



# Synthesis, stabilization, and applications of nanoscopic siloxane–metal particle conjugates<sup>☆</sup>

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Received 1 April 2003; accepted 28 May 2003

## Abstract

This account reports the new directions in the synthesis and characterization of polysiloxane-encapsulated metal nanoparticles and their applications to catalysis. These materials are prepared by sequestering metal ions with hydropolysiloxanes followed by chemical reduction to yield the corresponding zerovalent metal nanoparticles. The size and processability of such particles depends on the metal to polysiloxane ratios. Our method enables routine formation of stable nanometallic reservoirs in organic solvents avoiding particle aggregation during the storage as well as nucleation and growth process. Catalytic activity of nanoparticles vs metal complexes compares favorably for silaesterification reactions. We also demonstrate the utility of such reservoirs in grafting the surface properties of nanosized silver particles by ligand exchange reactions with thiols and phosphine oxide surfactants.

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**Keywords:** Polymer; Metallic nanoparticles; Silaesterifications; Polysiloxanes; Silver organosols

## 1. Introduction

Interest in condensed matter at size scales larger than atoms but much smaller than bulk solids has grown rapidly over the last few years. Matter containing from tens to thousands of atoms can have structures and properties significantly different from those of conventional materials [1]; consequently, the current research on nanostructured materials is principally devoted to the synthesis, characterization, and understanding of changes in the fundamental properties.

Particularly interesting is the study of metal properties behavior on a nanometric scale [2,3]. Size-dependent changes in band-gap energy, excited-state electronic behavior, and optical spectra are generated that differ drastically from those known for the bulk limit. In addition, the new characteristics of this class of materials make them really attractive for a number of

technological applications [4–6], including photonic devices, catalysis, corrosion protection, solar energy conversion, and chemical or biochemical sensors.

Preparation and characterization of nanocrystallites is a very critical area of research for fundamental understanding and tailoring of materials properties of practical use. Nanocomposite materials require nanometric particles with uniform size, controlled dimensions, and regular shape. Such particles can be obtained by solution chemistry (chemical precipitation and sol–gel technique) and by vapor deposition (gas evaporation, laser ablation, and sputtering) [7]. However, solution chemistry is the only technique that provides a cost-effective method for the production of large quantities of nanoparticles and allows one to manipulate matter at the molecular level. Solution chemistry is the most practical route for the synthesis of nanoscale particles, but the control of size distribution, particle morphology, and crystallinity still need further investigation.

The synthesis of soluble transition-metal nanoclusters has been accomplished using five general methods [8,9]: (i) the chemical reduction of transition-metal salts; (ii) the electrochemical reduction of transition-metal salts; (iii) thermal or photochemical decomposition of transi-

<sup>☆</sup> Invited contribution for “What’s new in Silicon Chemistry in 2003”.

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tion-metal precursors; (iv) ligand reduction and displacement from organometallic compounds; and (v) metal vapor synthesis. Some synthetic techniques use a combination of these five methods; e.g., sonochemical [10] preparations of nanoclusters involve either (i) or (iii) or a combination of (i) and (iii) [10–15]. Of the five methods, the chemical reduction of transition-metal salts is by far the most common.

Transition-metal nanoclusters are only kinetically stable because the formation of bulk metal is the thermodynamic minimum [16,17]. Therefore, nanoclusters that are freely dissolved in solution must be stabilized in a way that prevents the nanoclusters from diffusing together and coalescing—any such agglomeration would eventually lead to the formation of the thermodynamically favored bulk metal [16]. Nanocluster stabilization is usually discussed in terms of two general categories of stabilization, electrostatic and steric [18,19]. Electrostatic stabilization is achieved by the coordination of anionic species, such as halides, carboxylates or polyoxoanions, to the coordinatively unsaturated surface metal atoms of the metal particles [18]. This results in the formation of an electrical double-layer (really a diffuse electrical multilayer) [20], which causes coulombic repulsion between the nanoclusters. Steric stabilization is achieved by the presence of bulky, typically organic materials that, due to their bulk, impede the nanoclusters from diffusing together [18]. Polymers, dendrimers, and large alkylammonium cations are examples of organic steric stabilizers. The choice of stabilizer also allows one to tune the solubility of the nanoclusters [21,22].

