

Nanoengineering of Metallic Solutions Through Silicone Constructs[†]

**Bhanu P. S. Chauhan,^{a,*} Rajesh Sardar,^a Umar Latif,^a Moni Chauhan,^b
and William J. Lamoreaux^c**

^a *Nanomaterials Laboratory of Center for Engineered Polymeric Materials (CePM), Department of Chemistry and Graduate Center, City University of New York at The College of Staten Island, 2800 Victory Boulevard, Staten Island, New York 10314.
Corresponding Author's E-mail: chauhan@mail.csi.cuny.edu*

^b *Queensborough Community College of City University of New York, Bay Side, New York*

^c *Department of Biology and Graduate Center, City University of New York at The College of Staten Island, 2800 Victory Boulevard, Staten Island, New York 10314*

Received 28-09-2005

[†] This paper is dedicated to Professor Philip Boudjouk for his seminal contributions to organosilicon chemistry.

Abstract

In this review, we present the summary of preliminary results of our recent investigations on the synthesis, stabilization and characterization of functional metallic nanoclusters and their assembly in various physicochemical environments. These investigations are based on the “meatball-spaghetti” strategy, devised in our laboratory, we are investigating silicon based nanoreactors (spaghetti) for generation and stabilization of nano-objects (meatballs). In the first part, a one pot, highly efficient reduction of silver acetate to stable nanosized silver particles is described. This new strategy involves utilization of poly(methylhydro)siloxane as reducing and stabilizing agent and permits routine formation of stable 2 nm size silver particles in common organic solvents at room temperature. The role of physicochemical and morphological property profile of polysiloxanes in nucleation, growth and stabilization processes is also discussed. The ligand exchange studies of nanosilver pools in grafting the surface properties of silver particles is also presented. In the second part, cyclic and cubic siloxanes templates are used for the generation of micellar network in presence of polyethylene glycol units. The micellar network is used for the room temperature reduction of Ag and Pd metal salts to metal colloids, in organic solvents, by “polyol like process”. The cases are presented, which demonstrate that network not only acts as a reducing agent, but as a stabilizer as well. Electron microscopy studies show non-aggregated metal nanoparticles with narrow size distributions, which are evenly trapped in micelles.

Key words: Nanoclusters, polysiloxane, collagen, nanoreactors and cyclic templates

Contents

Introduction	362
Hydropolysiloxane as Nanoreactors	363
<i>a) Exchange Reactions With Amine (Nanoparticle Functionalization)</i>	364
<i>b) Exchange Reaction in Presence of Collagen (Nanoparticle Functionalization)</i> .	364
Inorganic/Organic Hybrid Nanoreactors	365
Tris(trimethoxysilylpropyl) Isocyanurate Grafted “Pd”-Nanoclusters	368
Conclusions and Future Perspective	368
Acknowledgements	368
References	368

Introduction

Nanosized materials are of significant importance due to the uncommon chemical and physical properties associated with their size regime. Driven by the curiosity and potential of such materials for future applications, last two decades have seen a spur of activity in this area of research.^{1–2} The synthetic strategies for such materials, can be grouped in two groups generally referred as “top-down” and “bottom-up” methods. It has been recognized that bottom-up synthetic routes are more dependable and successful in controlling the matter at nanoscale but the studies of factors such as pre- and/or post- synthetic stability, size, morphology and dimensional control are still not mature.^{3–4} To investigate these issues, along with monomeric surfactant stabilizers macromolecules based stabilization has also been investigated intensively.^{5–6} Such stabilizers are envisioned to provide not only the stability but also the morphological and reactivity control at nanosize regime. In general, macromolecule (dendrimer, linear polymer and co-polymer) based stabilization of nanomaterials is achieved through co-ordinating functionalities present in such macromolecules. In this area of research, notable contributions from various research groups have shed light on the array of size-related electronic, optical and catalytic properties of “nanoobject-macromolecule” constructs.^{5–8}

Recent investigations in our laboratory^{9–11} have been driven by the need to generate functionally active nanoclusters, which are stabilized by very weak coordinative environments leading to functionalizable,

active and reactive nano-objects. These studies are inspired by our hypothesis that stabilization of active nanoclusters can be achieved by the “meatball-spaghetti” analogy. In this model, preparation of functional nano-objects (nanoclusters) is viewed as the preparation of “meatball-spaghetti” dish. This analogy is based on the premise that the aggregation of the *meatballs* (nanoclusters) can be prevented if enough *spaghetti* (flexible polymeric structures) is present to physically wrap the meatballs during the formation process. Due to very weak surface passivation imparted by stabilizing agent, such type of nanoclusters are expected to show superior activity and selectivity over the nanoparticles passivated by strong coordinating ligands. The fundamental difference of this strategy from other polymer-stabilized systems is that, in this hypothesis the polymer does not contain the coordinating ligands, which can strongly passivate the nanocluster surface. Moreover, the substituents of the polymer are used to induce the reduction of metal salts avoiding utilization of any external reducing agent.

Based on the “meatball-spaghetti” strategy, we are investigating silicon based nanoreactors (*spaghetti*) for generation and stabilization of nano-objects (*meatballs*). In this review, we present the summary of preliminary results (Scheme 1) of our recent investigations on the synthesis, stabilization and characterization of functional metallic nanoclusters and their assembly in various physicochemical environments. The results are divided in three sections on the basis of stabilizing structures (nanoreactors).

