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Communications to the Editor

Inorganic/Organic Hybrid Nanoreactors Based on Cyclic and Cubic Siloxane Scaffolds†

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Nanocrystalline materials and nanocomposites are subjects of current interest because of their unusual properties.[1] The synthesis and patterning of nanosized metal properties into organized structures is a potential route to chemical, optical, magnetic, and electronic devices with useful properties.[2,3] Development of simple methods for the fabrication of controlled organized structures is indispensable for preparing new nanodevices. Several approaches have been used to obtain three-dimensional aggregates of metal nanoparticles.[4] Ligands or polymers, especially solvent-soluble polymers, either natural or synthetic, with some affinity for metals are often used as stabilizers of metal nanoparticles. The stabilization of metallic colloids to preserve their finely dispersed state is a crucial aspect to consider during their synthesis.

In recent years, inorganic/organic hybrid composites have acquired a great interest for stabilization and controlling the morphology of nanosized metal particles and as precursors for their self-assemblies.[5] Inorganic−organic hybrids appear as a creative alternative for obtaining new multifunctional materials of unusual features.[6] The breadth of physical and chemical properties of inorganic frameworks can be greatly extended by the introduction of organic groups into the inorganic framework. Cyclic and cubic siloxanes, e.g. $[R_2SiO_2]_4$ or $[RSiO_3]_8$, where R can be a diverse number of organic groups, offer the opportunity to develop a wide range of hybrid materials. Because of their specific geometry, both cyclosiloxanes (D_4) and polyhedral silsesquioxanes (T_8) promise to be versatile cores for the construction of new and interesting classes of macromolecules having controlled architectures. If selective modification strategies can be devised, then through their multi-Si vertices, these siloxanes can be covalently linked to a plethora of organic functional groups creating libraries of single-phase inorganic/organic hybrids.[7] These materials must be soluble or liquid and readily polymerizable to be effective for single-phase composite processing.[8] In principle, such cores can provide a spatially well-defined, rigid, hard component. Through proper choice of polymerizable R groups, the organic component can be varied to control the cross-link density, the segment distances between cross-links, the packing of individual siloxane units with respect to each other, and also the stability of the siloxane/organic bond. This type of control offers the potential to probe the effects of variations in interfacial interactions on hybrid properties. Thus, cyclosiloxane/cubic siloxane-based hybrids may provide a method of careful assessment of the scope and potential of inorganic/organic hybrid materials.

Siloxanes are hydrophobic entities. By attaching hydrophilic organic moieties like poly(ethylene glycol) (PEG) to such moieties, hybrid networks can be formed which can self-assemble into micelles. Such micellar network can be further employed as nanoreactors for metal and semiconductor particle formation.[9] In this communication, we present a versatile approach to well-defined cyclic silicon oligomers substituted with poly(ethylene glycol) to create nanoreactors, which act as reducing agents and as templates to control the size, stability, and solubility of metal nanoparticles ranging in diameter from 1 up to 10 nm.