Monolithic ceramic and polymeric templates have also been used for preparing nanomaterials. For example, the well-defined pores in alumina or polymeric filtration membranes can be used to define the geometrical and chemical properties of metal, semiconductor, and polymeric nanomaterials [23]. In many cases, the template can be removed chemically or thermally, leaving behind the naked nanomaterial. The obvious advantage of this technique is that highly monodisperse particles with a variety of shapes, sizes, and chemical compositions can be prepared [24].

The polymer template usually serves to both control particle size and passivate the surface of the nanoparticles against agglomeration. A number of polymers can be used as protective agents (e.g. poly(vinylalcohol), poly(methylvinylether), sodium polyacrylate, poly(*N*-vinylpyrrolidone) (PVP)) [25]; such a component allows one to recover the fine particles as a polymer-based composite. Moreover, diblock copolymers with metal-ion affinities can be used to sequester metal ions into localized domains that can subsequently be converted into metal nanostructures. A wide range of metal particles has been formed within such polymer templates including Cu, Ag, Au, Pt, Pd, and Rh.

While our group is involved in devising versatile and practical routes to semiconductor and metallic nanocrystals and their property profiling, due to space limitations, we will limit our discussion to novel metals. In this account, we will summarize, the synthesis and characterization of polysiloxane-encapsulated metal nanoparticles their thermal, catalytic, optical, and photo-thermal properties.

## 2. Motivations and rationale for approach

Siloxane polymers are a very versatile class of polymers, which have been used as additives to produce or enhance a number of physical properties ranging from water repellency to thermal 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 [26]. On the other hand, investigations of polyhydrosilanes as reducing agents for the generation of nanosized silver particles have not been explored. Though, their property profile may provide the means of directing metallic particles into specific physicochemical environments in addition to their utility as reducing agents. In our approach, well-defined silicon polymers (polysiloxanes) are envisioned to act as reducing agents, as well as templates to control the size, stability, and solubility of nanoparticles ranging in diameter from less than 1 up to 10 nm.

Polysiloxanes are, particularly, well suited for hosting metal nanoparticles for the following reasons: (1) the selected polysiloxane templates themselves are of fairly uniform composition and structure, and, therefore, they may yield well-defined nanoparticle replicas, (2) unusual freedom of rotation around the Si–O bond allows these polymers a high degree of flexibility while maintaining their integrity, (3) polysiloxanes with Si–H functionalities can act as reducing agents and thus can eliminate the need for extra reducing agents, (4) the encapsulated nanoparticles are confined primarily by steric effects, and, therefore, a substantial fraction of their surface is unpassivated and available to participate in surfactant exchange and catalytic reactions, (5) the substituent branches can be used as selective gates to control access of small molecules (substrates) to the encapsulated (catalytic) nanoparticles, and (6) the terminal groups can be tailored to control solubility of the hybrid nanocomposite and used as handles for facilitating linking to surfaces and other polymers. As will be discussed later, these attributes take full advantage of the unique structural and chemical properties of polysiloxanes. Indeed, polysiloxanes/nanoparticle composites can represent an unusual case of the template and replica working in concert to exhibit functions that exceeds those of the individual components. That is, in

the studies reported here the polysiloxane templates play a role well beyond that of a simple casting mold.

### 3. Pd-nanoweb: synthesis and applications of Pd-polysiloxane conjugates

Recently, we have described a novel route to biodegradable polysilylestere, via esterification of polyhydro-siloxanes in presence of Pd(OAc)<sub>2</sub> (Scheme 1) [27].

During these studies, following observations led us to investigate this catalysis in detail [28]: (i) when hydro-silanes were added to the reaction mixture containing catalytic amounts of Pd(OAc)<sub>2</sub>, color of the solution turned black accompanied by gas formation presumably H<sub>2</sub>, (ii) after the transformation was complete, a black precipitate was formed and the solution became colorless, and (iii) the black precipitate can be redispersed in the solution and was found catalytically active for silylesterification reactions thus allowing recyclability.

