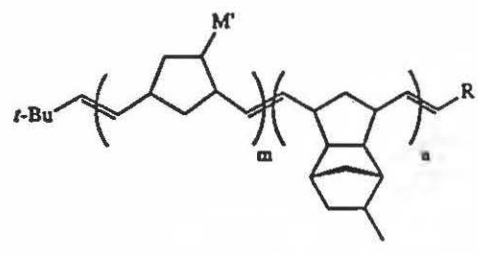
Composite Materials Containing Metal and Semiconductor Nanoclusters

Shurong Liang Literature Seminar November 24, 1992

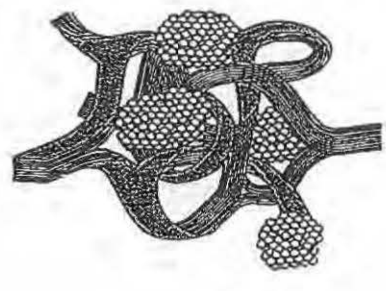
Nanostructures are assemblies of bonded atoms with dimensions in the range of 1 to 10^2 nanometers (1 nm = 10^{-9} M = 10 Å) [1]. Metallic or semiconducting materials of such small dimensions exhibit quantum size effects [2], and their electronic structures and properties are intermediate between atoms or molecules and those of bulk materials [3,4]. As a result, a regular array of these aggregates or clusters may have novel optical, electronic, magnetic or catalytic properties [3,4]. In their pure forms, however, these clusters readily undergo aggregation towards larger particles, and, in the last several years, much study has been conducted to disperse these clusters into appropriate media.

Metal vapor synthesis (MVS) has been employed to deposit metal clusters into organic polymers to form composite materials [5,6]. Metal nanoclusters are obtained by vacuum evaporation of bulk metal followed by condensation at low temperature. These clusters can be then dispersed into polymer solutions in various ways. In a recent study, nanosized gold clusters were dispersed in poly{5,7-dodecadiyne-1,12-diol-*co*-bis[((n-butoxycarbonyl)methyl)urethane]}, a well characterized nonlinear optical (NLO) polymer, and a 200-fold enhancement on the third-order NLO coefficient was observed [7].

Diblock copolymers **a** with organometallic complexes attached only to one block were synthesized by Schrock and coworkers via living ring-opening methathesis polymerization (ROMP) of functionalized norbornenes [8-14] using well-characterized W or Mo alkylidene catalysts [15]. Polymer films were prepared by static casting. Subsequent treatments of the films with molecular hydrogen or H_2S under mild conditions produced nanosized metal or semiconductor clusters, respectively, dispersed in the copolymers. Under suitable conditions these copolymers underwent microphase separation, resulting in lamellar, cylindrical, and spherical morphologies [16]. The clusters formed in the copolymer films were predominantly within the original metal-complex containing microdomains.



a



b

Synthesis of platinum(0) nanocluster-doped glassy carbon has been reported [17]. Platinum was incorporated in a glassy carbon precursor on the molecular level by the reaction of poly(phenylenediacetylene) with (ethylene)bis(triphenylphosphine) platinum(0). Thermolysis of this precursor afforded the formation of a stable, electroconductive composite material which revealed electrocatalytic activity. The idealized structure is shown as **b**.

Composite membranes containing arrays of nanoscopic gold cylinders have been prepared electrochemically within the pores of nanoporous alumina templates [18,19]. The diameters of the gold cylinders were predetermined by the pore size of the templates which were prepared by electrooxidation of an aluminum substrate [20]. These materials were optically transparent throughout the near-infrared and into the visible region.

Metal nanoclusters have also been incorporated in a SiO_2 matrix using sol-gel processing [22-25]. Metal complexes were anchored to the xerogel through an alkoxysilane of the type $X(CH_2)_3Si(OEt)_3$ ($X = NH_2$, $NHCH_2CH_2NH_2$, CN), which can undergo copolycondensation with $Si(OR)_4$ upon hydrolysis [23-25]. The organic components in the xerogel were removed by oxidation. M_x/SiO_2 (M = Ag, Co, Cu, Ni, Pt, or Pd) composite materials were obtained by reduction of the corresponding oxidation products.

Studies on the properties and applications of these materials are underway. Future work in this field is to explore new synthetic pathways to make materials with controlled cluster sizes and narrow size distribution, as these are critical factors to the materials' properties. Economic synthesis of these composites in a relatively large scale remains as another challenge.

References

1. Whitesides, G. M.; Mathias, J. P.; Seto, C. T., "Molecular Self-Assembly and Nanochemistry: A Chemical Strategy for the Synthesis of Nanostructures,"*Science* **1991**, *254*, 1312.

2. Henglein, A., "Mechanism of Reactions on Colloidal Microelectrodes and Size Quantization Effects," *Top. Curr. Chem.* **1988**, *143*, 113.

3. Siegel, R. W.; Brus, L. E., et al, "Research Opportunities on Clusters and Cluster-Assembled Materials -- A Department of Energy, Council on Materials Science Panel Report," *J. Mater. Res.* **1989**, *4*, 704.

4. Steigerwald, M. L.; Brus, L. E., "Synthesis, Stabilization, and Electronic Structure of Quantum Semiconductor Nanoclusters," *Annu. Rev. Mater. Sci.* **1989**, *19*, 471.