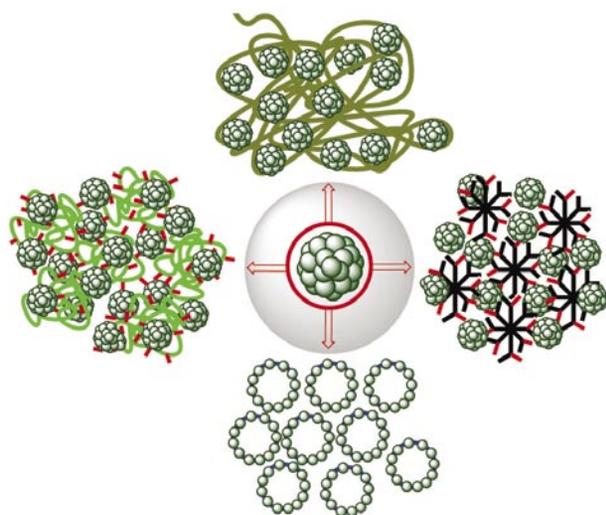
Biographical Sketches



Professor **Bhanu P. S. Chauhan** obtained his Ph.D. under the guidance of Professor Robert Corriu at Montpellier University (France) in 1995 for his work on silylene-transition metal complexes. Just after his Ph. D., he joined the group of Professor Masato Tanaka at “National Institute of Materials and Chemical Research” (NIMC). In NIMC-Japan, he was recipient of Agency of Industrial Science and Technology (AIST) Fellowship and NEDO research scientist fellowship and worked there for one and half year. In 1997, he moved to “Center for Main Group Chemistry” in the group of Professor Phil Boudjouk and worked with him for almost three years. He was appointed assistant professor at Catholic University of America in August 2000 and worked there for one year before joining City University of New York at CSI in 2001. His current research interests are in the area of nanoscale synthesis of metal and semiconductors, new avenues to silicon based macromolecules and nanoparticle mediated catalysis.

Rajesh Sadar was born in Calcutta, India. He got his B.S in chemistry from Calcutta University (Ramakrishna Mission College), India. He obtained his M.S. from IIT Kharagpur, India. He is currently a Ph. D. candidate in polymer science under the guidance of Professor Bhanu P. S. Chauhan at City University of New York, Graduate Center. His doctoral research involves investigations of the polyhydrosiloxane and its oligomeric counter parts as a reducing agent for the synthesis of noble metal nanoparticles.

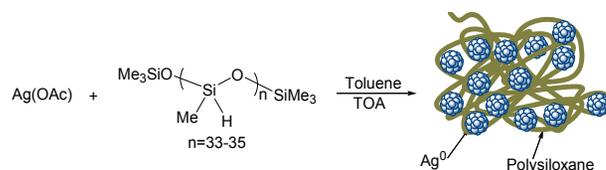




Scheme 1. Synthetic strategies to functional nanoclusters.

Hydropolysiloxane As Nanoreactors

In the context of metal catalyzed hydrosilylation of alkenes, hydrosilanes have been implicated as reducing agents of Pt, Pd, Ru and Rh metal complexes to corresponding nano-sized metallic particles.¹² These



Scheme 2. “meatball-spaghetti” strategy to stable nanosized silver particles.

works prompted us to investigate the possibility if polymeric hydrosilanes such as poly(methylhydro)siloxane (PMHS) can act as reducing as well as stabilizing agents fulfilling the role of spaghetti as proposed in our model.

Recently, utilizing polyhydrosiloxanes we have described a versatile method and first example of polyhydrosiloxane induced generation and stabilization of functionalizable monodisperse silver nanoparticles (Scheme 2).¹⁰

When poly(methylhydrosiloxane) PMHS was used as reducing agent, it was observed that reduction process was very slow and was accompanied by particles precipitation. In order to accelerate the reduction reaction an amine catalyst was added to the reaction mixture. Amines are known to polarize the $\text{Si}^{\delta+}\text{-H}^{\delta-}$

Biographical Sketches



Umar Latif received his B.S degree in Chemical Technology from Saint-Petersburg, Russia (1998). Later he moved to Czech Republic where he started his M.S. in Chemical Technology of Polymers at University of Pardubice. During his final semester (2001), he joined Ph. D. program in polymer chemistry at The City University of New York. Currently, he is pursuing the final level of his doctoral studies in Polymer Chemistry from Graduate Center of City University of New York under the supervision of Dr. Bhanu P. S. Chauhan. His research is focused on the generation of I/O hybrid nanoreactors for synthesis, stabilization, and catalytic application of metal nanoclusters. Another part of his research is to synthesize I/O hybrid porous materials for drug delivery applications.

Professor **Moni Chauhan** received her B.Sc. and M.Sc. from Christ Church College of Kanpur University and Joined IIT Kanpur after winning the CSIR fellowship. She obtained her Ph. D. in 1996 in the guidance of Professor Robert Corriu at Montpellier University for her work on the stabilization of cationic species of silicon and phosphorous. She briefly worked in Professor Tanaka's group at “National Institute of Materials and Chemical Research” in Japan before joining Professor Boudjouk's group at North Dakota State University in 1997. She was appointed Assistant Professor at Queensborough Community College of City University of New York in 2002. Her research interests are in the area of catalysis, nanodrug delivery and inorganic polymeric materials in general.



Professor **William L'Amoreaux** received his B.S. in Zoology from Arkansas State University and M.S. and Ph.D. in Biology from the University of Memphis. His postdoctoral research in neuroscience was directed by Drs. Anton Reiner and Malinda Fitzgerald at the University of Tennessee Center for Health Sciences. A cell biologist, Dr. L'Amoreaux's current research interest lies in the modification of extracellular matrix proteins (namely collagen) as it relates to aging and diabetes. His collaboration with Dr. Chauhan stems from a common interest in utilizing the features of native proteins as templates for drug delivery systems and creation of novel nanoscaffolds.