Based on these elucidations, we decided to investigate the possibility if “Pd” colloids were formed during this catalysis. Thus, in a Schlenk tube, Pd(OAc)<sub>2</sub> (0.004 gm, 0.02 mmol) and acetic acid (0.06 ml, 1.00 mmol) were dissolved in 2.5 ml of benzene, and the mixture was examined by UV–Vis spectroscopy. A peak at 400 nm indicative of Pd(OAc)<sub>2</sub> was observed (Fig. 1a). Poly-methylhydrosiloxane (**1**) (PMHS; 0.06 ml, 1 mmol, *M<sub>w</sub>* ~ 2000, 33–35 Si–H units) was added, which was accompanied by generation of a gas presumably H<sub>2</sub>. After 5 min of addition of **1**, Pd(OAc)<sub>2</sub> peak (400 nm) disappeared completely (Fig. 1) indicating formation of new metallic species.

One drop of the reaction mixture was deposited on formvar/carbon-coated grid and analyzed by transmission electron microscopy (TEM; Fig. 2). As is evident, from Fig. 2, “Pd” colloids were formed after the addition of PMHS and were stabilized by siloxane polymer network. Particle size analysis showed the average particle size of 6 nm with a standard deviation of 1 nm. High resolution TEM indicated that Pd-particles form web structures in the nanosize regime.

After completion of the catalysis, precipitated black sticky solid was analyzed by scanning electron microscopy (SEM), IR, and multinuclear NMR techniques. Silicon moieties were present in the solid as evidenced by <sup>29</sup>Si-NMR. The peaks at δ –36.15, –64.74, and –75.74 ppm correspond to a polymeric network containing Si–H (assigned after gated as well as off-resonance decoupling experiments), SiOCOR, and Si–OH moieties, respectively. The signal at δ –110.94 ppm

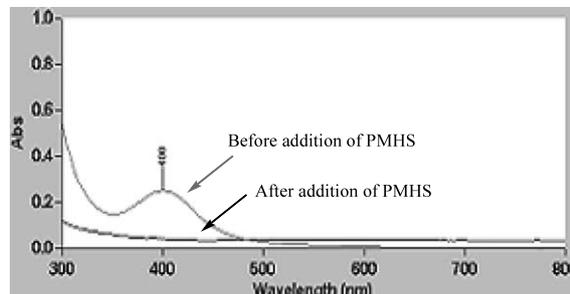


Fig. 1. UV–Vis spectra of the reaction mixture.

indicates fully condensed network. FT-IR spectra also displayed characteristic signals associated with SiH, and Si–O–Si bonds. SEM analysis (Fig. 3) of this solid was also undertaken. Particles were found to be in nanometer size regime (40–50 nm) and stabilized by polymeric network.

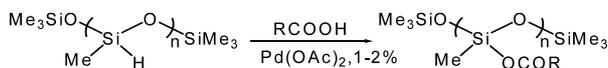
After product isolation, remaining sticky solid was washed with benzene and same catalysis was repeated again. A black solution was obtained after addition of the reactants. Catalysis was continued until total conversion to silylester, indicating that presence of silicon network stabilization facilitates the redispersion of catalytically active ‘Pd’ particles.

To further probe the identity of the “real catalyst”, poisoning experiments were also performed [29]. When the silylesterification was carried out in presence of PPh<sub>3</sub>, (3:1, PPh<sub>3</sub>:Pd(OAc)<sub>2</sub>), no reaction took place under standard conditions even after 18 h. If PPh<sub>3</sub> was added after the generation of the Pd-colloids, only 25% conversion of reactants to product was obtained after 24 h of reaction. Under identical reaction conditions, quantitative conversion to corresponding silylester takes place after 3.5–4 h.

Catalyst poisoning tests along with UV, TEM, and catalyst isolation (evacuation to dryness) and then reuse experiments firmly establish that Pd-colloids are the real catalysts in the present system. Based on these evidences, it seems plausible that the silicones play the role of intermediate host stabilizing agents.

We also investigated independent generation of “Pd” siloxane-networked particles by reacting **1** (0.06 ml, 1 mmol) with Pd(OAc)<sub>2</sub> (0.09 gm, 0.4 mmol) in 20 ml benzene. Preliminary evidence for this transformation was obtained from UV–Vis spectroscopy. UV–Vis spectra of Pd(OAc)<sub>2</sub> in benzene show a peak at 400 nm (Fig. 1). When PMHS was added to this solution, the color of the mixture changed from yellow to dark brown and was accompanied by generation of a gas presumably H<sub>2</sub>. After 5 min of addition of PMHS, Pd(OAc)<sub>2</sub> peak (400 nm) disappeared completely (Fig. 1), and a featureless transition indicating formation of new metallic species was observed.