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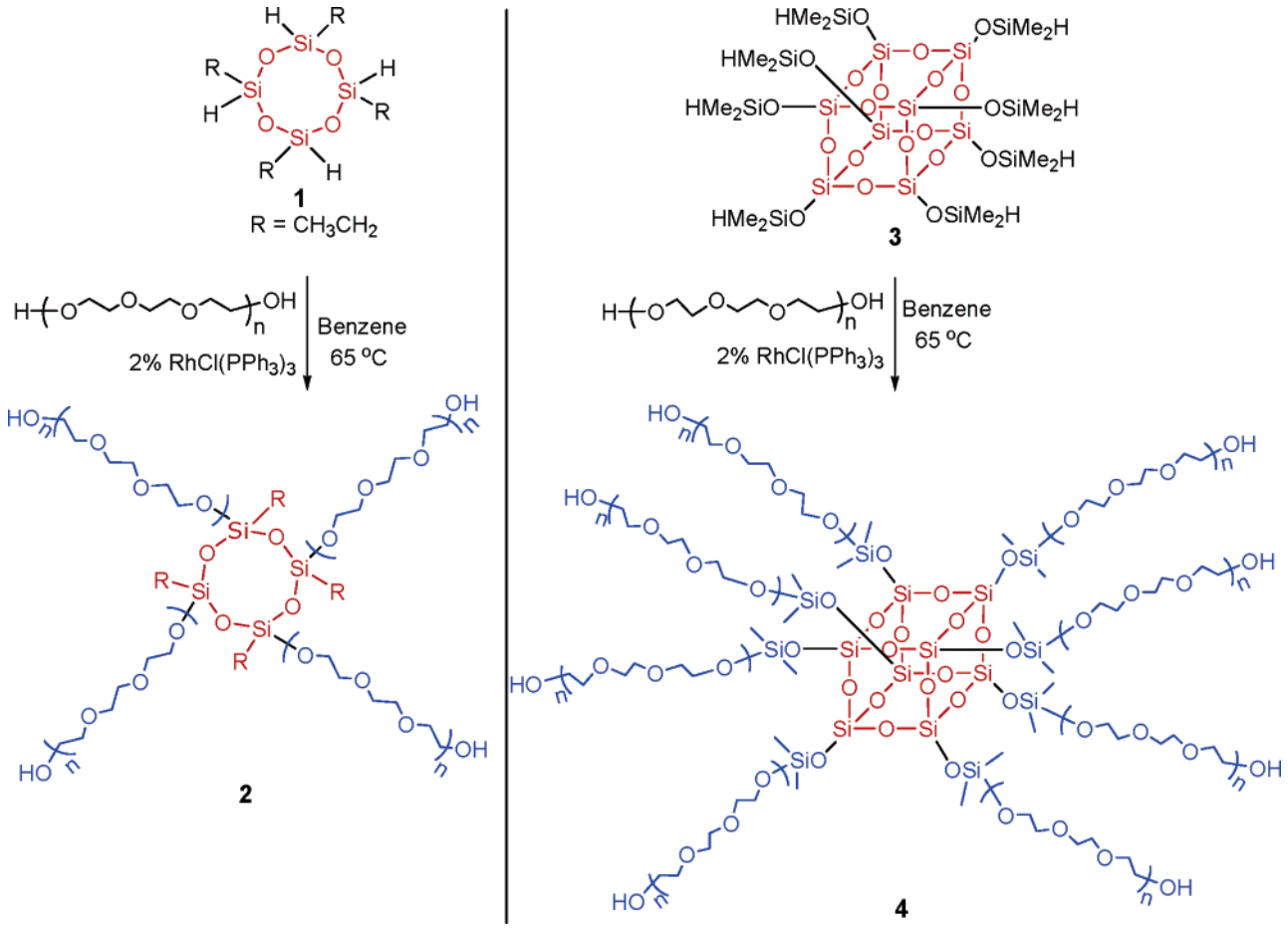
Scheme 1. Synthetic Route to PEG-Substituted Cyclic Siloxanes



In our synthetic strategy, the first task is the generation of covalently attached hydrophilic tail (poly(ethylene glycol)) to hydrophobic core (siloxanes). The synthesis of such a system was accomplished by the "Chauhan−Boudjouk alcoholysis" procedure, which can provide a one-step access to selective formation of PEG-substituted cyclic siloxanes.[10] Thus, the reaction of tetraethylcyclotetrasiloxane (**1**) (0.297 g, 1 mmol) and poly(ethylene glycol) (1.6 g, 4 mmol; $M_w \sim 400$) was examined in the presence of Wilkinson's catalyst $RhCl(PPh_3)_3$ (~20 mg, 0.02 mmol) in benzene under positive pressure of argon as shown in Scheme 1. The reaction mixture was heated at 65 °C and periodically monitored by IR, ^1H NMR, and ^{29}Si NMR. During the course of reaction, the reaction mixture became yellow, and evolution of a gas (presumably H_2) was observed. After 30 h of the reaction, complete consumption of **1** and formation of poly(ethylene glycol)-substituted siloxane **2** was observed in near-quantitative yield (Scheme 1). The detailed analysis of the product was carried out by spectroscopic and microscopic techniques.[11]