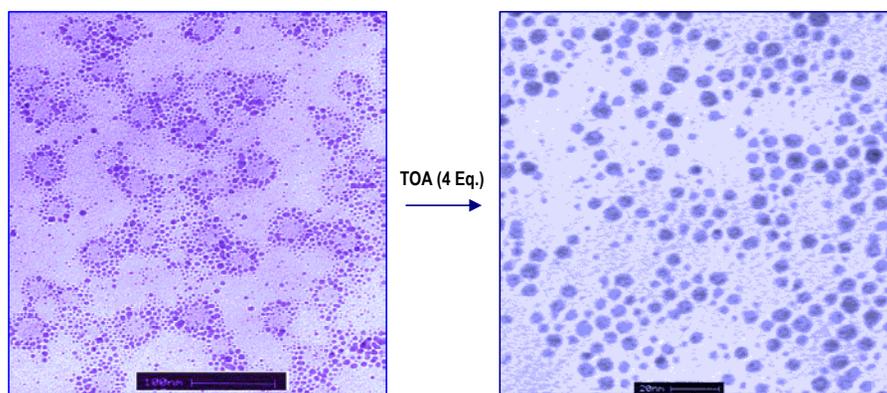


Figure 1. TEM image of the centrifuged reaction mixture of resulting silver nanonecklaces and their conversion to nanocrystals (Reprinted with the permission from ref. 10, copyright, 2004, American Chemical Society).

bonds via intermediate formation of hypercoordinated silicon species.¹³ The formation and stabilization process of polysiloxane-modified silver nanoparticles was traced by the UV-visible absorption method. 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. Due to the stability of these particles, without any other stabilizing agent present, we infer that polysiloxane wraps around the particles and prevents them from further agglomeration. This method enables routine formation of stable nanosilver reservoirs avoiding particle aggregation during the storage as well as nucleation and growth process.

a) Exchange Reactions With Amine (Nanoparticle Functionalization)

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. Surprisingly, individual nanoparticles as observed in the case of catalytic amounts of TOA were self-assembled in the form of nanosized necklaces, when two equivalent of TOA was used. Particle size analysis of the individual nanoparticles showed the particles to be rather monodispersed in two to three nanometer size regime. The ring diameter analysis showed that there were three types of necklaces (15–18 nm; 19–22 nm; 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, one or two to three polysiloxanes strands arranged in a spherical form can 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 type of nanoarchitectures.

In order to validate this hypothesis, under identical reaction conditions and molar ratio's of AgOAc and

PMHS, excess of TOA (6 equivalent to AgOAc) was used. The reaction was significantly faster and within one hour reduction was complete. TEM analysis of the reaction mixture showed the formation of self-assembled individual nanoparticles in 3 nm size regimes and complete disappearance of nanosized necklaces was observed (Figure 1). This result indicates 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 solution showing necklace morphology was incubated with excess of TOA, necklace morphology disappeared completely and almost identical TEM image (as in case of 6 equivalent to AgOAc amine) showing self-assembly of individual nanoclusters was obtained.¹⁰

b) Exchange Reaction in Presence of Collagen (Nanoparticle Functionalization)

The purpose of this study was to explore the possible application of such a facile exchange reaction in presence of biological molecules. We examined the exchange reactions in presence of collagen. Collagen is valued in medical applications for its superior biocompatibility, biodegradability, and weak antigenicity relative to other polymers used as biomaterials.¹⁴ It has been used in resorbable surgical sutures, hemostatic agents, and wound dressings for many years and nucleating silver nanoparticles with a collagen matrix could lead to many potential medical applications.¹⁵

Preliminary EM studies of the incubation of "PMHS-silver nanoparticle conjugates" with collagen, showed attachment of silver nanoparticles with collagen for all ratios of collagen: silver nanoparticles. Using a molar ratio of 2.5:1 collagen: silver particles, the incorporation of silver nanoparticles resulted in a tightly packed organization of the collagen-silver copolymers (Figure 2). Interestingly, when the ratio was increased to

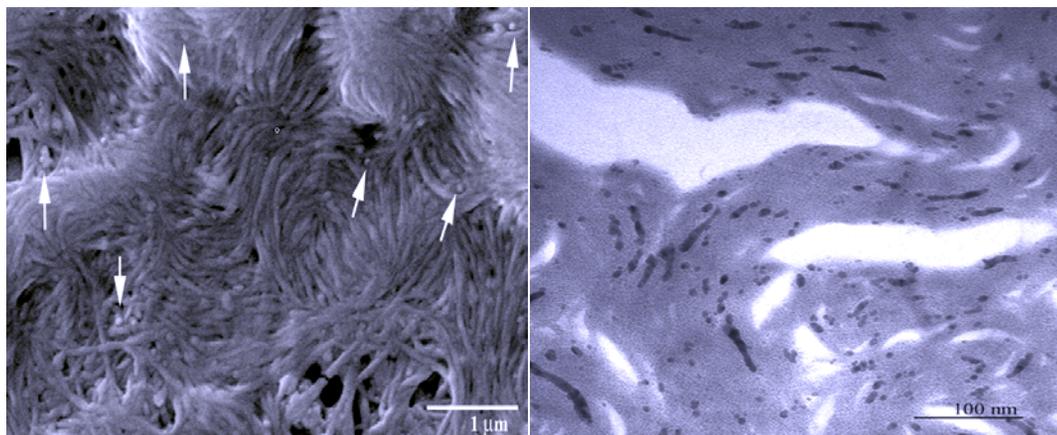


Figure 2. TEM image of the centrifuged reaction mixture silver nanoparticles incubated with collagen type 1.

favor silver (a ratio of 0.31:1), the fibrils were not closely packed, yet the numbers of associated nanoparticles were nearly perfectly aligned with the fibril.

