Sodium-Silicate Route to Submicrometer Hybrid PEG@Silica Particles

Hila Elimelech and David Avnir*

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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In a recent series of papers, a general methodology has been developed for the synthesis of polymer@silica submicrometer particles, which is based on the entrapment of a hydrophobic organic polymer in a polycondensating tetraethoxysilane (TEOS) oil-in-water (O/W) emulsion. As this system could not handle hydrophilic polymers, the development of a "mirror" W/O emulsion system was needed. Here we report the successful achievement of that goal, by demonstrating the synthesis of poly(ethylene glycol)@silica submicrometer particles from (the cheaper, greener) sodium silicate, which is a less common monomer compared to TEOS in submicrometer silica particle synthesis. Indeed, finding the right conditions for preparing these particles required screening of many procedures, some of which are briefly mentioned. Full characterization of the hybrid particles is provided. As both PEG and silica are biocompatible, so are the hybrid particles.

Background

Organic–inorganic hybrid materials offer endless opportunities for tailoring by design chemical, physical,[1] biochemical,[2] optical,[3] sensing,[4] and chromatographic[5] properties. General methodologies for the synthesis of such materials are therefore in constant need. In this framework we reported in a recent series of publications a novel general and facile synthetic route for the fabrication of hybrid submicrometer particles of hydrophobic polymers and silica (polymer@silica).[6–9] Unlike previous approaches to the synthesis of such particles which routinely started with silica particles and polymerized the organic component on/in it, our approach has been based on an opposite route: Entrapping the polymer in a forming silica particle, by performing the sol–gel polycondensation within a surfactant-stabilized oil-in-water (O/W) emulsion of a hydrophobic solution of the polymer in tetraethoxysilane (TEOS) with or without a cosolvent. A recent example is the preparation of high- or low-density polyethylene (PE)@silica particles, a molecular level hybrid material which has been unknown in any form.[8]

By the nature of this procedure, which utilizes TEOS as a polymer–solvent, only hydrophobic polymers could have been used, and polystyrene@silica[6,9] and high MW-PDMS@silica[7] are two additional examples. A needed extension to this procedure to generalize it further is a methodology for the preparation of *hydrophilic* polymer@silica, which is the topic of this report. This is particularly important, because many of the water-soluble polymers are biocompatible, and because silica is a GRAS (generally regarded as safe) material, so that their hybrids are biocompatible as well. Of course, TEOS cannot be used as an emulsified solvent is this case, and therefore a *hydrophilic* silica precursor which dissolves in water along with the polymer must be used: The classical sodium silicate was selected for that purpose, which also offers the advantages of being cheaper and greener compared to TEOS. A second accompanying change must be to reverse the emulsion, namely, to use the W/O system. This has been achieved: We report a simple one-step method for the fabrication of narrow size-distribution submicrometer biocompatible interpenetrating hybrid particles of poly(ethylene glycol) (PEG)@silica from sodium silicate.

It may come as a surprise, but the use of the low-cost and environmentally friendly sodium silicate as a precursor for the preparation of submicrometer silica particles is by far less common than the use of silicon alkoxides by Stöber-type procedures.[10,11] Examples include the use of a template molecule,[12] pyrolysis,[13] and the use of emulsions with

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* Corresponding author. E-mail: david@chem.ch.huji.ac.il.

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surfactants such as pluronic[14–19] and AOT.[20] A literature survey shows that the particles obtained from sodium silicate are usually in the micrometer scale[14] and that the size distribution is relatively wide.[20] PEG/silica composites are known in different architectures, for example, grafting of PEG on silica particles [21,22] or silica surfaces,[23,24] and as PEG-core/silica-shell micrometer sized particles.[25] Finally, a relevant reference is the study of Chang-Chien et al.,[26] who reported the preparation of porous carbon particles by entrapment of a blend of the hydrophobic poly(phenol-formaldehyde) and poly(ethylene oxide) in larger-than-micrometer particles.

