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New Materials for Synthesis of Quantum-Sized Semiconductors and Transition-Metal Particles. Microporous Polysilsesquioxanes as a Confinement Matrix for Particle Growth

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Sol-gel processing of bis(triethoxysilyl)alkylenes and -arylenes produces alkyl- and aryl-bridged polysilsesquioxanes, a new family of hybrid *amorphous* materials (Figure 1). These materials possess extremely high surface areas with narrow pore distributions confined to a range of 100 Å or lower.[1–9] The average pore size is controlled by the choice of molecular building block and by processing conditions. We now report that these microporous xerogels can serve as a *confinement matrix* for the controlled growth of quantum-sized semiconductor particles.[10–15] The average size of the semiconductor particle may be determined by the choice of polysilsesquioxane confinement matrix. Furthermore, the mild sol–gel conditions used to prepare these xerogels are compatible with incorporation of sol–gel processable zerovalent transition metal derivatives. Subsequent thermal treatment of the dried xerogels produces quantum-sized metal clusters[16–20] by a novel *internal doping mechanism.* Doping of these xerogels to produce two different quantum-sized cadmium sulfide particles and the *in situ* formation of microcrystalline chromium particles serve to illustrate both approaches.

The synthesis of microporous polyphenylene silsesquioxane (**X-1**) xerogels from 1,4-bis(triethoxysilyl)benzene (**M-1**) has been described previously.[1,3,4] Materials used in the present study had a BET surface area of 531 m^2/g and a relatively narrow distribution of pores with an average diameter of 34 Å (BJH theory).[21,22]

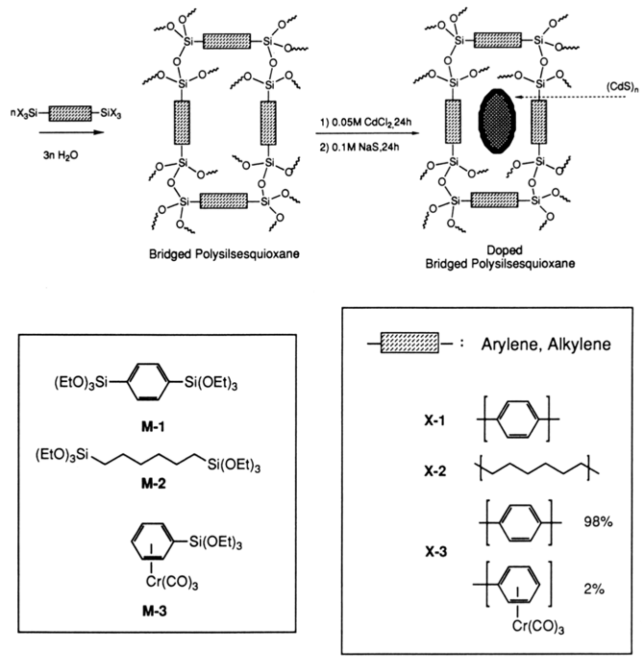

Figure 1. Schematic for sol–gel synthesis and doping of polysilsesquioxanes.

The CdS doping was performed on dried xerogels (100–250-μm particle size) by first soaking for two days in 0.05 M $CdCl_2$ ($EtOH/H_2O$, 1:4), filtering and washing with water followed by treatment with a 0.1 M solution of Na_2S. A pale yellow color appeared immediately. The material was filtered, washed with water, then dried (vacuum oven, 24 h, 25 °C). In contrast to the featureless nondoped materials, transmission electron microscopy (TEM) images of doped **M-1** showed xerogel particles that were distributed with spots of an average diameter of 58 ● 12 Å (Figure 2). Energy-dispersive X-ray analysis (EDAX) of individual spots revealed they contained Cd and S. Further characterization of the spots was obtained from the electron diffraction pattern which indicated the spots to be polycrystalline CdS in the β form. Independent evaluation of CdS particle size was obtained by analysis of the quantum-size effect of the UV absorption band edge following the method of Brus.[23] Representative samples were found by the UV method to have a calculated CdS particle diameter of 56 Å, in close agreement with the TEM micrographs.[24]