After 2 h of stirring at room temperature, obtained black precipitate was filtered and washed with excess of



Scheme 1. Pd-catalyzed silylester synthesis.

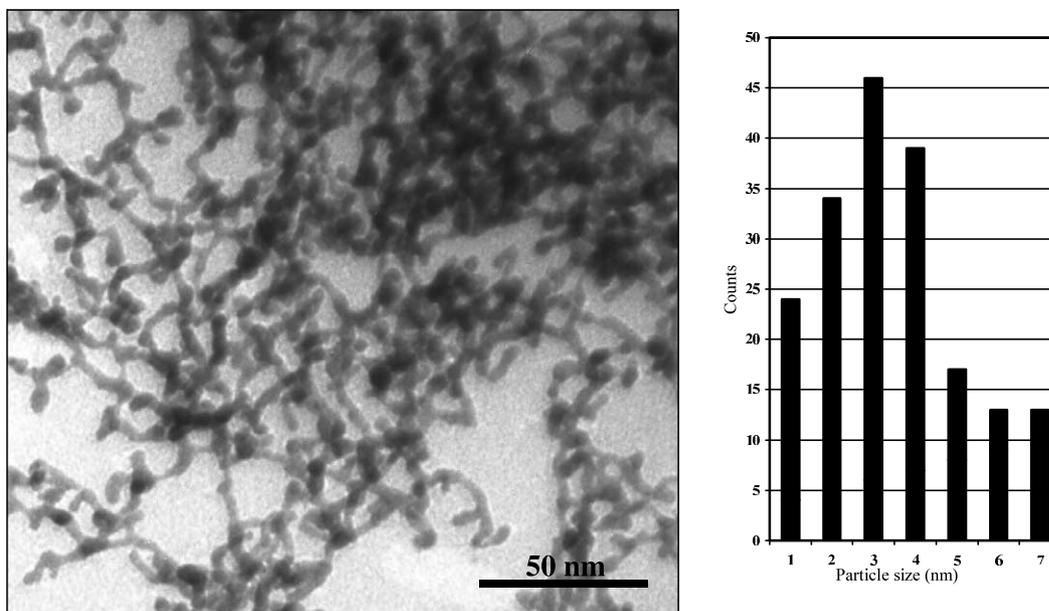


Fig. 2. TEM image and the particle size analysis of the “Pd” colloids obtained after the addition of starting materials (no staining was required).

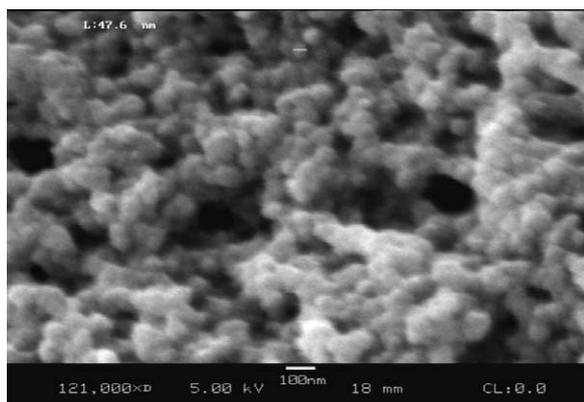


Fig. 3. SEM image of the gummy solid obtained after the catalysis.

benzene. SEM showed similar particle size distribution and,  $^{29}\text{Si}$  displayed peaks at same positions as in case of the solid obtained from catalytic reactions. This powder was used as catalyst for silaesterification reactions of polymer **1** and its monomeric model siloxane 1,1,1,3,5,5,5-heptamethyl trisiloxane (**2**). Under the identical reaction conditions and molar ratios, independently generated “Pd” colloids showed similar catalytic efficiency as in the case of previous experiments (see Table 1).