Experimental Details

Materials. Sodium silicate solution (27% SiO_2, 14% NaOH), 1,2-bis-(2-ethylhexyloxycarbonyl)-1-ethanosulfonate sodium salt (AOT), and PEG (molecular weights of 3000 and 8000) were purchased from Sigma-Aldrich.

Synthesis of PEG@Silica Particles. A total of 0.3 g of PEG-3000 was dissolved in 6.0 mL of sodium silicate solution diluted ×10 with distilled water using an ultrasonic bath for 5 min. This solution along with 3.0 mL of 3.0 M HCl was poured *simultaneously* into a solution of 100 mL *n*-heptane and 2.0 g of AOT under sonication. A white emulsion was formed immediately. The emulsion was kept under sonication for 1 h at room temperature. The composite particles were then collected by centrifugation for 15 min at 6000 rpm. The white powder was air-dried in a hood for 24 h. For PEG 8000@silica, slightly different quantities were used: 0.25 g of the polymer and 2.0 mL of HCl. Pure silica was prepared for comparison purposes by a procedure similar to that of PEG-3000@silica but with no polymer present. This successful procedure followed many attempts that yielded unsatisfactory results. Some of the main attempts are listed in the Results and Interpretations section.

Extraction of the Polymer. Extraction of PEG from the composite particles was affected with boiling DMSO in a Soxhlet extractor for 24 h. Although neat PEG-3000 readily dissolves in water, it could not be extracted from the composite using water in the Soxhlet apparatus.

Particle Characterization and Instrumentation. Transmission electron microscopy (TEM) observations were preformed on a Philips CM 12 (TECHNAi) microscope operating at 80–120 kV. Samples for TEM observation were prepared by redispersing the resultant powder in ethanol and placing a drop of that dispersion on a Formvar/carbon 300 mesh copper grid. The dispersion was air-dried for 1 min, and the excess solution was wiped off. High resolution scanning electron microscopy (HR-SEM) observations were performed with a Sirion (FEI) microscope, operating at 5 or 10 kV. Samples were prepared by placing the centrifuged, air-dried powder on an aluminum stub for SEM using a double sided tape. IR measurements were carried out using a Bruker Vector 22 spectrometer. The diameters of at least 70 particles were determined using the "Analysis" software, and statistical analysis was carried out with Origin software. The samples were tested in a disk form obtained by grinding the powder with KBr and pressing under 10 atm. BET specific surface area and BJH pore diameters were calculated from nitrogen adsorption/desorption isotherms determined at 77 K using a Micromeritics ASAP 2000 surface analyzer. Thermogravimetric analyses (TGA) were carried out with an SDT 2960 V3.0F (TA Instruments) under air at a rate of 10 °C/min. Zeta potential measurement were conducted using a Malvern Zetasizer 3000. The composite particles were suspended in an alkaline solution of pH 10.

Results and Interpretations

Obtaining the Particles and Microscopy. Typical SEM and TEM pictures of the resulting particles (Figure 1) show discrete, spherical particles, the sizes of which are in the submicrometer range. We have concentrated in this study on PEG-3000@silica, but higher PEGs can be used, as seen in Figure 1c. The typical particle size distribution of PEG-3000@silica, taken from 10 pictures, is shown in Figure 1d. It is seen that the most probable size is around 175 nm, with a tail into larger particle sizes. The main experimental difficulty which one had to overcome in the synthesis of such discrete particles from an inorganic source—sodium-silicate—is due to the rapid, disordered precipitation of silica as a result of the acidification. To attain the desired product, many experiments were preformed, using different types of precipitants and acids (such as ammonium bicarbonate,[27] Nafion, HNO_3,[20] and HCl), various surfactants (such as pluronic (PEG-PPG-PEG, HLB = 1–7 and 15–23), Brij 92, PGPR, Abil EM, PE-*block*-PEG, CTAC, Span60, Tween 80, and AOT), and various addition sequences of solutions containing various combinations of the main components, including the testing of emulsion−inversion procedures. All of these were screened for their ability to produce a stable homogeneous emulsion which would lead to spherical particles. Finally, the synthesis parameters listed in the Experimental Details, namely, a simultaneous addition of a PEG aqueous silicate solution and an HCl solution into the heptane solution of AOT, provided the desired product. An interesting observation has been that a blank experiment, carried out in the absence of the polymer, yielded continuous, rather than discrete, silica particles. This indicates that PEG has a significant role in forming the composite structure. The next analyses address this feature as well.

