

# Gold Nanorods Grown on Microgels Leading to Hexagonal Nanostructures

V. R. Rajeev Kumar, A. K. Samal, T. S. Sreepasad, and T. Pradeep\*

*DST Unit on Nanoscience (DST-UNS), Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai 600 036, India*

*Received April 9, 2007. In Final Form: June 4, 2007*

Hexagonal patterns of gold nanorods were made by assembling gold nanorod-coated poly(*N*-isopropyl acrylamide) microgels. The required population of nanorods on the microgels was achieved by attaching nanoparticle seeds on the latter and growing them to nanorods. The various materials prepared were characterized by UV–vis spectroscopy and transmission electron microscopy. Similar experiments with nanoparticle-coated or prefabricated nanorod-coated microgels did not give such hexagonal patterns. We suggest that the interlocking of nanorods leads to these regular structures. This is the first report of a solution phase method for assembling nanorods into a hexagonal pattern.

The way that nature makes beautiful, strong materials has always fascinated man. Nature does so by using biomolecules as templates. Examples of such architecture include shells of mollusks and teeth of vertebrates. The design of hybrid materials by combining the properties of organic and inorganic materials is an active area of research receiving considerable attention nowadays.<sup>1</sup> By mixing organic and inorganic components on the nanometer scale, one can construct hybrid materials with unusual hydrophobicity<sup>2</sup> and high hardness.<sup>3</sup> The synthesis of materials with well-defined porosity is possible by using soft organic templates. Organic templates such as surfactants,<sup>4</sup> carbon nanotubes,<sup>5</sup> and polymers<sup>6</sup> are commonly used as structure-directing agents to make inorganic materials. A well-known example is the synthesis of mesoporous silica using cationic surfactants.<sup>7</sup> Hexagonally fused microgel particles have been used to make macroporous architectures of silica.<sup>8</sup> A recent approach is to use low-molecular-weight gelators as templates for making inorganic structures.<sup>9</sup> Because gels form a rich variety of shapes, they can act as moulds for making inorganic materials with beautiful shapes that are otherwise difficult to prepare. Transcribing the shapes of organic materials into inorganic ones has opened up the possibility of using inorganic materials in

places where organic materials are dominant, such as in chiral separation. Spiral silica nanostructures have been made using chiral supramolecular fibers.<sup>10</sup> In this report, hexagonal patterns of gold nanorods are fabricated using nanorod-coated microgels. This is the first report of microgels as a template for making patterns in the solution phase.

The poly(*N*-isopropyl acrylamide) (PNIPAm) microgel particles required for the self-assembly experiments were prepared using precipitation polymerization (experimental details in Supporting Information).<sup>11</sup> The material showed a featureless absorption spectrum as expected, and the TEM image of the particles confirmed that they were monodisperse and redispersible (Figure S1). Cetyltrimethylammonium bromide (CTAB)-coated gold nanoparticles were used as the seed for preparing nanorods.<sup>12</sup> The absorption spectrum of CTAB-coated gold nanoparticles showed weak plasmon resonance characteristic of 4 nm particles (Figure S2). The microgel particles were loaded with CTAB-coated gold nanoparticles. A purified microgel dispersion (2 mL) was mixed with an equal volume of the as-prepared CTAB-coated gold nanoparticles. The mixture was equilibrated for 30 min, leading to the adsorption of the nanoparticles on the microgels, and it was centrifuged at 2000 rpm. The nanoparticle-loaded microgel particles settled at the bottom as a pellet. The supernatant containing unadsorbed particles was discarded, and the pellet was redispersed in water. The UV–vis spectrum of the nanoparticle-loaded microgel dispersion showed the weak surface plasmon resonance of the seed particles as a shoulder at 500 nm, with the structure being masked by the featureless absorption of the microgel particles (Figure S3). The seed-coated microgel was allowed to stand in distilled water for 2 days. This led to slow deposition of the particles. A TEM image of the deposited material showed patterns with large voids (Figure S3, inset). The microgel particles after seed loading were soaked in the growth solution. Nanorods grew on the nanoparticles attached to the microgels. The material was taken out of the solution by centrifugation at 2000 rpm. The UV–vis spectrum of the material after purification showed longitudinal and transverse surface plasmons (TSP and LSP) at 514 and 727 nm, respectively,

\* Author to whom all correspondence should be addressed. E-mail: pradeep@iitm.ac.in. Phone: ++91-44-2257 4208. Fax: ++91-44-2257 0545.