These preliminary results suggest that by altering the molar ratio of the components, it is possible to regulate the mesh size of the collagen fibers, yet retain the silver in nanometer size regime. Detailed studies are underway in our laboratory and will be disclosed in due time.

Inorganic/Organic Hybrid Nanoreactors

Our success with polysiloxane induced reduction and stabilization process inspired us to investigate inorganic-organic (IO) hybrid structures for nanoreactor applications. In recent years, IO hybrid composites have acquired a great interest for stabilization and controlling the morphology of nano-sized metal particles and as precursors for their self-assemblies.¹⁶ Inorganic-Organic hybrids appear as a creative alternative for obtaining new multifunctional materials of unusual features.¹⁷

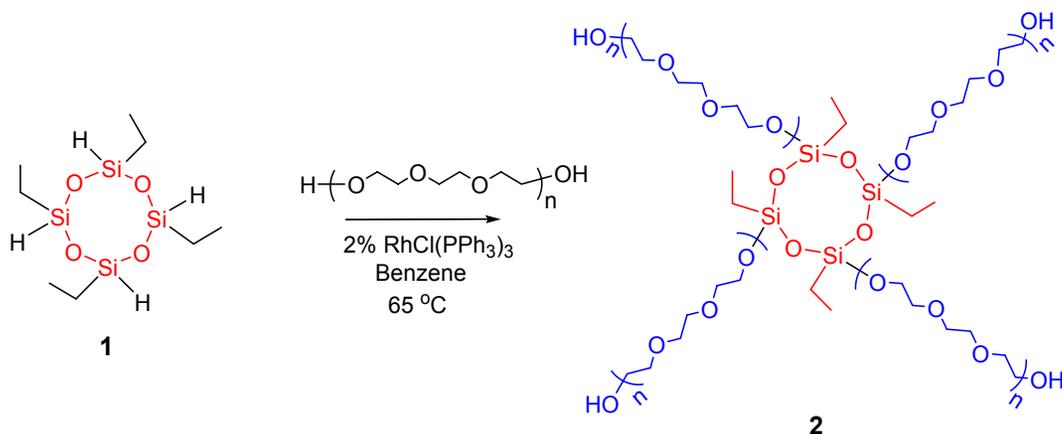
Cyclic siloxanes are hydrophobic entities. By attaching hydrophilic organic moieties like polyethylene glycol (PEG) to such moieties, hybrid networks can be formed which can self-assemble into micelles. We envisage that such micellar networks can be used as nanoreactors for metal and semiconductor particle formation and stabilization. In this part, we present preliminary results of this approach by devising cyclic silicon oligomers substituted with polyethylene glycol to create nanoreactors, which act as reducing agents, and as templates to control the size, stability, and solubility of metal nanoparticles.¹¹

In our synthetic strategy, the first task was the generation of covalently attached hydrophilic tail (polyethylene glycol) to hydrophobic core (siloxanes).

The synthesis of such a system was accomplished by the “Chauhan-Boudjouk alcoholysis” procedure, which provided a one step access to selective formation of PEG-substituted cyclic siloxanes.¹⁸ The reaction of tetraethylcyclotetrasiloxane **1** and polyethylene glycol (Mw~400) was examined in presence of Wilkinson’s catalyst $\text{RhCl}(\text{PPh}_3)_3$ in benzene under positive pressure of argon as shown in scheme 3. The reaction mixture was heated at 65 °C and periodically monitored by IR, ^1H , and ^{29}Si NMR. After 30h of the reaction, complete consumption of **1** and formation of polyethylene glycol substituted siloxane **2** was observed in near quantitative yield (Scheme 3). 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 3. ^{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-OCH₂CH₂O-moieties. As is evident from ^{29}Si NMR (Figure 3) 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

The morphology of the generated polymers was investigated by Transmission Electron Microscopy (TEM) technique. Polymer **2** (0.2 mmol) was diluted in 20 ml of benzene. After stirring for 10 min. in order to get a homogenous mixture, one drop of the solution was dropped on a formvar carbon-coated copper grid and the solvent was allowed to evaporate in open air. The TEM micrographs showed a well-defined micellar network (Figure 3).



Scheme 3. Synthetic Route to PEG-substituted Cyclic Siloxanes.

The PEG-substituted siloxane polymers were further used for the reduction of metal salts to metal nanoparticles. We envision that such polyethyleneglycol 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. The silver acetate was reacted with polymer **2** (0.377 g, 0.2 mmol) in toluene and 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. During a period of four hours, the solution color changed to yellow and then to brown. UV-vis spectrum of the solution showed a peak at 428, which is a characteristic feature of silver nanoparticles (Figure 4).¹⁹ To our surprise, unlike known harsh conditions for polyol reduction process²⁰ of metal salts, the reduction took place under very mild reaction conditions in four hours.¹¹