Based on initial evidences, the reaction scheme for producing nanoweb of palladium particles involves the reduction of the soluble Pd complex species, nucleation of metallic particles, and growth of the individual nuclei in the presence of a suitable reducing and protective agent. The presence of polysiloxane is essential for preventing the coalescence of the nuclei during the growth step. It is during the nucleation and growth

Table 1  
Comparison of the catalytic activity

Acid	Silane	Pd-colloids	2% Pd(OAc) <sub>2</sub>	Yield (%)
CH <sub>3</sub> COOH	<b>2</b>	Room temperature, 5 h	Room temperature, 8 h	95
CH <sub>3</sub> COOH	<b>1</b>	70 °C, 12 h	70 °C, 3.5 h	95
C <sub>6</sub> H <sub>5</sub> COOH	<b>2</b>	70 °C, 6 h	70 °C, 6 h	95
C <sub>6</sub> H <sub>5</sub> COOH	<b>1</b>	70 °C, 24 h	70 °C, 24 h	85

steps that particle–particle adhesion and sintering must be avoided. Prevention of particle sintering is achieved by adding a critical dosage of polysiloxane protective agent whose function is to cover the particles, thus effectively eliminating any possibility of palladium–palladium particle bond formation. The presence of this agent at the solid–liquid interface does not interfere with the palladium diffusion–surface deposition process, and the particles can grow to a definite size.

#### 4. Silver nanoparticles: synthesis and applications

Silver nanoparticles are of great interest due to their role in photographic processes [30], their utility as substrates for surface-enhanced Raman spectroscopy (SERS) [31], and also due to their application in catalysis [32]. 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 disper-

sions of silver in non-aqueous liquids (organosols) are rare and more difficult to prepare and stabilize.

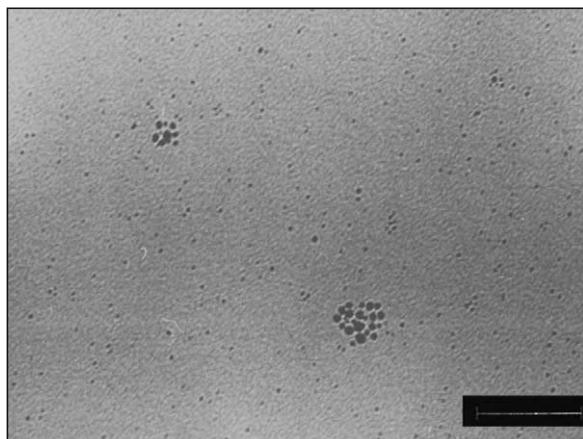
It has been observed that the stability, particle size, and properties of metal colloids strongly depend on the specific method of preparation and the experimental conditions applied. In most cases, nanoparticles are stabilized with strong coordinating surfactants to prevent the agglomeration and to provide specific surface properties [33]. On the other hand, utility and activity of such particles is 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 are stabilized by non-coordinating environments. Such preparations will provide flexibility to functionalize nanoparticles according to the need, 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.

In this part, we summarize a versatile method and first example of polyhydrosiloxanes-induced generation of functionalizable monodisperse silver sols [34]. This method enables routine formation of stable nanosilver reservoirs in organic solvents 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 ligand exchange reactions with thiols and phosphine oxide surfactants [34].

As in the case of  $\text{Pd}(\text{OAc})_2$  reduction process, when PMHS was added to a mixture of  $\text{AgOAc}$  and benzoic acid, reduction of silver salt to silver nanoparticles was observed. Surprisingly, in contrast to Pd-nanoweb, in



Toluene ↓ RT



Scheme 2. Generation and stabilization of silver nanosols.

this case, well-separated nanoscopic silver particles were obtained (Scheme 2).

This diversity led us to examine the metal salt reduction under various reaction conditions for tailoring the morphological features of the nanoparticles. In exploratory experiments, when 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), mixture turned faint yellow and showed a peak at 435 nm in UV–Vis spectra indicating formation of silver nanoparticles. But, it was observed that reduction process was slow (24 h) and was accompanied by particles precipitation.

In order to accelerate the reduction process and to develop the synergy between nucleation and growth process, an amine catalyst was added to the reaction mixture. This modification is based on the fact that dynamic coordination of amine to silicon hydrides leads to hypercoordinated silicon centers and thus very active siliconhydrides [35]. Thus, in an optimized procedure,  $\text{AgOAc}$  (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 for 1 h, and trioctylamine (0.005 ml, 0.01 mmol) was added as a catalyst. 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. A peak at 430–435 nm was observed after 30 min of reaction, indicating the formation of Ag nanoparticles. After 5 h of reaction, peak intensity became constant and mixture turned light yellow. At this juncture, yellow solution was centrifuged and analyzed.