(1) (a) Sanchez, C.; Julian, B.; Belleville, P.; Popall, M. *J. Mater. Chem.* **2005**, *15*, 3559. (b) Zayat, M.; Levy, D. *J. Mater. Chem.* **2005**, *15*, 3769. (c) Coronado, E.; Palomares, E. *J. Mater. Chem.* **2005**, *15*, 3593. (d) Mammeri, F.; Bourhis, E. L.; Rozes, L.; Sanchez, C. *J. Mater. Chem.* **2005**, *15*, 3787. (e) Schottner, G. *Chem. Mater.* **2001**, *13*, 3422.

(2) Bico, J.; Marzolin, C.; Quere, D. *Europhys. Lett.* **1999**, *47*, 743.

(3) Firla, M. T. *Dent. Spiegel* **1999**, *8*, 48.

(4) (a) Walsh, D.; Mann, S. *Nature* **1995**, *377*, 320. (b) Singh, P. S.; Kosuge, K. *Chem. Lett.* **1998**, 101. (c) Barel, S.; Schoen, P. *Chem. Mater.* **1993**, *5*, 145. (d) Hubert, D. H. W.; Jung, M.; Frederik, P. M.; Bomans, P. H. H.; Meuldijk, J.; German, A. L. *Adv. Mater.* **2000**, *12*, 1286.

(5) (a) Sathishkumar, B. C.; Govindaraj, A.; Vogl, E. M.; Basumallik, L.; Rao, C. N. R. *J. Mater. Res.* **1997**, *12*, 604. (b) Rao, C. N. R.; Sathishkumar, B. C.; Govindaraju, A. *Chem. Commun.* **1997**, 1581. (c) Sathishkumar, B. C.; Govindaraj, A.; Nath, M.; Rao, C. N. R. *J. Mater. Chem.* **2000**, *10*, 2115.

(6) (a) Caruso, F.; Spasova, M.; Susha, A.; Giersig, M.; Caruso, R. A. *Chem. Mater.* **2001**, *13*, 109. (b) Cha, J. N.; Stucky, G. D.; Morse, D. E. *Angew. Chem., Int. Ed.* **1999**, *111*, 826. (c) Iskander, F.; Mikrajuddin; Okuyama, K. *Nano Lett.* **2001**, *1*, 231. (d) van Bommel, K. J. C.; Jung, J. H.; Shinkai, S. *Adv. Mater.* **2001**, *13*, 1472.

(7) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538.

(8) Kresge, C. T.; Leonowicz, M.; Roth, W. J.; Vartuli, J. C.; Beck, J. C. *Nature* **1992**, *359*, 710.

(9) (a) Ono, Y.; Nakashima, K.; Sano, M.; Kanekiyo, Y.; Inoue, K.; Hojo, J.; Shinkai, S. *Chem. Commun.* **1998**, 1477. (b) Jung, J. H.; Ono, Y.; Sakurai, K.; Sano, M.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 8648.

(10) (a) Jung, J. H.; Ono, Y.; Shinkai, S. *Chem.—Eur. J.* **2000**, *6*, 4552. (b) Jung, J. H.; Ono, Y.; Hanabusa, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 5008. (c) Kobayashi, S.; Hamasaki, N.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2002**, *124*, 6550. (d) Ono, Y.; Nakashima, K.; Sano, M.; Hojo, J.; Shinkai, S. *Chem. Lett.* **1999**, 1119. (e) Llusar, M.; Roux, C.; Pozzo, J. L.; Sanchez, C. *J. Mater. Chem.* **2003**, *13*, 442.

(11) Debord, S. B.; Lyon, L. A. *J. Phys. Chem. B* **2003**, *107*, 2927.