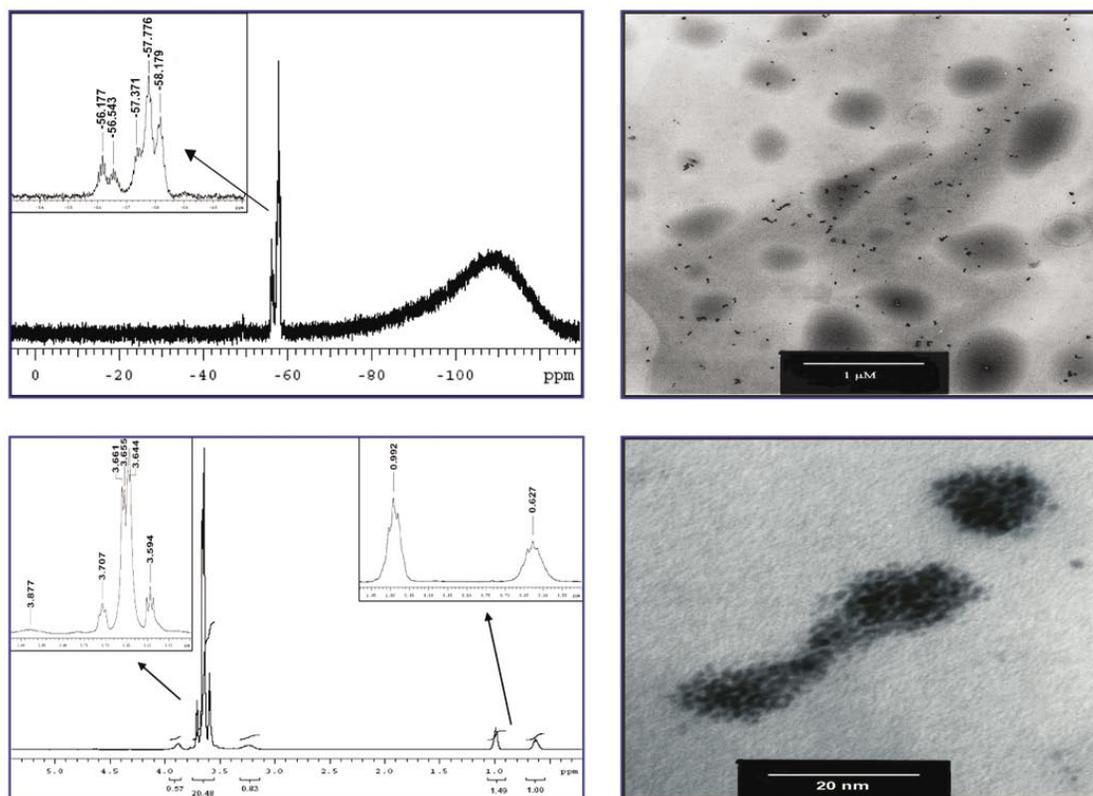


Figure 3. ²⁹Si-NMR and TEM images of PEG-substituted siloxane **2** (Reprinted with the permission from ref. 11, copyright, 2005, American Chemical Society).

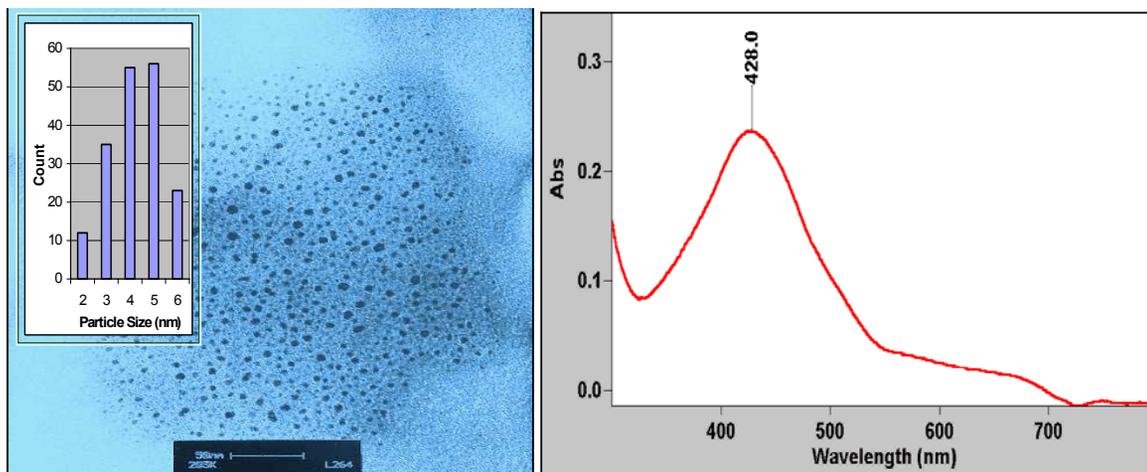


Figure 4. TEM, Particle Size and UV-vis Analysis of Ag Nanoparticles (Reprinted with the permission from ref. 11, copyright, 2005, American Chemical Society).

Palladium acetate solution is light yellow and shows a peak around ~ 400 nm in UV spectrum. For about one hour, after addition of polymer **2** to the palladium acetate solution, the color remained almost unchanged. After 2h of continuous stirring at room temperature, color of the reaction mixture started to change to brown. This was the first evidence of reduction of palladium acetate. During a period of four hours, the solution color changed to brown and finally turned black, which was a strong evidence of palladium nanoparticle formation. At this point, UV spectrum was taken and it showed a featureless absorption, a characteristic of palladium nanoparticles (Figure 5).

The TEM images showed formation of metal particles with narrow size distributions, which were stabilized by siloxane network as no other stabilizer was added (Figure 5). 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-polyethyleneglycol networks as effective stabilizing agents.