IR Spectroscopy. An immediate proof of the hybrid nature of the particles comes from the fingerprint region of the IR spectrum (Figure 2). The spectrum of the hybrid particles (Figure 2a) is a superposition of the spectra of silica (Figure

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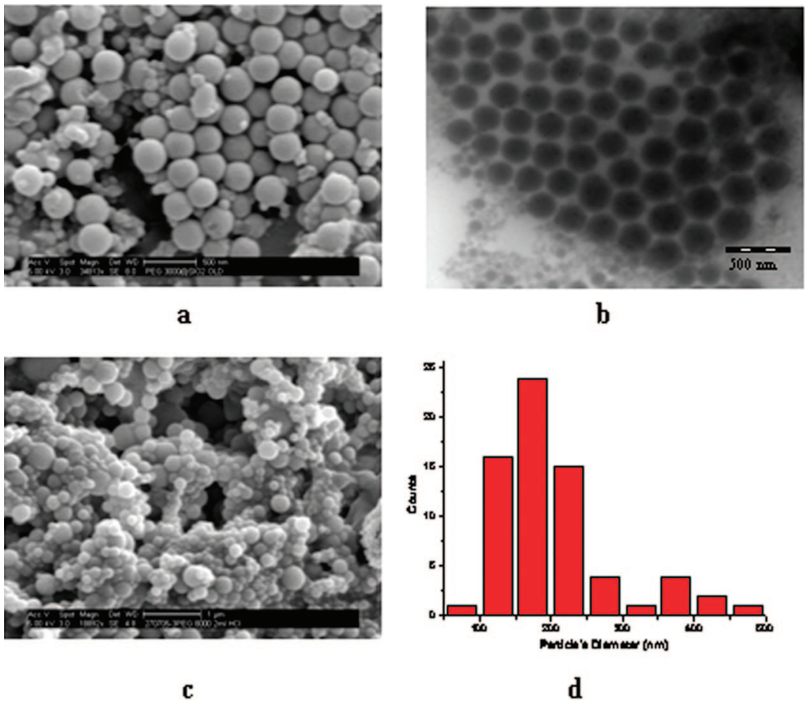

Figure 1. Micrographs of PEG@silica. (a) SEM and (b) TEM of PEG-3000@silica particles (bar: 500 nm); (c) SEM of PEG-8000@silica particles (bar: 1μm). (d) Particles size distribution for PEG-3000@silica.