(12) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389.

characteristic of gold nanorods (Figure S4). It is important to note that all of the nanoparticles were converted to nanorods. The TSP is apparently larger in intensity in comparison to nanorod dispersions because of the featureless spectrum of the microgels (Figure S1).

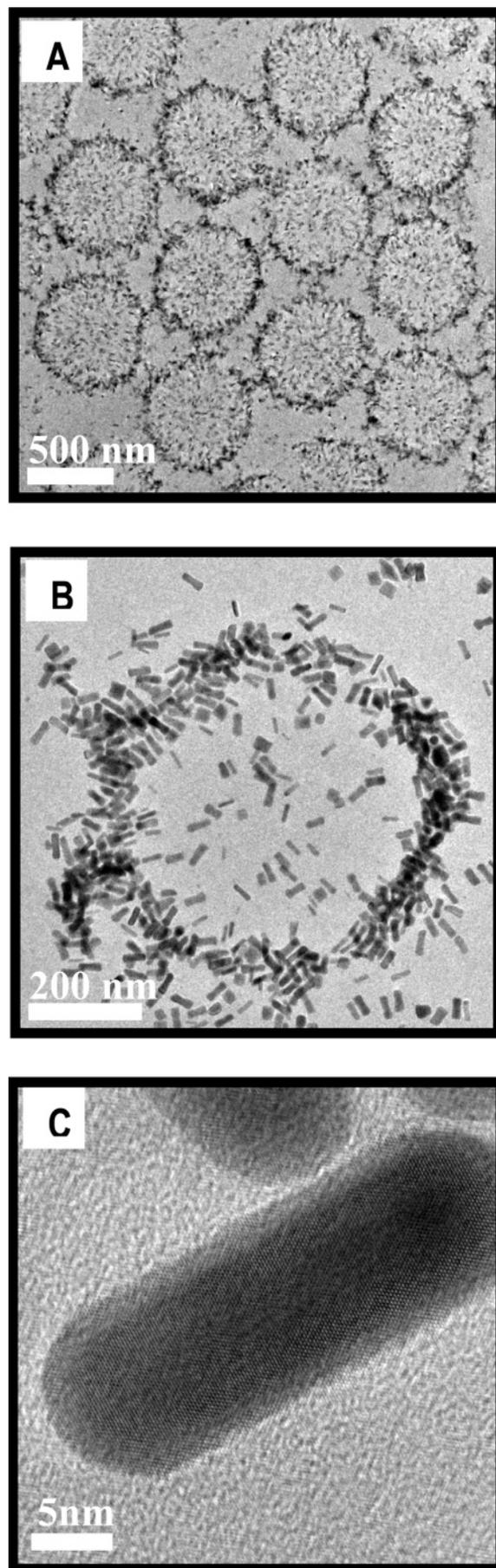
A TEM image of the material separated from the growth solution by centrifugation at 2000 rpm is shown in Figure 1A. The image clearly shows that the nanorod-coated microgels are well separated. An image of a single microgel decorated with nanorods is shown in Figure 1B. A high-resolution TEM image of the gold nanorod adsorbed on the microgel is shown in Figure 1C. The rods are of 11 nm average diameter and 35 nm average length. The particles are mostly rods, but a few cubes were also observed. Images suggest that the rods are growing on the surface of the microgels, and in a 2D projection, the edges show a large population of nanorods. It is also possible that the microgels have collapsed onto the grid yielding nanorods at the periphery.

The nanorod-coated microgels were allowed to stand in water for 2 days. During this period, the particles self-assembled to give hexagonally packed structures. The UV-vis spectrum of the precipitated material after redispersion showed longitudinal and transverse plasmon resonances indicating the presence of nanorods in them (Figure S5). The position of both LSP and TSP showed a red shift compared to the microgel before fusion. The new positions of the LSP and TSP were 764 and 522 nm, respectively. Such a large shift in the position of the longitudinal plasmon is expected when nanorods aggregate.<sup>13</sup>

Figure 2 shows the TEM images of the hexagonal pattern. The fusion of microgels is clearly visible because of the decoration of the microgel with the nanorods. The population of the nanorods is higher at the junction compared to that at the center of the microgel. Figure 2A shows a large-area image of the material. Each microgel particle is in contact with six others. Hexagonal close packing is preferred in view of the packing efficiency considerations. Figure 2B shows the image of a single hexagonal assembly. The nanorods adsorbed on the microgels are clearly visible in this image.

