Self-Assembled Stable Silver Nanoclusters and Nanonecklace Formation: Poly(methylhydrosiloxane)-Mediated One-Pot Route to Organosols†

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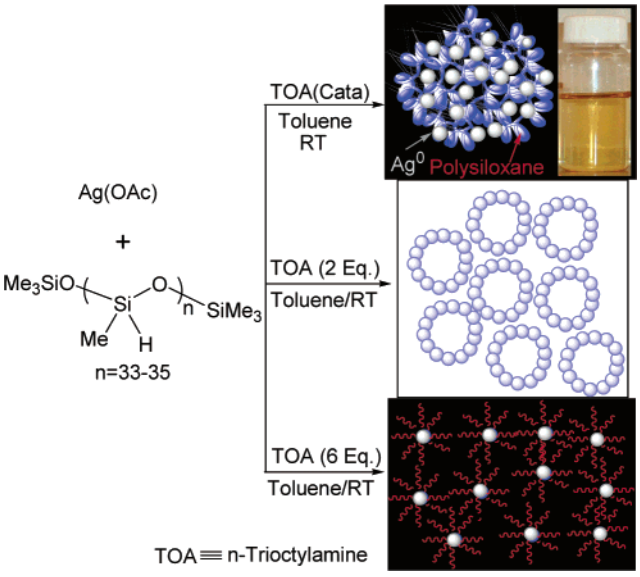
Nanometer-sized particles of metals and semiconductors have been investigated intensively in recent years.[1] In this context, silver nanoparticles are of great interest due to their role in photographic processes,[2] their utility as substrates for surface-enhanced Raman spectroscopy (SERS),[3] and also their application in catalysis.[4] Silver nanocrystallites, mostly hydrosols, have been widely studied because of the ease of their preparation. Since most of the catalytic reactions are performed in organic solvents, it is desirable to design synthetic methods which lead to the stabilization of metal nanoparticles in such solvents. Colloidal dispersions of silver in nonaqueous liquids (organosols) are rare and more difficult to prepare and stabilize. It has been observed that the stability, particle size, and properties of metal colloids strongly depend on the specific method of preparation and the experimental conditions applied. In most cases, nanoparticles are stabilized with strong coordinating surfactants to prevent the agglomeration and to provide specific surface properties.[5] On the other hand, utility and activity of such particles are compromised due to the difficulty in ligand exchange reactions in catalytic processes. In this context it is desirable to develop synthetic strategies to fabricate nanoparticles which provide flexibility to functionalize nanoparticles according to the need and hence tailoring of nanoparticle surfaces. Moreover, for catalytic applications such conjugates may have superior activity and selectivity over the nanoparticles passivated by strong coordinating ligands.

Nanosized colloidal metal nanoparticles protected by polymers exhibit intriguing optical, catalytic, or electronic properties due to the "size effect" and additionally provide the option of influencing the materials' properties by selection of the polymeric matrix.[6,7] A large number of preparative methods for these colloidal metal dispersions involve the presence of the polymer during the reduction from the metal precursors. In this way, the polymer can profoundly influence the particle features of the resulting metal colloids as well as their long-term colloidal stability. Monomeric hydrosilanes are known reducing agents and have been successfully used for the generation of Pt, Pd, and Rh nanosized particles in the context of metal-catalyzed hydrosilylation of alkenes.[8] On the other hand, investigations of polymeric analogous such as polyhydrosilanes as reducing agents for the generation and in-situ stabilization of nanosized metal particles have not been explored. Though, their property profile may provide the means of directing metallic particles into specific physicochemical environments[9a] in addition to their utility as reducing agents. Moreover, combining the ease of processability of polysiloxane polymers with the improved mechanical and optical properties of metal nanoparticles is of practical use for the fabrication of many new devices.[9b]

In this Communication, we describe a versatile method and first example of polyhydrosiloxane-induced generation and stabilization of functionalizable monodisperse silver sols (Scheme 1). This method enables routine formation of stable nanosilver reservoirs, avoiding particle aggregation during the storage as well as nucleation and growth process. We also demonstrate the utility of such reservoirs in grafting the surface properties of nanosized silver particles by exchange reactions with trioctylamine.