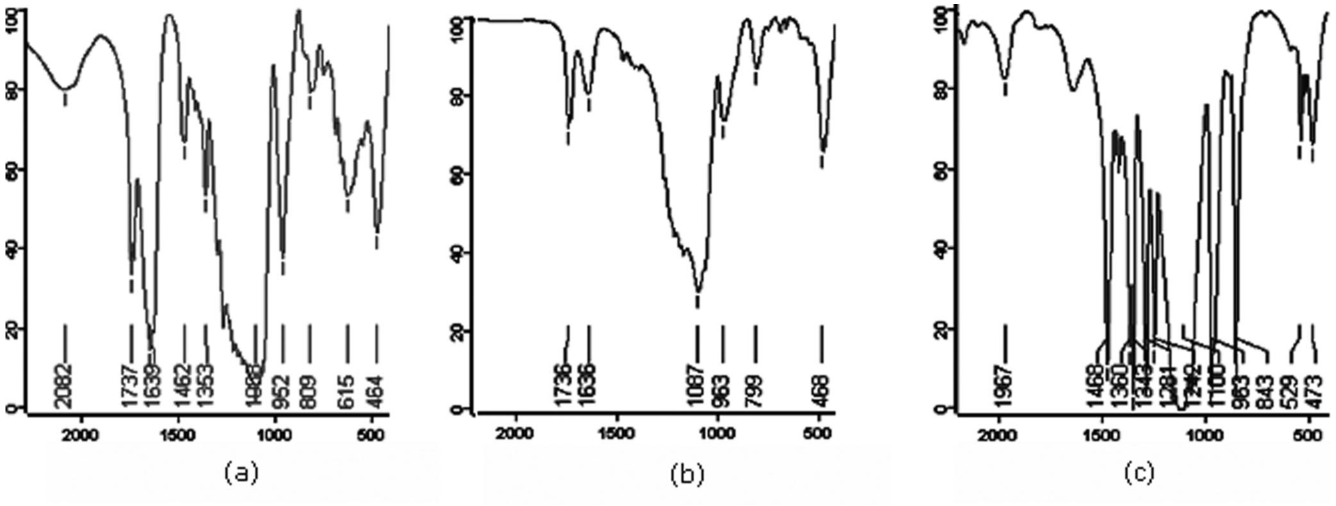

Figure 2. Fingerprint portion of the IR spectra: (a) PEG-3000@silica; (b) blank silica with no polymer; and (c) free PEG-3000.

2b) and of the polymer (Figure 2c). For instance, the peaks at 464, 1088, 1639, and 1737 cm^{-1} are those of silica, and at 1353 and 1462 cm^{-1} are of PEG (with slight shifts[28,29]). We recall that the polymer could not be extracted with water, which is a good solvent for it. Indeed, the spectral shifts indicate a strong interaction between the two components, which further indicates the hybrid nature (as opposed to two distinctly separated phases). Finally, no bands indicative of the surfactant were found.

TGA. Another proof of the composite nature is TGA, which also serves to determine the percentage of the organic phase within the composite. Figure 3 shows the result, along with two blanks: the free polymer and the sample after DMSO-extraction of the polymer. Free PEG decomposes sharply at 300 °C (curve c), and after extraction (b), the only weight loss is of solvents (~100 °C), indicating that extraction indeed left silica behind (few percents of its dehydration are seen at higher temperatures). Curve a, of the hybrid, shows a 35% weight loss at ~400 °C. The known strong interactions between PEG and silica[30] stabilize the polymer, and its oxidative decomposition is delayed by 100 °C compared with the free polymer. The final step at 950 °C is typical of sodium carbonate, which forms under the

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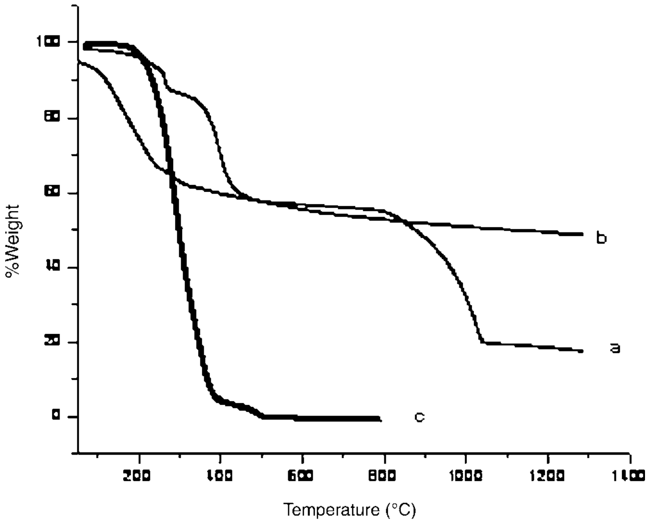

Figure 3. TGA of (a) PEG-3000@silica; (b) the sample after extraction of PEG; and (c) free PEG-3000.