The family of bridged polysilsesquioxanes provide a range of materials with "engineered" microporosity.[1–4] Utilization of this flexibility is demonstrated by the growth of CdS particles in a hexamethylene bridged polysilsesquioxane **X-2**, a material prepared by sol–gel processing of 1,6-bis(triethoxysilyl)hexane (**M-2**).[7] This dried xerogel has a BET surface area of 533 m^2/g with an average pore diameter of 43 Å. Utilizing doping techniques identical to those of the previous example, microcrystalline CdS particles were produced with an average particle diameter

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(1) Shea, K. J.; Loy, D. A.; Webster, O. W. *Chem. Mater.* **1989,** *1,* 572.
(2) Shea, K. J.; Loy, D. A.; Webster, O. W. *Proc. ACS Div. Polym. Mater., Sci. Eng.* **1990,** *63,* 281.
(3) Shea, K. J.; Webster, O. W.; Loy, D. A. *Better Ceramics through Chemistry IV, MRS Symp. Proc.* **1990,** *180,* 975.
(4) Shea, K. J.; Loy, D. A.; Webster, O. W. *J. Am. Chem. Soc.* **1992,** *114,* 6700.
(5) Loy, D. A.; Shea, K. J.; Russic, E. M. *Better Ceramics through Chemistry V, MRS Symp. Proc.* **1992,** *271,* 699.
(6) Loy, D. A.; Shea, K. J.; Small, J. H. *J. Non-Cryst. Solids,* in press.
(7) Oviatt, H. W. Jr.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993,** *5,* 943.
(8) Loy, D. A.; Buss, R. J.; Assink, R. A.; Shea, K. J.; Oviatt, H. W. Jr. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1993,** *34,* 244.
(9) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Wong, C. M. M. *Chem. Mater.* **1992,** *4,* 1217.
(10) Wang, Y.; Suna, A.; Mahler, W. *Mater. Res. Soc. Symp. Proc.* **1988,** *109,* 187.
(11) Watzke, H. J.; Fendler, J. H. *J. Phys. Chem.* **1987,** *91,* 854.
(12) Hoffman, A. J.; Mills, G.; Yee, H.; Hoffman, M. R. *J. Phys. Chem.* **1992,** *96,* 5546.
(13) Rossetti, R.; Ellison, J. L.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1984,** *80(9),* 4464.
(14) Lippens, P. E.; Lannoo, M. *Phys. Rev. B* **1989,** *39(15),* 10935.
(15) Alfassl, Z.; Bahnemann, D.; Henglein, A. *J. Phys. Chem.* **1982,** *86,* 4656.
(16) Ozin, G. A.; Gil, C. *Chem. Rev.* **1989,** *89,* 1749.
(17) Stucky, G. D.; MacDougall, J. E. *Science* **1990,** *247,* 669.
(18) Henglein, A. *Chem. Rev.* **1989,** *89,* 1861.
(19) Kuczynski, J.; Thomas, J. K. *J. Phys. Chem.* **1985,** *89,* 2720.
(20) Uchida, H.; Curtis, C. J.; Kamat, P. V.; Jones, K. M.; Nozik, A. J. *J. Phys. Chem.* **1992,** *96,* 1156.
(21) (a) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951,** *73,* 373. (b) Oscik, J.; Cooper, I. L. In *Adsorption*; John Wiley & Sons: New York, 1982.
(22) The pore diameter was calculated from an average of both adsorption and desorption isotherms.
(23) Brus, L. E. *J. Phys. Chem.* **1986,** *90,* 2555.
(24) The absence of a strict correspondence between *average* pore size as established by analysis of the N_2 adsorption/desorption isotherm and the direct methods is not surprising since the BJH treatment assumes cylindrical pores. The actual pore shape in the polysilsesquioxanes is unknown at present but preliminary results from X-ray and neutron scattering suggest highly irregular rough surfaces that may arise by fractal growth of polymer chains. Loy, D. A.; Schaefer, D. W.; Beaucage, G.; Shea, K. J., unpublished results.