Scheme 1. Synthetic Strategy to Polysiloxane-Stabilized Silver Sols and Their Surface Grafting



In an exploratory experiment, when poly(methylhydrosiloxane) (PMHS; 0.024 mL, 0.4 mmol, $M_w \sim 2000$, 33−35 Si−H units) was added to the 50 mL toluene suspension of silver acetate (0.032 g, 0.2 mmol), the mixture turned faint yellow and showed a very broad peak at 445 nm in UV−vis spectra, indicating formation of silver nanoparticles.[10] But, it was observed that the reduction process was very slow (24 h) and was accompanied by particles precipitation.

To accelerate the reduction reaction, an amine catalyst was added to the reaction mixture. Amines are known to polarize the $Si^{\delta+}-H^{\delta-}$ bonds via intermediate formation of hypercoordinated silicon species.[11] Thus, in an optimized procedure, AgOAc (0.032 g, 0.2 mmol) was suspended in 50 mL of toluene and PMHS (0.072 mL, 1.2 mmol) was added while stirring gently at room temperature under nitrogen. The solution was stirred

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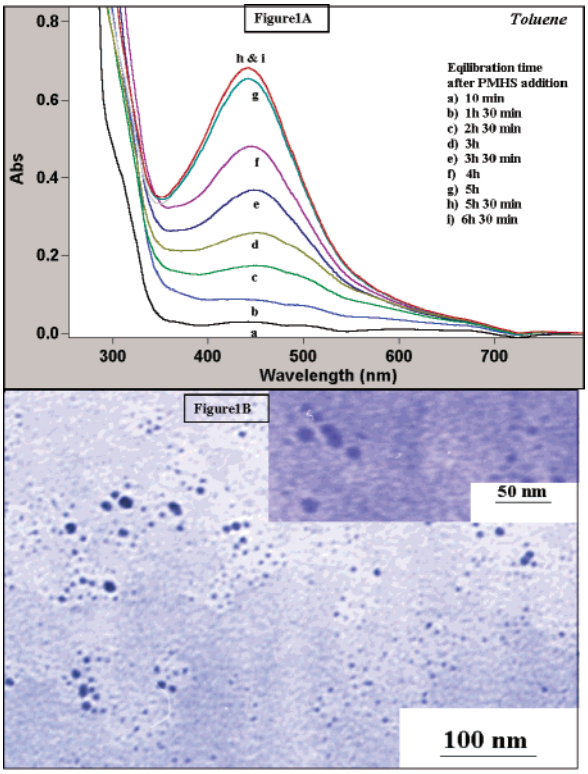

Figure 1. UV−vis spectra monitoring of the absorption changes at different time intervals (A) and TEM analysis (B) of the polysiloxane-stabilized silver nanoparticles.

for 1 h, and trioctylamine (TOA) (0.005 mL, 0.01 mmol) was added as a catalyst. The solution was stirred intermittently for around 5 min after every half an hour, and the formation of silver nanoparticles was probed by monitoring the absorption changes at different time intervals (Figure 1). The formation and stabilization process of polysiloxane-modified silver nanoparticles was traced by the UV−vis absorption method. Figure 1A shows the shifts of the peak positions and the shapes of the absorption spectra during the whole reduction process. Just after 10 min of the injection of the reducing agent, a very broad almost featureless UV−vis band was observed, which was very similar to the solution absorption spectrum before the reducing agent was added. When the reaction was continued for 3 h, a broad asymmetric peak centered at 445−448 nm appeared, indicating the formation of polydisperse nanoparticles. After 4 h of the reaction, the broad peak becomes more symmetric (indicating narrow size distribution) and blue shifts from 445 to 448 to 438 nm (indicating smaller particle size). After total 6 h of the reaction, the plasmon band (λ_{max}: 435 nm) becomes symmetric, and no further intensity increase was observed. At this juncture, the yellow solution was centrifuged and analyzed.

One drop of the solution was deposited on a Formvar-coated carbon grid and visualized by a transmission electron microscope (TEM), without any additional staining. TEM analysis demonstrated that indeed silver particles were formed. The average particle size was found to be 2 nm with a standard deviation of 0.6 nm (Figure 1B). Careful visualization at higher resolution indicated that all the particles were rapped by a lighter matrix, most probably polysiloxane. However, it was difficult to achieve enough contrast (PMHS is not visible at such resolutions) to conclude this observation. As-prepared toluene solutions were found to be stable for 3 months. Because of the stability of these particles, without any other stabilizing agent present, we infer that polysiloxane raps around the particles and prevents them from further agglomeration.