One drop of the solution was deposited on formvar-coated carbon grid and visualized by 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. Careful visualization at higher resolution indicated that all the particles were wrapped by lighter matrix most probably polysiloxane. Though, it was difficult to achieve enough contrast (PMHS is not visible at such resolutions) to conclude this observation. Due to the stability of these particles, we infer that polysiloxane wraps around the particles during the formation stage and prevents them from further agglomeration.

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. Hence,

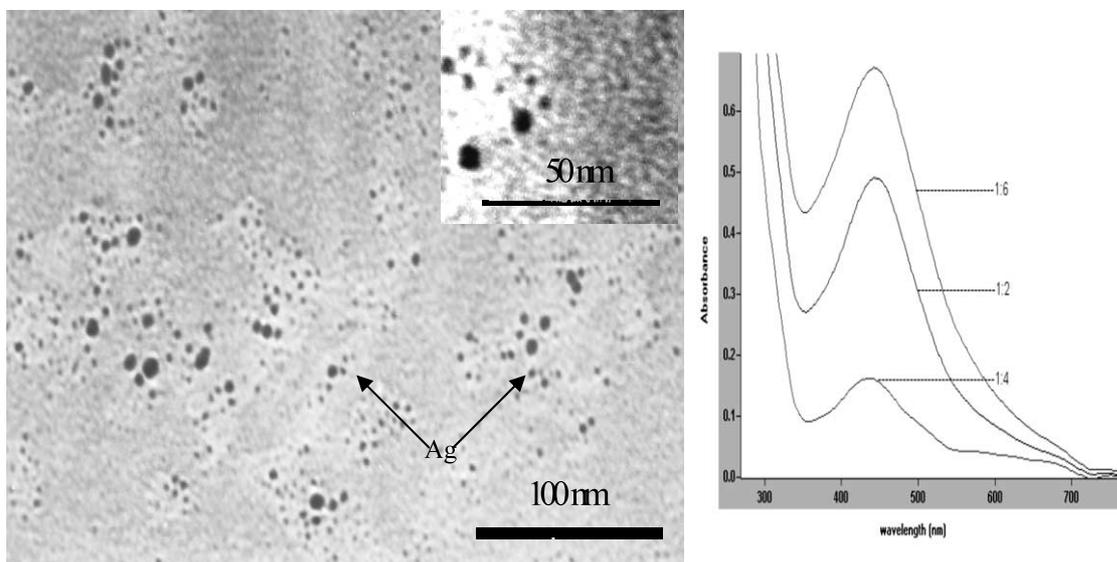


Fig. 4. TEM and UV-Vis spectrum of as-prepared polysiloxane-stabilized silver nanoparticles. No additional staining was required.

advantage of this property can be taken for the application of the particles to the preparation of thin films.

Reduction process was examined with various amounts of polysiloxane reducing agent. In the cases of 1:2 and 1:6 (AgOAc:PMHS) ratios, particles were found to be stable and almost monodisperse ( $\sim 2$  nm). On the other hand, in the presence of 1:4 AgOAc:PMHS ratio, reduction process was also accompanied by particles precipitation (Fig. 4, UV-Vis spectra).

In order to investigate the utility of polysiloxane-silver conjugates, surface grafting studies were performed. In as-prepared samples of polysiloxane-conjugated silver particles, trioctylphosphineoxide (TOPO;

0.8 mmol) was added and solution was kept at room temperature for 24 h and analyzed by TEM, NMR, IR, and UV-Vis spectroscopy. The color of the sol changed to golden yellow and UV-Vis analysis indicated forma-

Table 2  
Comparison of absorption maxima and average particle size<sup>a</sup>

Entry	Silver sols	UV-absorbance	Color	Particle size
1	Ag-PMHS	435–440 nm	Faint yellow	2.00 (0.60)
2	Ag-TOPO	421–425 nm	Golden yellow	3.63 (0.96)
3	Ag-DDT	Very weak 422 nm	Dark yellow	4.40 (1.19)

<sup>a</sup> In all the cases, ca. 150 particles were counted and then combined into histograms to obtain the size distributions.