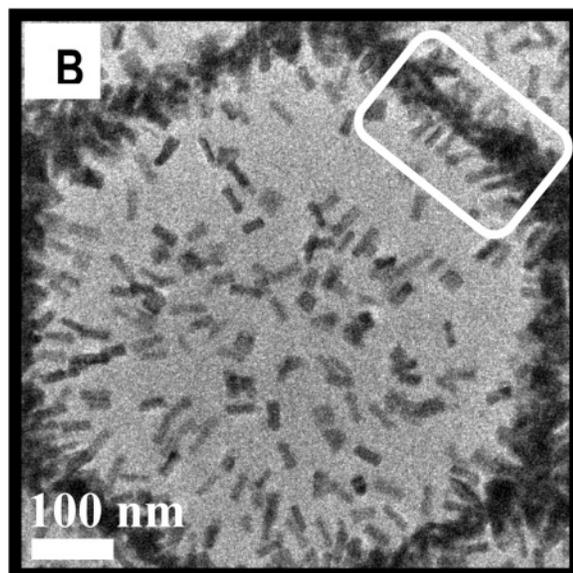
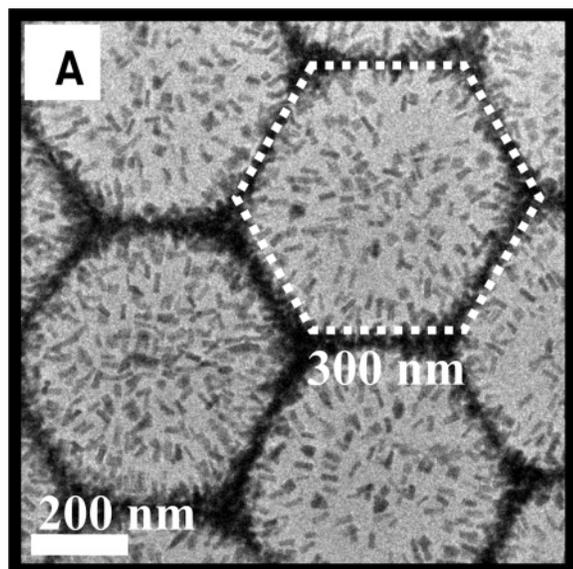
A pictorial representation of the events is given in Figure 3. Initially, the nanorod-coated microgels have a spherical shape. When such spherical particles come close to each other, the nanorods present on the surface start interacting. This facilitates the fusion of microgels, which is marked by a high population of nanorods between the microgel particles. The high density of nanorods on the surface of the microgel helps in filling the void space effectively. This is followed by an annealing step. The annealing process includes the effective packing of spheres and a change in shape. The packing defects are possibly removed in the solution itself. The shape change can happen when the material is removed from the solution or when it forms a film. From TEM, it may be inferred that strong interaction between the nanorods occurs, possibly by interpenetration of the nanorods (Figure S6). A high-resolution TEM image showing the interpenetration of nanorods is given in Figure S7. However, because of the difficulty in arranging all of the nanorods perpendicular to the surface, other possibilities such as tip-to-tip interaction and sidewise organization of nanorods lying parallel to the surface of microgels are possible, which makes the junction highly heterogeneous in organization.

A large-area image of the hexagonally fused nanorod pattern is shown in Figure 4. The sides of the hexagonal pattern had an average length of 300 nm. The average width of the wall is ~65

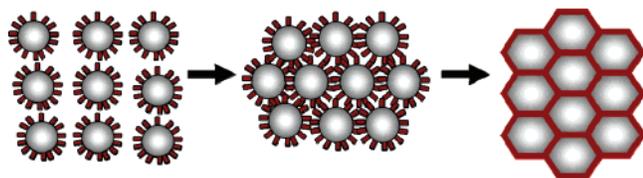


**Figure 1.** TEM images of the gold nanorod-PNIPAm composite at different magnifications.

(13) (a) Thomas, K. G.; Barazzouk, S.; Ipe, B. I.; Joseph, S. T. S.; Kamat, P. V. *J. Phys. Chem. B* **2004**, *108*, 13066. (b) Jain, P. K.; Eustis, S.; El-Sayed, M. A. *J. Phys. Chem. B* **2006**, *110*, 18243.