On the basis of these preliminary results, we can roughly elucidate the polysiloxane-induced generation, growth, and stabilization process as follows: At the beginning of the reaction silver ions which are reduced to atoms aggregate rapidly together to form small nanoparticles, which aggregate to become large nanoparticles due to the high density of the small nanoparticles. Formed large particles are not stable and are broken into small particles, which due to the protection provided by siloxane polymers become stable. Alternatively, it is also possible that the dynamics of the protection provided by siloxane polymer is such that it cannot wrap the particles in the time, which allows nucleation-growth phenomena to occur. On the basis of the preliminary UV−vis and TEM studies of the reaction mixture, the whole reduction process seems to be a dynamic one; that is, during the increase in the particle size there are some larger particles which decompose into smaller nanoparticles, and during the decrease in the particle size some smaller nanoparticles aggregate to become larger. However, more experimental and theoretical work is underway to understand the formation process.

After optimization of reaction conditions, the role of PMHS and catalyst TOA was examined in detail since both can also function as a stabilizing agent for nanoparticles. Reactions with varying amounts of TOA were performed. Thus, a suspension of AgOAc (0.2 mmol, 0.032 g) was prepared in 50 mL of toluene, and PMHS (1.2 mmol, 0.072 mL) was injected to this suspension at room temperature. Vigorous stirring was continued for 0.5 h, during which the color of the solution changed to faint yellow (UV−vis spectroscopy, λ_{max} at 444 nm). At this juncture TOA (0.4 mmol, 0.17 mL) was injected into the reaction mixture. After 10 min of addition of TOA, the color of the solution turned dark yellow (UV−vis spectroscopy, λ_{max} at 440 nm). After of 2 h of total reaction at room temperature, the mixture was centrifuged, and one drop of the reaction mixture was deposited on a carbon-coated grid and analyzed by TEM (Figure 2A). Surprisingly, individual nanoparticles as observed in the case of catalytic amounts of TOA were self-assembled in the form of nanosized necklaces. Particle size (Figure 2B) analysis of the individual nanoparticles showed the particles to be rather monodispersed in the 2−3 nm size regime. The ring diameter analysis (Figure 2C) showed that there were three types of necklaces (15−18, 19−22, and 23−26 nm) present in the reaction mixture. The calculated length of the PMHS (n = 33−35) used in this reduction process is approximately 12−13 nm. Incidentally, if one or two to three polysiloxane strands arranged in a spherical form, it will lead to the formation of such spheres. The existence of the pearl-necklace aggregates suggests that the reduced silver particles even in the presence of other stabilizing agents are in interaction with polysiloxane, leading to new types of nanoarchitectures.

To validate this hypothesis, under identical reaction conditions and molar ratios of AgOAc and PMHS, an excess of TOA (6 equiv to AgOAc) was used. The reaction was significantly faster, and within 1 h reduction was complete (Figure 3A). After 1 h of the reaction, the mixture was centrifuged and analyzed by TEM (Figure