The ^{29}Si NMR and transmission electron microscopy (TEM) analysis of the product **2** is shown in Figure 1. ^{29}Si NMR of starting siloxane **1** shows four peaks centered at −30 ppm arising from O−SiMeH−O− units. After glycolysis, the ^{29}Si NMR analysis of resulting product **2** showed peaks centered at −56 to −57 ppm, reflecting the change in electronic environment of Si units due to the formation of new $SiMe-OCH_2CH_2O-$ moieties. As is evident from ^{29}Si NMR (Figure 1), no residual signals due to Si−H bonds were observed, indicating complete consumption of the Si−H bonds. The IR spectral analysis also confirmed the disappearance of the characteristic bands due to Si−H bonds.[11]

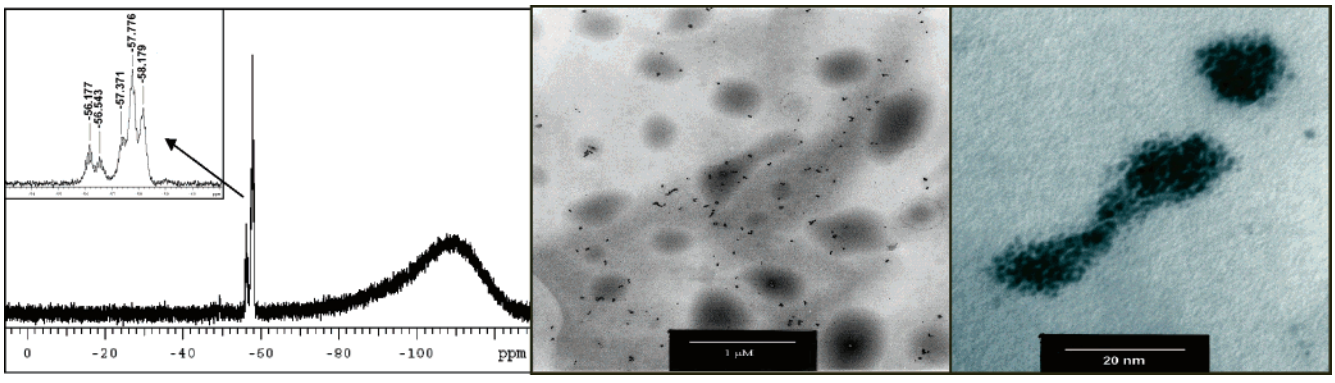


Figure 1. ^{29}Si NMR and TEM images of PEG-substituted siloxane **2**.