These studies indicate towards 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 presence of only poly(ethylene)glycol. Under identical reaction

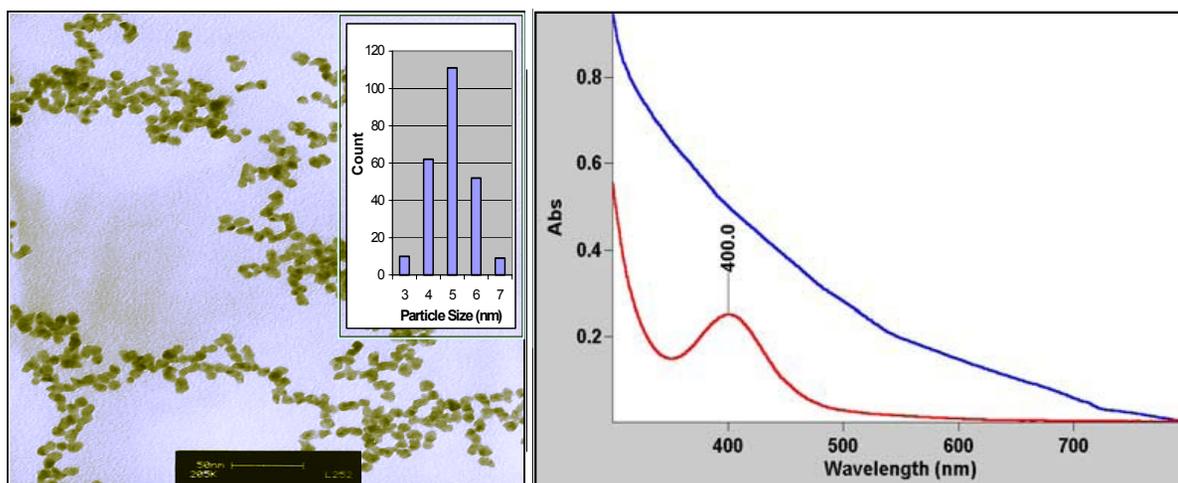


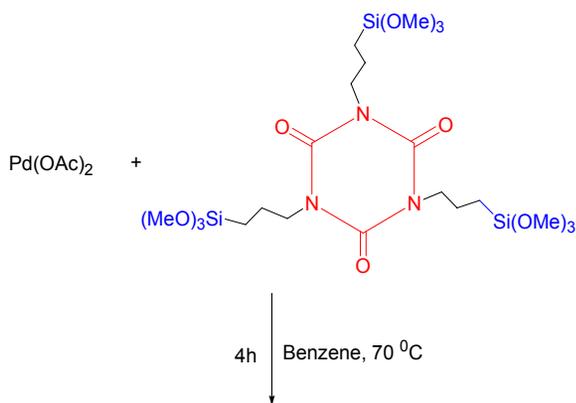
Figure 5. TEM, Particle Size and UV-vis Analysis of Pd-Nanoparticles (Reprinted with the permission from ref. 11, copyright, 2005, American Chemical Society).

conditions and molar ratio's (as in case of polymer 2) formation of nanoparticles was not observed even after continuous stirring for several hours. 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 polyol like process.

Tris(trimethoxysilylpropyl) isocynurate Grafted "Pd"-nanoclusters

In this approach, siloxane oligomers containing isocynurate functionality are envisioned to act as reducing agents, as well as templates to control the size, stability, and solubility of nanoparticles. Herein, we describe a new synthetic strategy and first examples of one pot synthesis of palladium nanoparticles achieved by tris(trimethoxysilylpropyl) isocynurate induced reduction of $\text{Pd}(\text{OAc})_2$ and present comparative studies of their stabilization. We also provide the evidence that this strategy enables a tight control over the chemical nature of encapsulated Pd nanoparticles.

In a typical experiment, $\text{Pd}(\text{OAc})_2$, TTPI were dissolved in 50 ml of benzene (Scheme 4). The color of the reaction mixture turned black after 15–20 minutes of heating at 70 °C, indicating the conversion of $\text{Pd}(\text{OAc})_2$ to Pd nanoclusters. The color change was corroborated by UV-vis analysis of reaction mixture. After 4h of reaction, peak at 397–399 nm, which was indicative of $\text{Pd}(\text{OAc})_2$, completely disappeared and a featureless absorption was observed. The color changes and absorption spectra correlates well with the UV-vis spectra of "Pd" colloids simulated by Creighton and co-workers.¹¹ At this stage, one drop of the reaction mixture was analyzed by Transmission Electron Microscopy (TEM). Indeed formation of rather monodisperse Pd-nanoparticles was observed. A representative TEM micrograph of the crude reaction mixture is showed in Scheme 4.



Scheme 4. Synthetic Scheme for Generation of Nanoparticles.

The particles were stable for several weeks without any other added stabilizing agent indicating that TTPI not only plays an important role as reducing agent but also as a stabilizing agent. Efforts are underway to study the mechanism of formation in detail.

Conclusions and Future Perspective

All the three strategies described in this article lead to metallic particles of various sizes and morphologies. Though, the catalytic and physical properties of these materials are not the scope of this review but we have shown that polysiloxane-metallic nanoconjugates really act as potent catalysts for various processes such as silaesterification, hydrosilylation and reduction reactions of conjugated alkenes. A large body of work still remains to be carried out in order to understand detailed mechanistic pathways of reduction reactions, and also the determination of the influence of polysiloxane structures on the shape and size of resulting metal nanoparticles. Another aspect of silicone structures, which we are exploring in our laboratory, is the investigations of the parameters, under which chemical processes can be performed and controlled inside the siloxane networks and cavities in a desired and predefined manner.

Acknowledgements

BPSC acknowledges financial support from NYSTAR-Cart program for "Center for Engineered Polymeric Materials", CUNY-Collaborative Grant, NIST-research grant, GRTI (*The Graduate Research and Technology Initiative*) grant, and Merck-AAA award. Acknowledgements are also due to the other co-authors from nanomaterials laboratory whose names appear in the references.