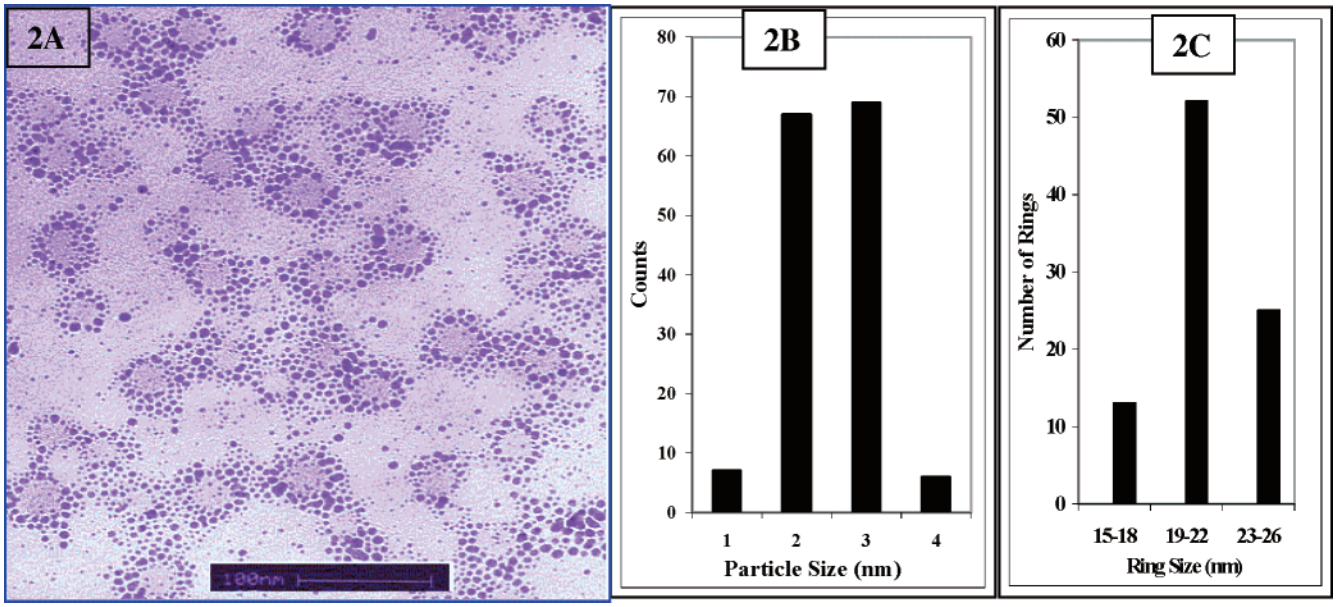

Figure 2. TEM image of the centrifuged reaction mixture (A), particle size (B), and ring size analysis (C) of resulting silver nanonecklaces.

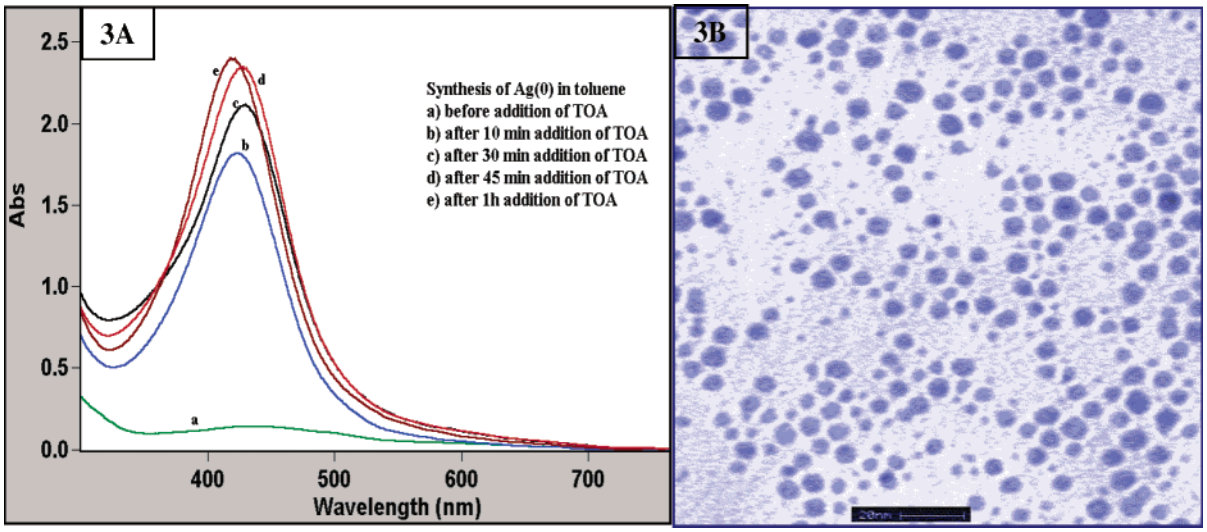

Figure 3. Reaction progress as evidenced by UV−vis spectrum (A) of reactions mixture in the presence 6 equiv of amine and TEM image of nanoclusters (B) after centrifugation of the product.

3B). TEM analysis of the reaction mixture showed the formation of self-assembled individual nanoparticles in 3 nm size regimes, and the complete disappearance of nanosized necklaces was observed. This result shows that when enough coordinating (stabilizing) agents are present, PMHS is completely dissociated from the nanoparticle periphery and surfactant-stabilized nanoparticles are obtained. Further validity for this line of thought was obtained from the following experiment: In a separate experiment, when a solution showing necklace morphology was incubated with an excess of TOA, necklace morphology disappeared completely, and an almost identical TEM image (as in the case of 6 equiv to AgOAc amine) showing self-assembly of individual nanoclusters was obtained.