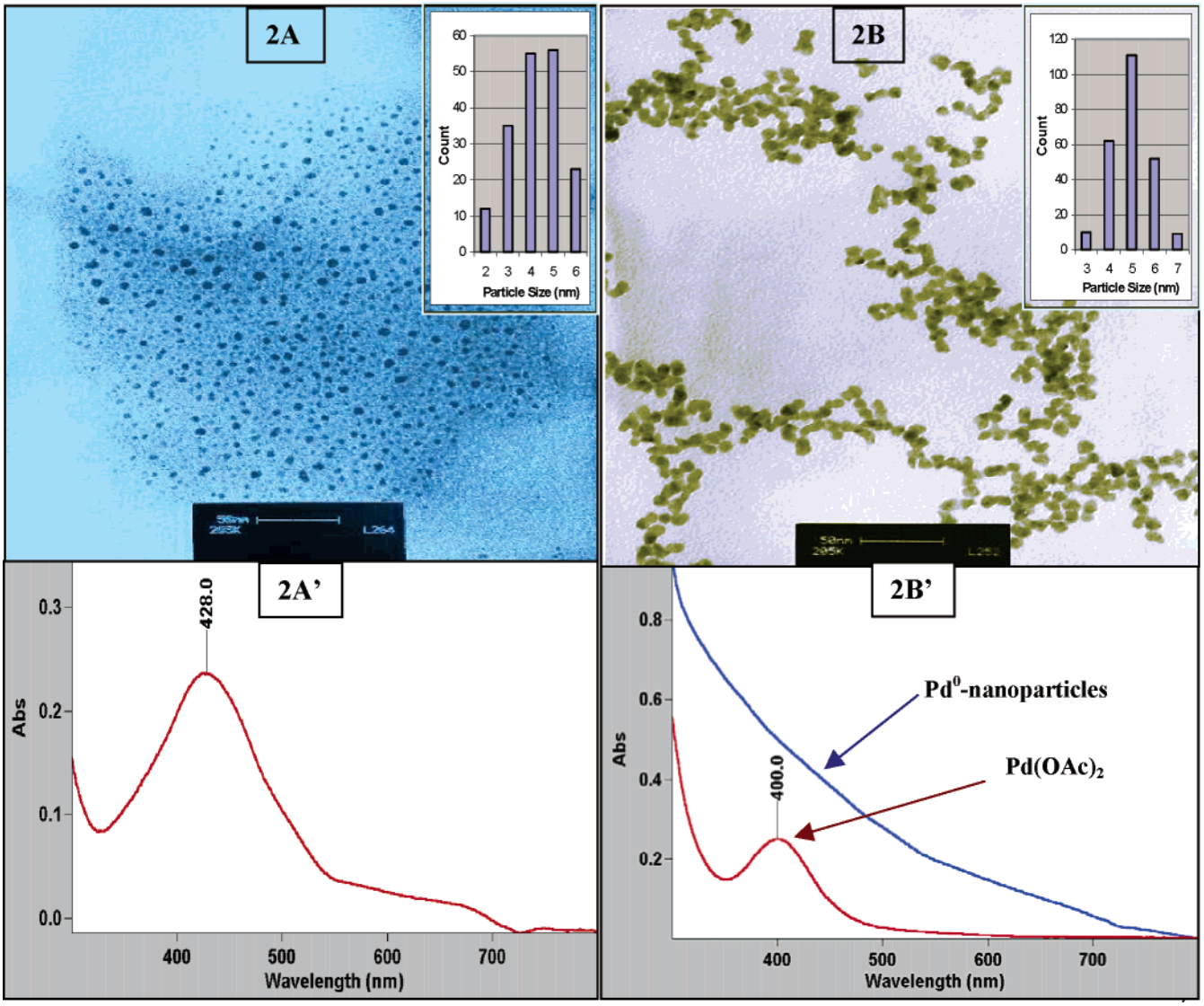


Figure 2. TEM, particle size, and UV−vis analysis of Ag (A, A′) and Pd (B, B′) nanoparticles.

The morphology of the generated polymers was investigated by the transmission electron microscopy (TEM) technique. Polymer **2** (0.377 g, 0.2 mmol) was diluted in 20 mL of benzene. After stirring for 10 min in order to get a homogeneous mixture, one drop of the solution was carefully dropped on formavar-coated copper−carbon grid, and solvent was allowed to evaporate at room temperature in open air. The TEM micrographs showed a well-defined micellar network (Figure 1). In a similar fashion, reaction of cubic siloxane **3** with 8 equiv of PEG led to formation of the corresponding PEG-substituted cubic siloxane polymer **4** in near-quantitative yield (Scheme 1). The detailed analysis of the polymer indicated selective formation of the desired product without any side reactions.[11]

The PEG-substituted siloxane polymers were further used for the reduction of metal salts to metal nanoparticles. We envision that such poly(ethylene glycol)-substituted siloxane-based macromolecules can not only act as the reducing agent for metal salts to metal nanoparticles, but they can also stabilize these metallic nanoparticles and create well-defined self-assembled networks loaded with metal colloids. Thus, the reduction of silver acetate and palladium acetate to corresponding nanoparticles was examined using polymers **2** and **4**.