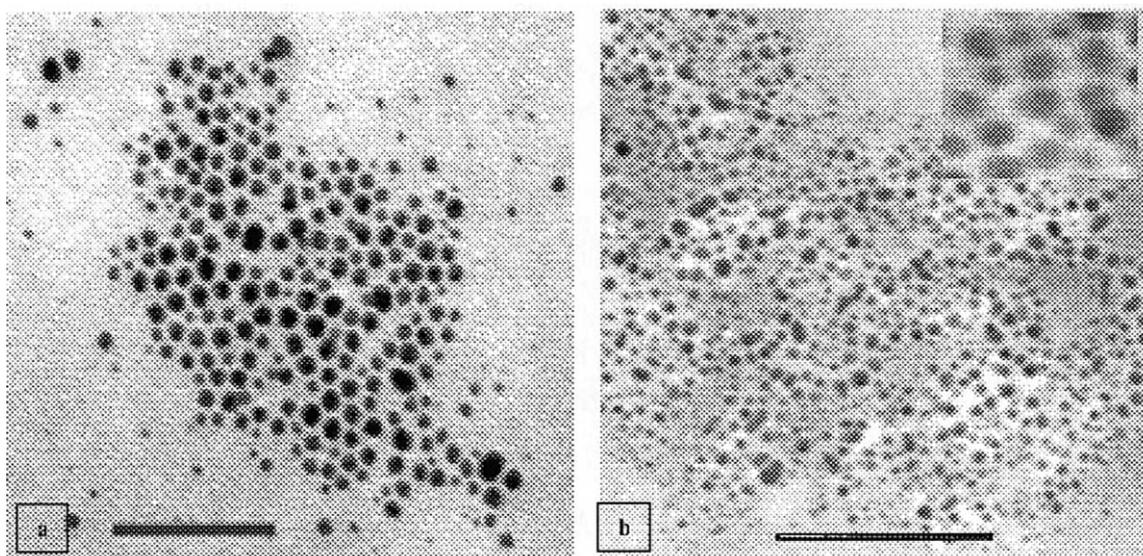


Fig. 5. TEM of (a) TOPO, and (b) DDT-functionalized silver particles.

tion of new type of silver sols (421 nm,  $\lambda_{\text{max}}$ ). TEM analysis (Fig. 5a) showed that TOPO-capped silver nanoparticles spontaneously self assemble, when deposited on a copper grid. The average particle size was found to be 3.6 nm. Spontaneous self-assembly has been observed before for highly monodispersed TOPO-capped semiconductor nanoparticles [10]. In a similar fashion and under identical molar ratios, addition of 1-dodecanethiol (DDT) led to the formation of thiol functionalized silver sols (Fig. 5b).

Functionalized nanosized silver particles can also be synthesized via one pot in situ reduction. Thus, PMHS (0.072 ml, 1.2 mmol) was added to the 50 ml toluene suspension of silver acetate (0.032 g, 0.2 mmol) and stirred at room temperature. After 10 min of reaction at room temperature, TOPO (0.30 g, 0.8 mmol) was introduced to the reaction mixture, and reaction progress was followed by UV–Vis spectroscopy. The peak positions were determined to be at 431, 423, and 420 nm, corresponding to time intervals of 15, 30, and 45 min, respectively. After 6 h of reaction at room temperature TOPO-functionalized silver particles were obtained. In a similar fashion and in identical molar ratios of reactants, DDT-stabilized silver particles were also synthesized. Surfactants-stabilized yellow solutions of silver nanoparticles were found to be stable for months and always displayed an intense absorption peak around  $\sim 420$  nm. A comparative study of UV–Vis absorption spectra and particle size analysis is summarized in Table 2.

## 5. Conclusions and future perspectives

In conclusion, a one-step conversion of metallic salts to stable nanosized metal particles is achieved under mild conditions in high yields. We have shown that physicochemical and morphological property profile of polysiloxanes lead to controlled nucleation, growth, and stabilization of nanoparticles and provide new opportunities in nanoscale synthesis of metal particles. In addition, facile surface tailoring reactions open new avenues in the field of surfactant exchange reactions.

## Acknowledgements

BPSC acknowledges support from NIST-research grant, NSF-instrumentation grant, GRTI (The Graduate Research and Technology Initiative) grant, Merck-AAA grant, PSC-CUNY grant, and CSI-CUNY startup grant. We also thank “Deans Summer Scholarships Program”. Our thanks are also due to Professor Bill L’Amoreaux for helping with EM analysis.

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