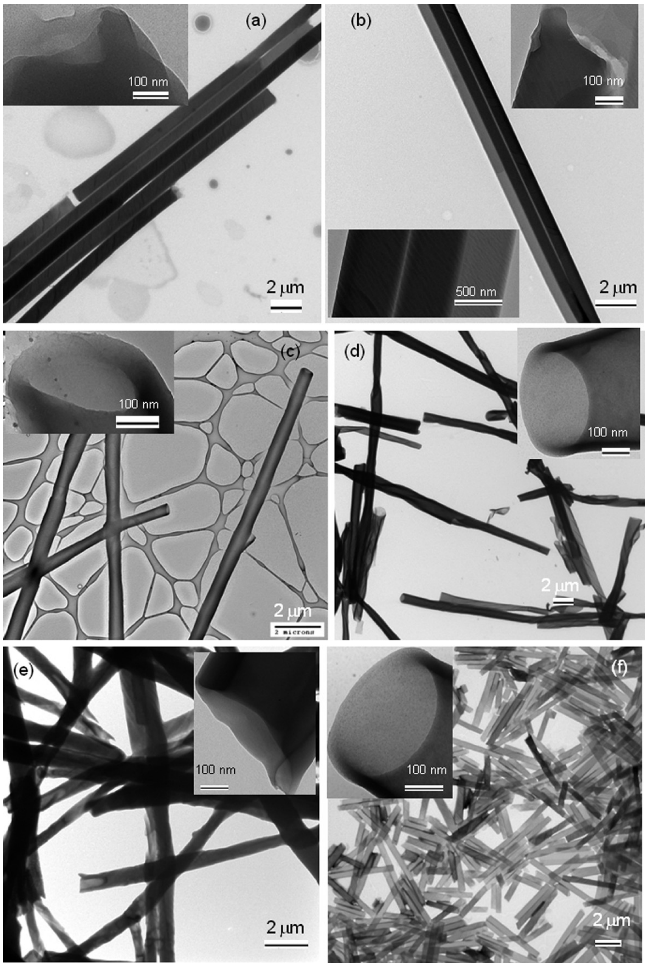

Figure 1. TEM images of the self-assembled lipid−germania tubules formed from diacetylenic phospholipid (10 mg) with a different amount of $Ge(OEt)_4$: (a) 5 μL, (b) 10 μL, (c) 15 μL, (d) 20 μL, and (e) 30 μL. (f) TEM image of tubules synthesized under ultrasonic environment at the same formulation with Figure 1d. Insets of each image show high magnification.

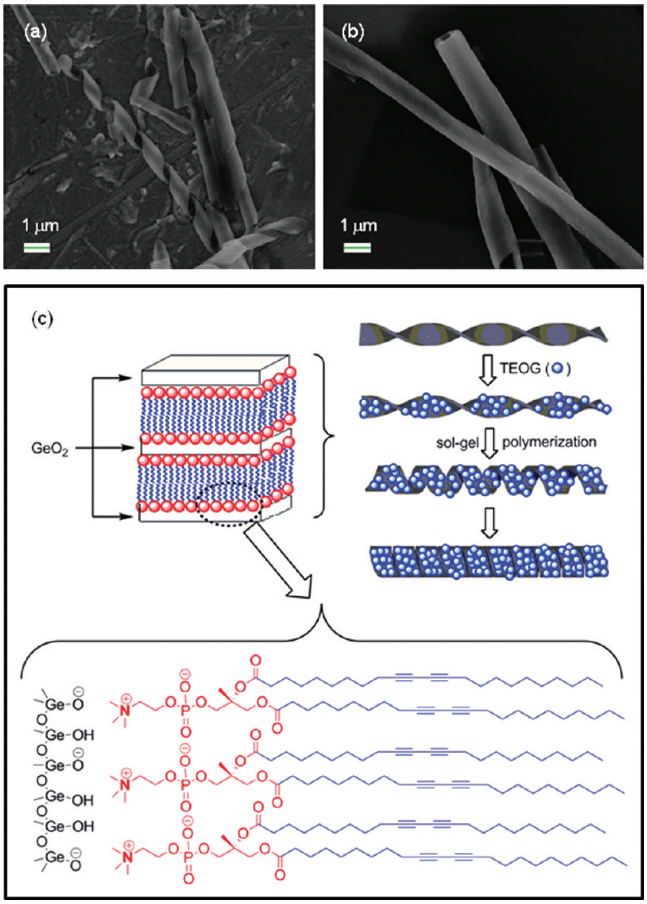

Figure 2. SEM images of the self-assembled lipid−germania tubules formed from diacetylenic phospholipid (10 mg) with a different amount of $Ge(OEt)_4$, (a) 30 μL and (b) 10 μL, and (c) schematic representation showing a helical germania-lipid composite with coiled multilamellar architecture formed by interactions between the lipid headgroup and anionically charged germania surface.