The silver acetate (0.0083 g, 0.05 mmol) was suspended in toluene, and polymer **2** (0.377 g, 0.2 mmol) was added to the reaction mixture at room temperature. The progress of the reaction was monitored by UV−vis spectroscopy and TEM. After 45 min of addition of polymer to silver acetate suspension in toluene, the solution color changed to light yellow. This was the first evidence of silver colloid formation. During a period of 4 h, the solution color changed to yellow and then to brown. The UV−vis spectrum of the solution showed a peak at 428 nm, which is a characteristic feature of silver nanoparticles (Figure 2).[12] To our surprise, unlike known harsh conditions for polyol reduction process[13] of metal salts, the reduction took place under very mild reaction conditions in 4 h.[14]

Palladium acetate solution is light yellow and shows a peak around ~400 nm in the UV spectrum. For about 1 h, after addition of polymer **2** to the palladium acetate solution, the color remained almost unchanged. After 2 h of continuous stirring at room temperature, the color of the reaction mixture started to change to brown. This was the first evidence of reduction of palladium acetate. During a period of 4 h, the solution color changed to brown and finally turned black, which was a strong evidence of palladium nanoparticle formation. At this

Table 1. Comparison of Nanoreactor to Metal Salt Ratios on the Size of Resulting Nanoparticles[a]

entry	metal salt	metal salt to polymer **2** ratio (mmol)	reaction time (h)	particle size[b] (nm)	UV−vis absorption maxima (nm)
1	Ag(OAc)	1:4	4	4.7 (0.9)	428
2	$Pd(OAc)_2$	1:4	6	5.8 (0.9)	featureless
3	Ag(OAc)	1:6	2.5	4.2 (1.2)	425
4	$Pd(OAc)_2$	1:6	5.5	5.5 (0.9)	featureless
5	Ag(OAc)	1:20	2	2.6 (0.7)	434
6	$Pd(OAc)_2$	1:20	4	2.3 (0.5)	featureless

[a] On average, 200 particles were counted for each particle size analysis study. [b] The figures in parentheses indicate the standard deviation.

point, the UV spectrum was taken, and it showed a featureless absorption, a characteristic of palladium nanoparticles (Figure 2B).

The reaction mixtures were centrifuged for 10 min at 3000 rpm to remove unreacted metal salts. One drop of the colloidal solution was carefully dropped on a farmavar-coated copper−carbon grid and examined by TEM. Solvent was allowed to evaporate at room temperature in open air for about 10 min. These images showed formation of metal particles with narrow size distributions, which were stabilized by siloxane network as no other stabilizer was added (Figure 2A,B). Particle size distribution analysis showed silver and palladium nanoparticles with an average size range of ∼5 nm.

The nanoparticle solutions of silver and palladium were found to be quite stable, signifying the role of siloxane−poly(ethylene glycol) networks as effective stabilizing agents. To examine the efficiency of nanoreactors, the reduction reactions were performed with varying amounts of polymers (1:4, 1:6, and 1:20). The results of TEM study and particles size analysis are summarized in Table 1. It was observed that with lower metal-to-polymer ratios reduction reactions took longer time and did not produce much population of nanoparticles. By increasing polymer amounts, reduction time decreased, and a significant increase in the particle population was observed (Table 1). Moreover, the particle size also decreased with higher polymer to metal salt ratios (entries 5 and 6, Table 1). These studies indicate toward the potential of this methodology for generation of spherical metallic nanoparticles in various size regimes from the same nanoreactor (polymer).

The resulting hybrids can be regarded as processable reservoirs of nanosized metal, which inherit the profitable solution behavior of silicon-based polymers and the catalytic activity of metal colloids. The studies are underway to examine the catalytic activities of these nanoparticles.