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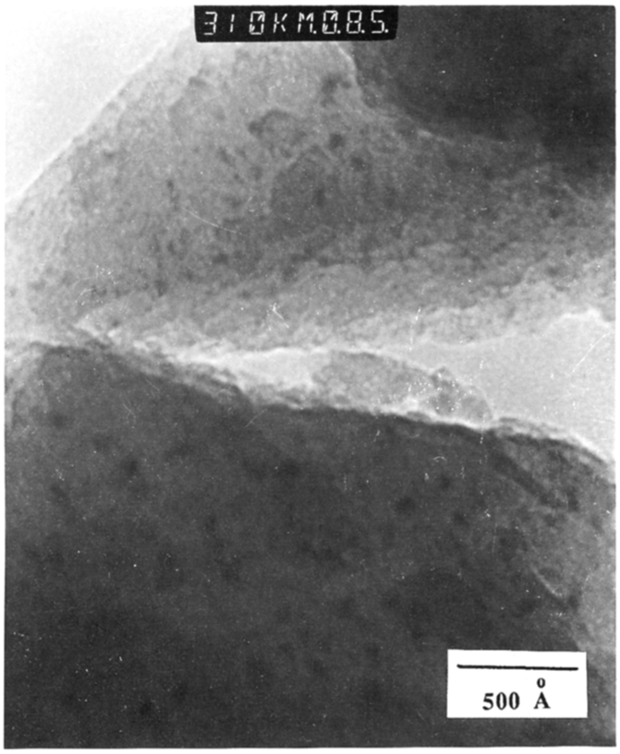

Figure 2. HRTEM image of xerogel **X**-1. The dark spots (average diameter 58 Å), which are absent in undoped samples, are microcrystalline CdS particles. The sample contains approximately 1 wt% CdS.

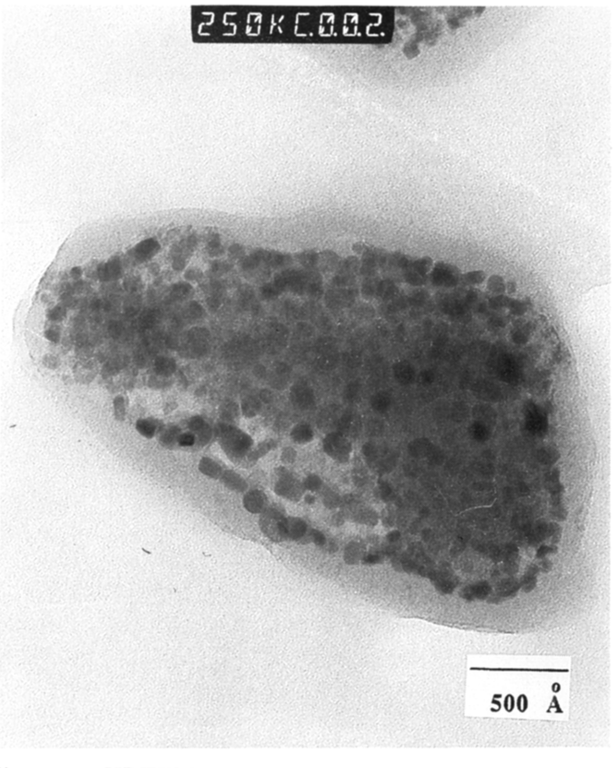

Figure 3. HRTEM image of a xerogel **X**-2. The dark spots within the fragment (average diameter 90 Å) are microcrystalline CdS particles. CdS comprises approximately 2% of the sample.

of 90 ± 16 Å as measured directly from TEM images (Figure 3) and from analysis of the shift in the UV band edge. The identity of the CdS spots observed in the TEM images was confirmed in **X**-2 by EDAX and the electron diffraction pattern. In contrast to the two previous examples, when *nonporous xerogels* were employed,[25] the doping procedures did not produce CdS particles of any size in the materials. Only bulk CdS precipitate on the exterior of the particles which could be mechanically removed to reveal a cadmium sulfide-free polysilsesquioxane was observed.