various silica surfaces has been noted in the past.[22] This has been attributed to electrostatic attraction between the negatively charged silica surface[23] and positively charged quaternary tetramethylammonium headgroup of the phosphatidylcholine lipid present in the cell membranes.[24] The phospholipid $DC_{8,9}$-PC has the same headgroup as phosphatidylcholine, and therefore the adsorption of germania particles on the tubule surface can also originate from electrostatic attraction, assuming the similarity of germania and silica. The germania particles on the tubule surface gel, leading to a thin film, indicate significant neutralization of their charges subsequent to adsorption on the tubule surface to form an open secondary hybrid architecture rather than a closed tube.

Since the sol−gel reaction proceeds in an aqueous medium according to “a surface-mediated mechanism”[13] on the outer and inner sides of the single bilayers, the minimal amount of positive charges, due to the thin organic wall, depresses the random accumulation of negatively charged germania oligomers. In addition a large amount of germania anions prevents $DC_{8,9}$-PC from self-assembling freely. TEM images of lipid−germaina hybrid tubules formed with a large amount of TEOG ($[DC_{8,9}\text{-PC}]/[TEOG]$ = 179 (Figure 1c), 119 (Figure 1d), and 80 (Figure 1e)) illustrate predominantly single bilayer walls, in particular in the presence of a larger amount of TEOG. These results demonstrate that the thicknesses of the hybrid tubules are controllable by the relative amount of $DC_{8,9}$-PC to TEOG, while the length and diameter are not. The secondary structure becomes more distorted as TEOG amount increases, as expected. The distorted structure can be seen more clearly by scanning electron microscopy (SEM) as shown in Figure 2. Figure 2c shows a plausible illustration of the formation of a $DC_{8,9}$-PC/germania helical and finally tubular composites from multilamellar achitecture formed by interations between $DC_{8,9}$-PC headgroup and polymerized germania surface. High-resolution TEM images in insets in Figure 1d,e and in Figure 3a,b show areas of the helical tubules in which the lipid bilayers were fortuitously oriented approximately parallel to the electron beam that continuous lattice fringes were observed with spacings of about 4.5 nm that were consistent

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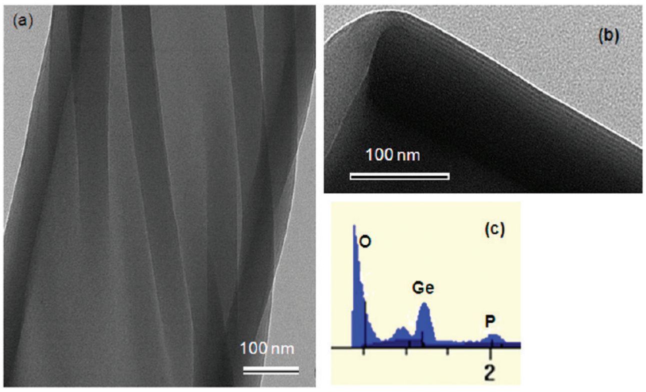

Figure 3. (a) TEM image of the self-assembled lipid−germania tubules formed from diacetylenic phospholipid (10 mg) with Ge(OEt)$_4$ (20 μL), (b) lattice image of tube edge oriented end-on to the electron beam showing regular fringes with 4.5 nm spacing corresponding to the superlattice structure of the layered germania, and (c) EDX analysis recorded from individual tubules showing the formation of composite tubules.

with a twisted multilamellar hybrid mesophase in which the lipid bilayers were intercalated with thin sheets of amorphous germania.