The stability of silver particles was also investigated in common organic solvents. PMHS- and TOA-stabilized yellow solutions of silver nanoparticles were found to be stable for months and always displayed an intense characteristic absorption peak around ~435 nm without any trailing at higher wavelengths (see Supporting Information). There was, however, an effect against this colloidal stability, namely adsorption on the walls of silica containers, especially for the higher concentrations. This effect is mostly observed for quartz, while it is hardly noticeable if the dispersions are stored in glass vials. This tendency to attach onto silica surfaces represented a serious problem for the spectroscopic study of the kinetics of particle formation. (After each measurement, the dispersion had to be removed from the cuvette and cleaned with KOH to dissolve any remaining of silver attached to the quartz walls.) Although, an advantage of this property can be taken for the application of the particles to the preparation of thin films. This will be reported in a further study.

In conclusion, a one-step conversion of silver acetate to stable nanosized silver particles is achieved under mild conditions in high yields. We have shown that the physicochemical and morphological property profile of polysiloxanes leads to controlled nucleation, growth, and stabilization of nanoparticles and provides new opportunities in nanoscale synthesis of metal particles. In

addition, facile surface tailoring reactions open new possibilities in the field of surfactant exchange reactions.

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Supporting Information Available: UV spectrum for stability studies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612 (b) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226 (c) Belloni, J. *Curr. Opin. Colloid Interface Sci.* **1996**, *2*, 184. (d) Brus, L. *Curr. Opin. Colloid Interface Sci.* **1996**, *2*, 197. (e) Banin, U.; Lee, J. C.; Guzelian, A. A.; Kadavanich, A. V.; Alivisatos, A. P. *Superlattices Microstruct.* **1997**, *22*, 559. (f) Fendler, J. H.; Meldrum, F. C. *Adv. Mater.* **1995**, *7*, 607. (g) Bonnemann, H.; Richards, R. M. *Eur. J. Inorg. Chem.* **2001**, 2455.

(2) Mostafavi, M.; Marignier, J. L.; Amblard, J.; Belloni, J. *Radiat. Phys. Chem.* **1989**, *34*, 605.

(3) Matejka, P.; Vlckova, B.; Vohlidal, J.; Pancoska, P.; Baumrunk, V. *J. Phys. Chem.* **1992**, *96*, 1361.

(4) (a) Sun, T.; Seff, K. *Chem. Rev.* **1994**, *94*, 857. (b) Verykios, X. E.; Stein, F. P.; Coughlin, R. W. *Catal. Rev.—Sci. Eng.* **1980**, *22*, 197.

(5) (a) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41. (b) Schmidt, G. *Chem. Rev.* **1992**, *92*, 1709.

(6) (a) Karim, A.; Yurkeli, K.; Meredith, C.; Amis, E.; Krishnamoorti, R. *Polym. Eng. Sci.* **2002,** *42*, 1836. (b) For an excellent overview, see: Schmidt, G.; Malwitz, M. M. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 103 and references therein. (c) Grohn, F.; Kim, G.; Bauer, A. J.; Amis, E. J. *Macromolecules* **2001**, *34*, 2179. (d) Crooks, R. M.; Zhao, M.; Sun, L.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181. (e) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226.

(7) (a) Chauhan, B. P. S.; Rathore, J. S.; Chauhan, M.; Krawicz, A. *J. Am. Chem. Soc.* **2003**, *125*, 2876. (b) Chauhan, B. P. S.; Rathore, J. S.; Sardar, R.; Tewari, P.; Latif, U. *J. Organomet. Chem.* **2003**, *686*, 24. (c) Chauhan, B. P. S.; Sardar, R.; Tewari, P.; Sharma, P. Third International Workshop on Silicon-Containing Polymers, Troy, ISPO 2003, June 23−25, T-13.

(8) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693 and references therein.

(9) (a) For an excellent review see: Ganicz, T.; Stanczyk, W. A. *Prog. Polym. Sci.* **2003**, *28*, 303. (b) Stucky, G. D.; McDougall, J. E. *Science* **1990**, *247*, 669.

(10) UV−vis absorption spectroscopy has been proved to be quite sensitive to elucidate the formation of silver colloids. An intense absorption peak around 400−440 nm is generally observed and attributed to the surface plasmon absorption of Ag nanoparticles. Such resonance occurs when the incident photon frequencies match with the collective oscillations of the metal nanoparticles.

(11) (a) Corriu, R. J. P.; Lanneau, G. F.; Perrot, M. *Tetrahedron Lett.* **1988**, *29*, 1271. (b) Corriu, R. J. P.; Lanneau, G. F.; Perrot, M.; Mehta, V. D. *Tetrahedron Lett.* **1990**, *31*, 2585.

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