The structural features of the polymers play an important role in the reduction process. To verify this observation, in a separate experiment reaction of silver and palladium acetate was examined in the presence of only poly(ethylene glycol). Under identical reaction conditions and molar ratios (as in the case of polymer 2) formation of nanoparticles was not observed even after continuous stirring for several hours. The reaction mixtures were heated at 80 °C for 4 h, but the color as well as UV−vis spectrum remained unchanged. These preliminary experiments indicate that substitution of glycol units to a cyclosiloxane core and formation of a micellar network plays an important role in reduction of metal salts by a polyol-like process. The resultant stable colloids with narrow size distribution further confirm that the network is acting not only as a reducing agent but also as an efficient host agent for nanoparticles.

In conclusion, we have demonstrated a new one-pot, mild, high yielding approach to generation of inorganic/organic hybrid nanoreactores and verified their utility and efficiency for the synthesis of silver and palladium nanoparticles. Investigations of the mechanistic details and generalization of such an approach for stable nanoparticles and semiconductors are underway in our laboratory and will be reported in due course.

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(11) The siloxane network was synthesized via dehydrogenative coupling of tetraethylcyclotetrasiloxane (**1**) with poly(ethylene glycol) (PEG, $M_w \sim 400$). Reaction was carried out in a 25 mL Schlenk tube. Wilkinson's catalyst (20 mg, 0.02 mmol) and poly(ethylene glycol) (1.60 g, 4 mmol, $M_w \sim 400$) were mixed under an argon atmosphere and dissolved in benzene (3.0 mL) at room temperature. This mixture was stirred for 5.0 min, and **1** (0.297 g, 1 mmol) was added. The resulting reaction mixture was heated at 65 °C and monitored by NMR and IR spectroscopy. Total conversion to desired product **2** was observed after 30 h of the reaction. The reaction mixture was centrifuged to separate the catalyst and analyzed by IR, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR. Yield: 98%. ^{1}H NMR (δ, ppm): 0.627 (m), 0.992 (m), 3.594 (s), 3.655 (m), 3.707 (m), 3.877 (m). ^{13}C NMR (δ, ppm): 4.358 (m), 5.322 (m), 6.793 (m), 61.591 (s), 62.198 (s), 70.547 (s), 72.352 (s), 73.012 (s). ^{29}Si NMR (δ, ppm): −57.776 (m), −56.177 (m). IR (ν, cm^{-1}): 2878.26, 1947.83, 1647.83, 1469.57, 1352.17, 1300.00, 1252.17, 1104.35. In a similar fashion and identical molar ratios polymer **4** was synthesized. Yield: 96%. ^{1}H NMR (δ, ppm): 0.012 (m), 3.11 (m), 3.48 (m), 3.65 (s). ^{13}C NMR (δ, ppm): −1.79 (s), 61.23 (s), 70.18 (d), 72.21 (s). ^{29}Si NMR (δ, ppm): −8.41 (d), −109.80 (s). IR (ν, cm^{-1}): 2878.26, 1947.83, 1647.83, 1452.17, 1343.48, 1291.30, 1243.48, 1095.65.

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(14) In a typical reduction procedure, silver acetate (0.0083 g, 0.05 mmol) was suspended in toluene (20 mL) in a 100 mL Schlenk tube equipped with a magnetic stirrer. After continuous stirring for about 10 min, polymer **2** (0.377 g, 0.2 mmol) was added, and resulting mixture was stirred at room temperature. After 45 min, the color of reaction mixture changed to light yellow. The color change indicated that the reduction of silver acetate to silver nanoparticles has ensued. In the course of 4 h, the color changed to dark yellow and then to brown, indicating the complete reduction of silver acetate to silver colloids. The resulting nanoparticle solution was centrifuged at 3000 rpm for 10 min in order to remove unreacted silver acetate. The formation of silver nanoparticles was confirmed by UV−vis spectroscopy and transmission electron microscopy. In a similar fashion, reduction reactions with various ratios of polymer were examined. In case of palladium, stable black homogeneous colloidal solution was obtained.

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