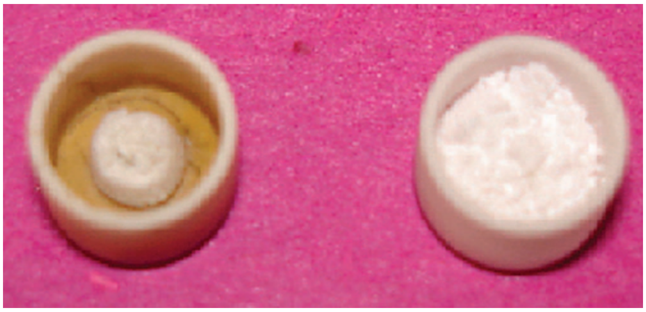

Figure 4. Densification of PEG@silica powder (right) into a dense compact solid (left) upon heating.

TGA conditions CO_2, water, and sodium ions.[31] An interesting observation which follows the TGA heating, is seen in Figure 4: the sample turns from a dispersed powder into a dense compact solid. We have not observed this phenomenon in the other hydrophobic polymer@silica composites we prepared.[6–9] This phenomenon may hint to the formation of Si−O−C bonds between the components during the heating. Indeed, the facile formation of that bond by a nucleophilic attack of the oxygen of COH on the silicon of SiOH has been suggested before.[30]

Surface Area and Porosity. Comparative surface area and porosity analysis was performed on the hybrid PEG@silica particles, on a sample from which PEG was extracted, and on a reference pure silica sample prepared by the same synthesis but without the polymer. The data obtained is collected in Table 1. The low surface area and very low pore volume of the hybrid particles indicate that these particles are practically full and nonporous. Extraction of the PEG results in a ∼10-fold jump in these parameters, and the emerging porosity is of an average size of ∼16 nm. This formed porosity may indicate the typical size of the PEG component in the hybrid particles, although, like pore size distribution, there is a domain-size distribution that starts at the level of very few, perhaps one PEG molecule. Silica prepared without PEG has completely different characteristics—classical ones for silica—of much higher surface area and pore volume and much narrower pores (Table 1). Thus, it is evident that PEG interferes actively in the silica polycondensation reaction. This is unlike the entrapment of the very hydrophobic PE, where it was shown that the PE does not interfere in the typical silica structure formation in the PE@silica hybrid.[8] This comes as no surprise because, as already indicated above, PEG interacts strongly with silanols and therefore affects the polycondensation of the silicic acid species (we recall again that PEG could not be extracted from the composite using boiling water).

Table 1. Surface Area and Porosity Data

	pore volume (mL/g)	pore diameter (Å)	surface area (m^2/gr)
PEG@silica	2.6×10^{-3}	60	1.4
extracted sample	4.8×10^{-2}	160	12
reference silica without polymer	1.3×10^{-1}	38	119

Zeta Potential. Finally, the particle zeta potential was determined to be −4.5 mV. This is a low value which is not characteristic to silica (around −50 mV[32]). This relatively low charge density on the particles surface helps indicate that a certain population of the PEG molecules is entrapped at the interface of the particle, masking the negatively charged silanols. This is a reflection of the action of PEG as an emulsifying cosurfactant in the synthesis of these particles.

In conclusion, we have further generalized the methodology of forming polymer@silica hybrid particles in silica-forming emulsions, by developing a procedure for a hydrophilic polymer. Using a W/O emulsion (rather than O/W emulsion, which has been used so far) allowed the use of sodium silicate solution as the dispersed phase, which contained also the PEG to be entrapped. PEG@silica particles are of potential use wherever biocompatibility is required, because both components are safe from that point of view. Evidence is provided that the PEG and silicas interpenetrating phases in these hybrid particles interact much stronger with each other, compared to the interactions in hydrophobic polymers@silica particles.

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