Elemental mapping of germanium (Ge), oxygen (O), and phosphine (P) on the wall of the DC$_{8,9}$-PC/germania hybrid nanotubes investigated by means of energy-dispersive X-ray (EDX) analysis coupled with TEM measurements shows the presence of Ge, O, and P from the lipid headgroups associated with the mineralized tubules (Figure 3c). In addition thermogravimetric analysis indicated that they contain about 70 wt % lipid moiety. The formation of germania has also been confirmed by IR spectra. The very strong absorption peak around 860 cm^{-1} and the significant band in the region 500−600 cm^{-1} are assigned to Ge−O−Ge stretching vibrations and mixed stretching−bending motions, respectively.[25] These findings strongly support that the gel formation is induced by templating the DC$_{8,9}$-PC assemblies and that the germania has thereby been deposited on the surfaces of the organic nanotubules. The inner and external surfaces of the tubules were coated with an electron-dense material to reveal an interfacial region of low electron density that runs along the length of the self-assembled microstructure in various ways; for example, straight (Figure 3a) or twisted (Figure 3b), and which corresponds to a 50−70 nm wide wall of approximately 9−12 lipid bilayers. The outer walls of the tubules were coated with a continuous and smooth overlayer around 30−60 nm in thickness, with no evidence of discrete gemania particles.

To get further insight on the mechanism of the DC$_{8,9}$-PC/germania hybrid nanotube formation, a series of controlled sol−gel reactions have been performed. The DC$_{8,9}$-PC (10 mg) was dissolved in 3.5 mL of absolute ethanol and then mixed with 20 μL (90.4 nmol) of TEOG at room temperature. A sol−gel reaction was started by introducing 1.5 mL of water into the mixture by using a syringe pump (10 μL/min). Figure 4 shows representative