5. Andrews, M. P.; Ozin, G. A., "Wrapping Oligomers and Polymers around Metal Atoms, Metal Clusters, and Metal Colloids," *Chem. Mater.* **1989**, *1*, 174.

6. Klabunde, K. J.; Habdas, J.; Cárdenas-Triviño, G., "Colloidal Metal Particles Dispersed in Monomeric and Polymeric Styrene and Methyl Methacrylate,"*Chem. Mater.* **1989**, *1*, 481.

7. Olsen, A. W.; Kafafi, Z. H., "Gold Cluster Laden Polydiacetylenes: Novel Materials for Nonlinear Optics," *J. Am. Chem. Soc.* **1991**, *113*, 7758.

8. Sankaran, V.; Cummins, C. C.; Schrock, R. R.; Cohen, R. E.; Silbey, R. J., "Small PbS Clusters prepared via ROMP Block Copolymer Technology," *J. Am. Chem. Soc.* **1990**, *112*, 6858.

9. Cummins, C. C.; Beachy, M. D.; Schrock, R. R.; Vale, M. G.; Sankaran, V.; Cohen, R. E., "Synthesis of Norbornenes Containing Tin (II), Tin (IV), Lead (II), and Zinc (II) and their Polymerization To Give Microphase-Separated Block Copolymers," *Chem. Mater.* **1991**, *3*, 1153.

10. Sankaran, V.; Cohen, R. E.; Cummins, C. C.; Schrock, R. R., "Morphology of Diblock Copolymers of Norbornene and Organometallic Derivatives of Norbornene," *Macromolecules* **1991**, *24*, 6664.

11. Ng Cheong Chan, Y.; Schrock, R. R., "Synthesis of Silver and Gold Nanoclusters within Microphase-Separated Diblock Copolymers," *Chem. Mater.* **1992**, *4*, 24.

12. Cummins, C. C.; Schrock, R. R.; Cohen, R. E., "Synthesis of ZnS and CdS within ROMP Block Copolymer Microdomains," *Chem. Mater.* **1992**, *4*, 27.

13. Ng Cheong Chan, Y.; Craig, G. S. W.; Schrock, R. R.; Cohen, R. E., "Synthesis of Palladium and Platinum Nanoclusters within Microphase-Separated Diblock Copolymers," *Chem. Mater.* **1992**, *4*, 885.

14. Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E., "Synthesis of Single Silver Nanoclusters within Spherical Microdomains in Block Copolymer Films," *J. Am. Chem. Soc.* **1992**, *114*, 7295.

15. Schrock, R. R., "Living Ring-Opening Metathesis Polymerization Catalyzed by Well-Characterized Transition-Metal Alkylidene Complexes," *Acc. Chem. Res.* **1990**, *23*, 158.

16. Bates, F. S., "Polymer-polymer Phase Behavior," *Science* **1991**, *251*, 898.

17. Pocard, N. L.; Alsmeyer, D. C.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R., "Nanoscale Platinum(0) Clusters in Glassy Carbon: Synthesis, Characterization, and Uncommon Catalytic Activity," *J. Am. Chem. Soc.* **1992**, *114*, 769.

18. Tierney, M. J.; Martin, C. R., "Transparent Metal Microstructures," *J. Phys. Chem.* **1989**, *93*, 2878.

19. Foss, C. A., Jr.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R., "Optical Properties of Composite Membranes Containing Arrays of Nanoscopic Gold Cylinders," *J. Phys. Chem.* **1992**, *96*, 7497.

20. Despic, A; Parhutik, V., in *Modern Aspects of Electrochemistry* ; Bockris, J. O'M.; White, R. E., Eds.; Plenum Press: New York, **1989**, p. 401.

21. Tour, J. M.; Pendalwar, S. L.; Cooper, J. P., "Homogeneous Deposition of Palladium (0) into Sol-Gel-Derived Materials," *Chem. Mater.* **1990**, *2*, 647.

22. Breitscheidel, B.; Zieder, J.; Schubert, U., "Metal Complexes in Inorganic Matrices. Nanometer-sized, Uniform Metal Particles in a SiO_2 Matrix by Sol-Gel Processing of Metal Complexes," *Chem. Mater.* **1991**, *3*, 559.

23. Schubert, U.; Breitscheidel, B.; Buhler, H.; Egger, C.; Urbaniak, W., "Metal Complexes in Oxidic Matrices," in *Better Ceramics through Chemistry V* (Mat. Res. Soc. Proc. **271**), Hampden-Smith, M. J.; Klemperer, W. G.; Brinker, C. J., Eds.; Materials Research SocietyL: Pittsburgh, Pennsylvania, **1992**, p. 621.

24. Rousseau, F.; Duan, Z.; Hampden-Smith, M. J.; Datye, A., "Formation of Highly Dispersed Metals on Functionalized Silica Supports," in *Better Ceramics through Chemistry V* (Mat. Res. Soc. Proc. **271**); Hampden-Smith, M. J.; Klemperer, W. G.; Brinker, C. J., Eds.; Materials Research Society: Pittsburgh, Pennsylvania, **1992**, p. 633.