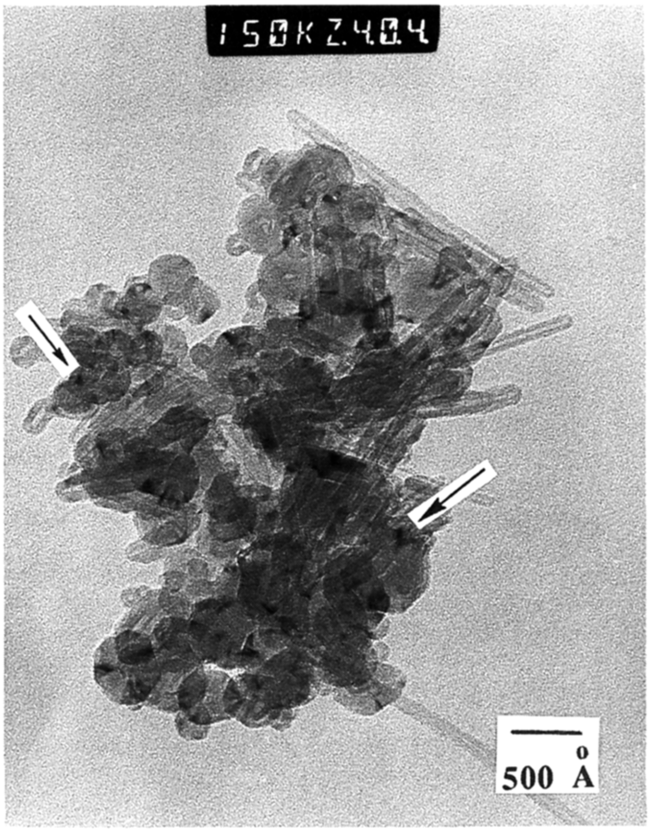

Figure 4. HRTEM image of a xerogel particle in **X-3**. The dark spot irregular regions of approximate dimensions 25–100 Å (see arrows), are microcrystalline Cr particles.

These results establish that microporous polysilsesquioxanes can be used as a confinement matrix for the growth of quantum-sized semiconductor particles and that the morphology of the individual xerogel "controls" the size of the resulting quantum-sized particles.[24] Since optically transparent monoliths with *nominal* pore sizes that range from 5 to >100 Å are available by this technique, a wide range of semiconductor particle sizes may be prepared.

The mild methods for preparing alkyl- and aryl-bridged polysilsesquioxanes (dilute aqueous acid or base) are compatible with many sol–gel processable organometallic compounds that can serve as metal atom precursors. Following sol–gel processing and drying, the microporous xerogel can be heated or photolyzed to liberate metal atoms. Subsequent migration and aggregation of metal atoms, a process confined by the microporous matrix, can allow for preparation of quantum-sized metal (or bimetallic) cluster compounds imbedded in a microporous polysilsesquioxane.

The first demonstration of this approach is illustrated by preparing a polysilsesquioxane xerogel doped with microcrystalline chromium particles. A microporous xerogel (**X-3**), prepared from chromium tricarbonyl monomer **M-3** and 1,4-bis(triethoxysilyl)benzene[26] (2:98), 0.2 M concentration of triethoxysilyl monomers, NH_4OH

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(25) Nonporous xerogels can be produced at high monomer and catalyst concentrations. Their chemical composition is otherwise identical to the microporous materials.[7]

catalyst, H_2O, THF, produced, after drying, a pale green xerogel (surface area 983 m^2/g). The xerogels were heated at $<10^{-3}$ Torr at 60 °C for 24 h. TEM images (Figure 4) revealed the appearance of irregularly shaped dark features that ranged in size from 25 to 100 Å. Focusing on these new dark features, the EDAX and the electron diffraction pattern confirmed their elemental composition and microcrystallinity of the chromium clusters. The particle shape and other features of these internally doped microporous materials may reveal structural information of the internal porosity. This result demonstrates the novel approach of "internal doping" and matrix confinement of the developing metal clusters within a microporous material.

The extension of this approach to the preparation of highly active metal cluster catalysts and a combination of both methodologies for preparation of transition metal "coated" semiconductor particles is underway.

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Supplementary Material Available: Experimental details (8 pages). Ordering information is given on any current masthead page.

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(26) This compound gave elemental and spectroscopic properties consistent with its assigned structure.