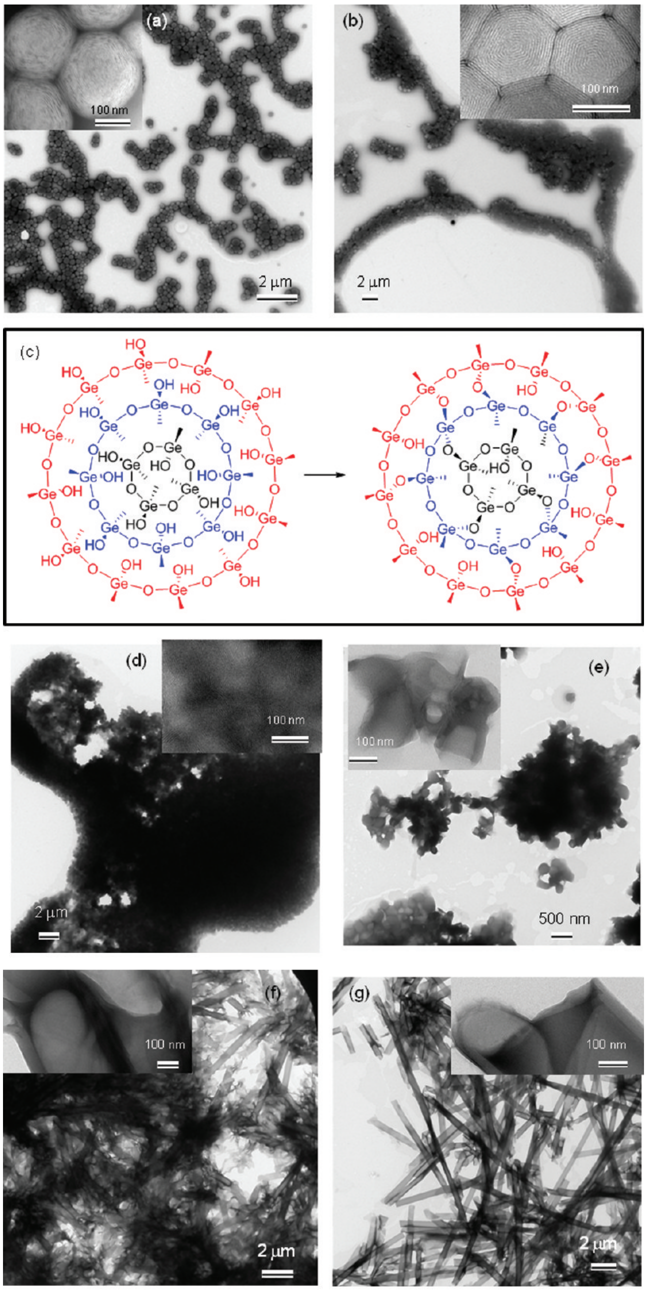

Figure 4. TEM images showing step-by-step procedures forming lipid-germania tubules from the reaction of diacetylenic phospholipid (10 mg) with 20 μL of Ge(OEt)$_4$ in ethanol solution (3.5 mL) in the presence of different amounts of water: (a) 0 μL, (b) 10 μL, (d) 30 μL, (e) 0.3 mL, (f) 0.5 mL, and (g) 1.5 mL. (c) Schematic illustration of the condensation polymerization of Ge(OEt)$_4$ in aqueous ethanol solution resulting in the development of a vesicular mesophase. Insets of each image show high magnification.

TEM images of the samples collected during the reaction. As shown in Figure 4a, negatively charged TEOG molecules accrete from solution mainly to the positively charged headgroup region of adsorbed lipid bilayer to form multilamellar vesicle-like morphologies sized from 100 to 300 nm. The internal structure of the vesicles resembles the annual concentric ring structure found in trees with each ring less than 1 nm thick. A very small amount of water (10 μL) induces sol−gel reaction along the lipid bilayer and makes the rings clearer and thicker (~2.5 nm), which indicates TEOG molecules are

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polymerized to form GeO_2 (Figure 4b). Figure 4c illustrates the development of multilamellar vesicle-like morphologies by TEOG condensation. A silica sphere with similar internal morphology was prepared by aerosol templating.[26] Addition of 30 μL of water made the mixture bulkier due to the severe aggregation of the polymerized TEOG, and at the same time the polymerized GeO_2 was mixed completely with the lipid layer (Figure 4d). High magnification TEM images show that the line of the ring becomes bigger (~4.5 nm) and the spheres collide with neighboring ones, and finally the individual spheres are not discernible (see lower inset in Figure 4d).

The germania coated hybrid nanotubules start to form from the aggregated mixture when the water amount reached around 0.3 mL as shown in Figure 4e. The $DC_{8,9}$-PC molecules are evidently a template to drive this secondary structure. The growth of the tubule out of the bulky $DC_{8,9}$-PC/GeO_2 mixture (primary structure) could be seen clearly when the water amount reached to around 0.5 mL (Figure 4f). Figure 4g shows that the formation of germania nanotubules is completed when 1.5 mL of water is introduced into the mixture. This image is comparable to Figure 1d.

Intrinsically formed TEOG spheres arranged along the head groups of lipid bilayer are easily hydrolyzed by nucleophilic reactions with water. Condensation occurs when the hydroxide molecules bind together as they release water molecules and a gel network of the hydroxide is obtained first within arrayed spheres. Considering that those metals with lower electronegativities undergo hydrolysis and condensation faster than those with higher electronegativities, the rates of these reactions of TEOG are expected to be larger than those of TEOS. As these reactions proceed in a larger amount of water, the resulting germanate species become homogenized with lipid molecule, in particular along the polar head groups of the lipid. The lipid molecule may play a crucial role in functioning as a very mild acid catalyst by yielding weakly acidic pH conditions as well as distributing positive charges all over the surfaces. These two conditions are crucial for the homogeneous deposition of negatively charged germanate precursors. The intrinsic ability of the lipid molecule to form tubules by self-assembly drives the bulky and shapeless sol materials to a well-defined gel structure. It was found that the metal alkoxide precursors could not get into the lipid molecule if the hydrolysis occurs too fast. For example, it was impossible to get TiO_2 deposited tubules in a similar procedure with $Ti(OR)_4$.