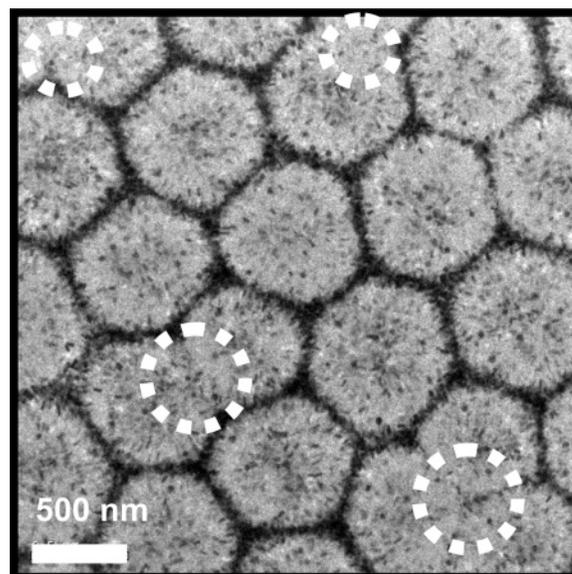


**Figure 2.** TEM images of the gold nanorod–PNIPAm composite at different magnifications. Panel B shows that the anisotropic structures sitting on the microgels are gold nanorods. The rectangle in B shows the largely parallel arrangement of nanorods at the junction.



**Figure 3.** Formation of a hexagonal pattern by the fusion of nanorod-coated microgels.

nm, which is a few nanometers less than twice the length of a single nanorod. This indicates that the interpenetration of nanorods may be creating the walls. Nanorods were observed in regions other than the junctions with lesser density. Even though the pattern occurs over a large area, it does show some defects. The defects appear either as pentagonally shaped microgels or as fusion without nanorod markings. The defects are likely to be due to unevenly coated microgels.



**Figure 4.** Large-area image of the hexagonal pattern. The defect sites are shown by dashed circles.

We also tried to load prefabricated nanorods directly onto the microgel particles by adsorption. The purified microgel particle dispersion (2 mL) was mixed with the as-prepared nanorod dispersion (2 mL) and was allowed to stand for 1 day. The nanorod-coated microgel particles were centrifuged out of solution, and the material after purification was allowed to stand in distilled water. The UV–vis spectrum of the material showed two plasmons indicating that microgels are coated with nanorods (Figure S8). The TEM images also confirmed the adsorption of nanorods (Figure S9). As we can see from the images, the number of nanorods adsorbed on a single microgel particle was very small. These particles did not produce hexagonal patterns. It appears that the lower density of nanorods is the reason for the lack of such ordered assemblies.

In conclusion, hexagonal patterns of gold nanorods were made by growing them on the surface of microgels and subsequently allowing the nanorod-loaded microgels to self-organize. The material was characterized by UV–vis spectroscopy and transmission electron microscopy. Because of the reduced number density of the nanoparticles, similar attempts with nanoparticle-coated and prefabricated nanorod-coated microgels did not form such patterns. We believe that interpenetration of the nanorod structures leads to such hexagonal assemblies. This opens up a new possibility for making patterns in high yield through solution-phase methods.

**Acknowledgment.** T.P. thanks the Department of Science and Technology (DST) for supporting his research program on nanomaterials.

**Supporting Information Available:** UV–vis spectra and TEM images of PNIPAm microgel particles, CTAB-coated gold nanoparticles, gold nanoparticle-adsorbed microgel particles, and prefabricated gold nanorod-coated PNIPAm microgels. UV–vis spectrum of gold nanorod-coated microgel particles and a hexagonally fused gold nanorod–PNIPAm composite. Large-area and high-resolution TEM images of a hexagonally fused gold nanorod–PNIPAm composite. The material is available free of charge via the Internet at <http://www.pubs.acs.org>.

LA701028A