References

- (a) L. M. Liz-Marz, P. V. Kamat *Nanoscale Materials*; Kluwer Academic Publishers: Boston, MA, 2003. (b) G. Schmid, *Nanoparticles: From Theory to Application*; Wiley-VCH: Weinheim, Germany, 2003. (c) Y. Waseda, A. Muramatsu, A. Muramatsu *Morphology Control of Materials and Nanoparticles: Advanced Materials Processing and Characterization*; Springer Series in Materials Science; Springer: Berlin, Germany, 2004.
- (a) A. Wieckowski, E. R. Savinova, C. G. Vayenas, *Catalysis and Electrocatalysis at Nanoparticle Surfaces*; Dekker: New York, 2003. (b) M. Wilson, *Nanotechnology: Basic science and Emerging Technologies*; Chapman & Hall/CRC: Boca Raton, FL, 2002. (c) M. Rieth, *Nano-engineering in Science and Technology: an Introduction to the World of Nano-design*; World Scientific: River Edge, NJ, 2003.

- (d) S. Yang, P. Sheng, *Physics and Chemistry of Nanostructured Materials*; Taylor & Francis: London, U.K., 2000.
3. (a) For excellent reviews see: H. Bonnemann, R. M. Richards *Eur. J. Inorg. Chem.* **2001**, 2455–2480. (b) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757–3778.
4. Books related to the topic see: (a) M. Antonietti, *Colloid Chemistry II*; Springer: Berlin, Germany, 2003. (b) W. A. Goddard, III. *Handbook of Nanoscience, Engineering, and Technology*; CRC Press: Boca Raton, FL, 2003. (c) J. Z. Zhang, *Self-assembled Nanostructures*; Kluwer Academic/Plenum Publishers: New York, 2003. (d) J. H. Fendler, *Nanoparticles and Nanostructured Films: Preparation, Characterization and Applications*; Wiley-VCH: Weinheim, Germany, 1998.
5. (a) R. M. Crooks, V. Chechik, B. I. Lemon, L. Sun, L. K. Yeung, M. Zhao, In *Metal Nanoparticles, Synthesis, Characterization, and Applications*; Feldheim, D. L., Foss, C. A., Eds.; Marcel Dekker: New York, 2002; Chapter 11. (b) R. M. Crooks, M. Zhao, L. Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res.* **2001**, *34*, 181–190 and references cited therein. (c) M. Zhao, L. Sun, R. M. Crooks, *J. Am. Chem. Soc.* **1998**, *120*, 4877–4878. (d) M. E. Garcia, L. A. Baker, R. M. Crooks, *Anal. Chem.* **1999**, *71*, 256–258. (e) R. W. J. Scott, A. K. Datye, R. M. Crooks, *J. Am. Chem. Soc.* **2003**, *125*, 3708–3709.
6. (a) D. A. Tomalia, *Prog. Polym. Sci.* **2005**, *30*, 294–324 and references cited therein. (b) Tomalia, D. A. *Aldrichimica Acta* **2004**, *37*, 39–57. (c) D. A. Tomalia, H. M. Brothers II, L. t. Pihler, H. Dupont Durst, D. R. Swanson, *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5081–5087. (d) L. Balogh, D. A. Tomalia, *J. Am. Chem. Soc.* **1998**, *120*, 7355–7356. (e) N. C. Beck Tan, L. Balogh, S. F. Trevino, D. A. Tomalia, J. S. Lin, *Polymer* **1999**, *40*, 2537–2545.
7. M. A. El-Sayed, *Acc. Chem. Res.* **2004**, *37*, 326–333. (b) M. A. El-Sayed, *Acc. Chem. Res.* **2001**, *34*, 257–264 and references cited therein. (c) E. Nakamura, H. Isobe, *Acc. Chem. Res.* **2003**, *36*, 807–815. (d) K. Esumi, R. Isono, T. Yoshimura, *Langmuir* **2004**, *20*, 237–243. (e) K. Esumi, A. Suzuki, N. Aihara, K. Usui, K. Torigoe, *Langmuir* **1998**, *14*, 3157–3159. (f) K. Esumi, A. Suzuki, A. Yamahira, K. Torigoe, *Langmuir* **2000**, *16*, 2604–2608. (g) F. Grohn, X. Gu, H. Grull, J. C. Meredith, G. Nisato, B. J. Bauer, A. Karim, E. J. Amis, *Macromolecules* **2002**, *35*, 4852–4854.
8. (a) R. Shenhar, V. M. Rotello *Acc. Chem. Res.* **2003**, *36*, 549–561 and references cited therein. (b) B. L. Frankamp, A. K. Boal, V. M. Rotello, *J. Am. Chem. Soc.* **2002**, *124*, 15146–15147. (c) S. Srivastava, B. L. Frankamp, V. M. Rotello, *Chem. Mater.* **2005**, *17*, 487–490.
9. (a) B. P. S. Chauhan, J. S. Rathore *J. Am. Chem. Soc.* **2005**, *127*, 5790–5791. (b) B. P. S. Chauhan, J. S. Rathore, T. Bando, *J. Am. Chem. Soc.* **2004**, *126*, 8493–8500. (c) B. P. S. Chauhan, J. S. Rathore, M. Chauhan, A. Krawicz, *J. Am. Chem. Soc.* **2003**, *125*, 2876–2877. (d) B. P. S. Chauhan, R. Sardar, P. Tewari, P. Sharma, Third International Workshop on Silicon-Containing Polymers, Troy, ISPO 2003, June 23–25, T–13.
10. B. P. S. Chauhan, R. Sardar, *Macromolecules* **2004**, *37*, 5136–5139.
11. B. P. S. Chauhan, U. Latif, *Macromolecules* **2005**, *38*, 6231–6235.
12. L. N. Lewis, *Chem. Rev.* **1993**, *93*, 2693–2730 and references therein.
13. (a) R. J. P. Corriu, G. F. Lanneau, M. Perrot, *Tetrahedron Lett.* **1988**, *29*, 1271–1274. (b) R. J. P. Corriu, G. F. Lanneau, M. Perrot, V. D. Mehta, *Tetrahedron Lett.* **1990**, *31*, 2585–2588.
14. M. Maeda, S. Tani, A. Sano, K. Fujioka, *J. Control. Release* **1999**, *62*, 313–324.
15. (a) C. H. Lee, A. Singla, Y. Lee, *Int. J. Pharm.* **2001**, *221*, 1–22. (b) S. Förster, T. Plantenberg, *Angew. Chem., Int. Ed. Eng.* **2002**, *41*, 677–714.
16. (a) K. Naka, H. Itoh, Y. Chujo, *Nano Lett.* **2002**, *2*, 1183–1186. (b) V. Chandrasekhar, A. Athimoolam, *Org. Lett.* **2002**, *4*, 2113–2116. (c) R. M. Laine, A. Sellinger, *Chem. Mater.* **1996**, *8*, 1592–1593. (d) M. Yokoyama, K. Kataoka, N. Nishiyama, T. Aoyagi, T. Okano, Y. Sakurai, *Langmuir*, **1999**, *15*, 377–383. (e) A. Martino, S. A. Yamanaka, J. S. Kawola, D. A. Loy, *Chem. Mater.* **1997**, *9*, 423–429.
17. (a) A. L. Douglas, J. Kenneth, *Chem. Rev.* **1995**, *95*, 1431–1442. (b) K. M. Kim, D. K. Keum, C. Yoshiki, *Macromolecules* **2003**, *36*, 867–875. (c) P. Innocenzi, G. Brusatin, *Chem. Mater.* **2001**, *13*, 3126–3139. (d) J. Pyun, K. Matyjaszewski, *Chem. Mater.* **2001**, *13*, 3436–3448. (e) F. Grohn, G. Kim B. J. Bauer, E. J. Amis, *Macromolecules* **2001**, *34*, 2179–2185.
18. (a) B. P. S. Chauhan, T. E. Ready, Z. Al-Badri, P. Boudjouk, *Organometallics* **2001**, *20*, 2725–2729. (b) P. Boudjak, T. E. Ready, B. P. S. Chauhan, *US Patent No: US 6,482,912* **2002** (Nov.19). (c) T. E. Ready, B. P. S. Chauhan, P. Boudjouk, *Macromol. Rapid Commun.* **2001**, *22*, 654–657. (d) P. Boudjouk, M. H. Z. AL-Badri, B. P. S. Chauhan, *J. Organomet. Chem.* **2004**, *689*, 3468–3471.
19. (a) C. Petit, P. Lixon, M. P. Pileni, *J. Phys. Chem.* **1993**, *97*, 12974–12983 (b) J. A. Creighton, C. G. Blatchford, M. G. Albrecht, *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 790–798. (c) M. Kerker, D. S. Wang, H. Chew, *Appl. Opt.* **1980**, *19*, 4159–4174. (d) M. Kerker, O. Siiman, D. S. Wang, *J. Phys. Chem.* **1984**, *88*, 3168–3170.
20. (a) J. Chen, T. Herricks, M. Geissler, Y. Xia, *J. Am. Chem. Soc.* **2004**, *126*, 10854–10855. (b) C. Liu, X. Wu, T. Klemmer, N. Shukla, X. Yang, D. Weller, A. G. Roy, M. Tanase, D. Laughlin, *J. Phys. Chem. B.* **2004**, *108*, 6121–6123. (c) J. Yang, T. C. Deivaraj, H.-P. Too, J. Y. Lee, *Langmuir* **2004**, *20*, 4241–4245. (d) G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lacaze, F. Fievet-Vincent, F. Fievet, *Chem. Mater.* **2003**, *15*, 486–494. (e) K. Sridhar, L. Dongsheng, N. Bharat, K. Hiraoki, S. B. Amar, *Langmuir* **2002**, *18*, 5959–5962.