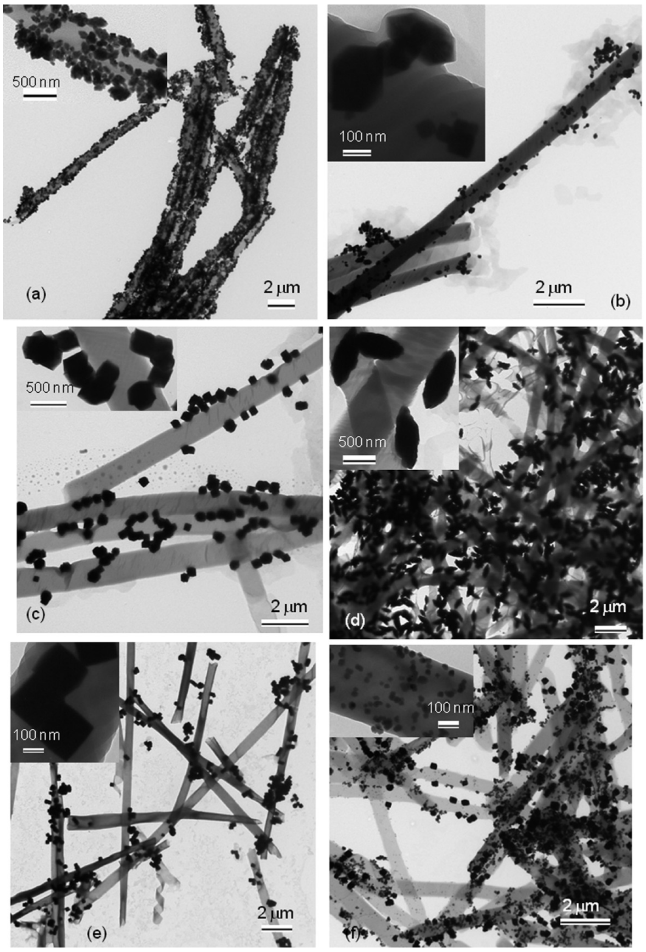

Figure 5. TEM images showing the formation of germania nanoparticles on the surface of lipid-germania tubules in the presence of different amounts of $Ge(OEt)_4$: (a) 50 μL, (b) 70 μL, (c) 100 μL, and (d) 120 μL or (e) $Ge(O^iPr)_4$ (100 μL). (f) TEM image of nanoparticles synthesized under ultrasonic environment at the same formulation with Figure 1c. Insets of each image show high magnification.

The value of $DC_{8,9}$-PC as a template to design a nanostructure of germania can also be addressed by the fine control of TEOG amount in the reaction mixture. It is interesting to note that 10 mg of $DC_{8,9}$-PC can accommodate only about 30 μL of TEOG (TEOG/$DC_{8,9}$-PC ~ 1.25 mol % or ~ 0.34 wt %) on its surface without precipitating germanate particles. Clear solution obtained by increasing the amount of TEOG to 50 μL (0.226 μmol) in the mixture of 10 mg of $DC_{8,9}$-PC (10.8 μmol) and 5 mL of 70% ethanol solution at 50 °C was subjected to slow cooling to room temperature. The TEM image (Figure 5a) shows that germania nanoparticles (50−200 nm) are precipitated predominantly on the surface of $DC_{8,9}$-PC/GeO_2 hybrid tubules. The apparent morphology of these crystalline nanoparticles is random. Increasing the amount of TEOG to 70 μL at the same sol−gel reaction conditions yields similar sized nanoparticles of more uniform morphology. Surprisingly cube shaped particles were obtained with 100 μL of TEOG (0.452 μmol) (Figure 5c). The germania nanocubes are monodisperse with one side size about 200 nm. Further increase the TEOG amount to 120 μL (0.542 μmol) yielded predominantly rugby football shaped particles (~500 nm long and ~200 nm short) with some star shaped particles that were most probably grown from the football shaped particles. Substituting TEOG for other precursors such as tetraisopropyl germanium and tetrabutyl germanium at similar reaction conditions gave similar results. For example, cube-shaped particles could be obtained by using 0.452 μmol of tetraisopropyl germanium as in the case of using TEOG as a precursor (Figure 5e). In an effort to control the particle size, the

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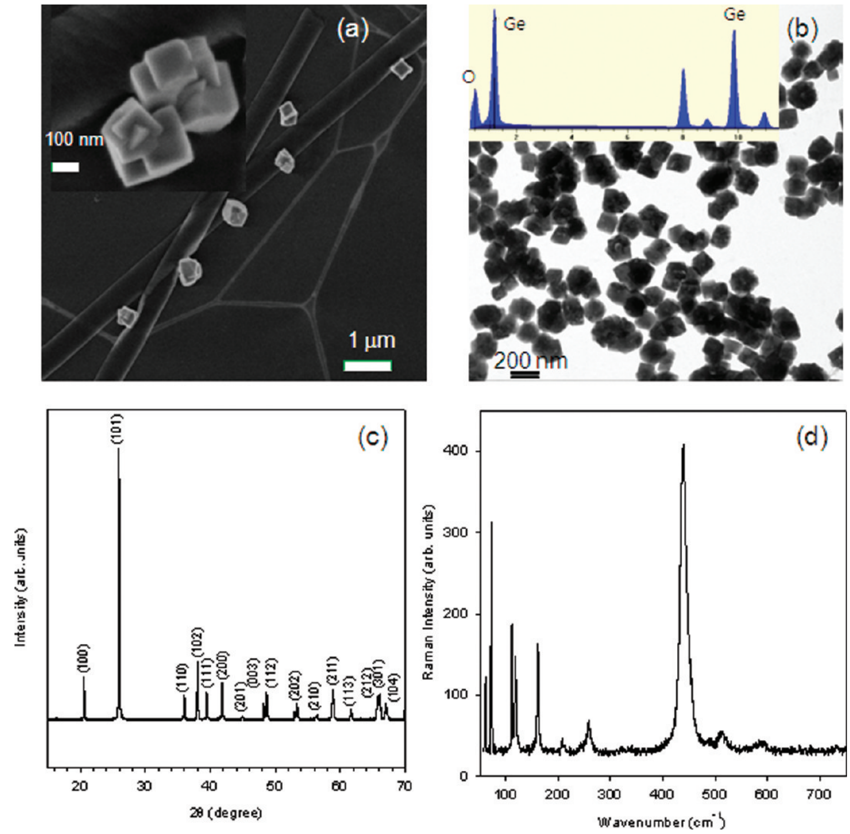

Figure 6. SEM image of germania nanoparticles growing on the surface of germania nanotubules (a) and TEM image of separated germania nanoparticles (b). EDX analysis of the particles is shown in the inset. (c) XRD and (d) Raman spectra of hexagonal GeO_2 particles.

same sol–gel reactions were performed with ultrasonic treatment. Under otherwise normal reaction conditions, a clear solution obtained by mixing 100 μL of TEOG, 10 mg of $DC_{8,9}$-PC, and 5 mL of 70% ethanol solution at 50 °C was subjected to slow cooling to room temperature under ultrasonification. Figure 5f shows the TEM image of the resulting mixture. Multimodal distribution of particle sizes was observed; some are cube-shaped particles of the similar size with those in Figure 5c or Figure 5e, while others are disintegrated into small cube-shaped particles ranging from about 10 to 100 nm. It is noted that the hybrid tubules are formed even under ultrasound condition due to the strong self-assembling behavior of $DC_{8,9}$-PC and that the size of germania nanoparticles might be tunable by employing suitable sol–gel reaction conditions.

The surface morphology of germania nanotubules bearing germania nanocubes on their surfaces can be seen more clearly in the SEM image (Figure 6a). The cube-shaped nanoparticles could be separated by dissolving the tubules that consist of 70% organic components in chloroform. As shown in Figure 6b, the resulting nanoparticles are uniform. EDX analysis coupled with TEM measurement showed that the amount of Ge and O was perfectly fitted with an expected formula, GeO_2. X-ray powder diffraction pattern (XRD) of the particles showed that there were no other peaks demonstrating the existence of other crystalline phases except hexagonal structure (Figure 6c). The positions of the XRD peaks are in good agreement with those of the hexagonal GeO_2 (α-phase quartz-like structure) listed in the standard handbook of XRD spectra. The Raman spectrum (Figure 6d) of the germania particles demonstrates that the sample is represented by a trigonal GeO_2 having germanium in fourfold coordination and that it is in good agreement with those reported in the literature.[27]

Conclusion

A very facile protocol has been shown to prepare highly crystalline germania nanoparticles from hierachically organized $DC_{8,9}$-PC/germania hibrid nanotubules using a high fidelity self-assembly and functionality of a tubular $DC_{8,9}$-PC template. The TEOG molecules are hydrolyzed on the surface of lipid bilayer and mixed completely with lipid molecules, and then the resulting $DC_{8,9}$-PC/germania hybrid mixture brings up to the secondary structure by the self-assembling driving force of the lipid molecules. The weakly acidic lipid headgroup is responsible for the characteristic formation of the germania nanotubules. Excess amount of TEOG above the range that the lipid can afford on their tubules' surface resulted in precipitating well-defined crystalline hexagonal germania nanoparticles.

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