Povzetek

Predstavljamo povzetek preliminarnih rezultatov naših nedavnih raziskav o sintezi, stabilizaciji in karakterizaciji funkcionalnih kovinskih nano-klastrov in njihovo vključevanje v različna fizikalno-kemična okolja. Te raziskave bazirajo na tako imenovani "špageti-z-mesnimi-kroglicami" ("meatball-spaghetti") strategiji, ki smo jo razvili v našem laboratoriju. Gre za nanoreaktorje na osnovi silicija (špageti), ki pomagajo pri tvorbi in stabilizaciji nano delcev (mesne kroglice). V prvem delu opisujemo zelo učinkovito redukcijo srebrovega acetata za pripravo stabilnih srebrovih delcev nanovelikosti. Ta nova strategija vključuje uporabo poli(metilhidro)siloksana kot reducirnega sredstva in stabilizatorja in omogoča tvorbo stabilnih 2 nm velikih srebrovih delcev, v pogostih organskih topilih in pri sobni temperaturi. Opisujemo vlogo fizikalno-kemičnih in morfoloških lastnosti polisiloksanov v tvorbi, rasti in stabilizaciji delcev. V drugem delu so ciklične in kubične siloksanske šablone uporabljene za nastanek micelnih tvorb v prisotnosti polietilenskih glikolnih enot. Micelne tvorbe so uporabljene za redukcijo srebrovih in paladijevih kovinskih soli v kovinske koloide v organskih topilih pri sobni temperaturi. Predstavljamo primere, ki jasno kažejo, da mreža nima vloge le kot reducent, pač pa tudi kot stabilizator. Študije z elektronskim mikroskopom kažejo neagregirane kovinske delce z ozko distribucijo velikosti, ki so enakomerno ujeti v micelle.