

Supporting information for the paper:

Gold nanorods grown on microgels leading to hexagonal nanostructures

V. R. Rajeev Kumar, A. K. Samal, T. S. Sreeprasad 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

Email: pradeep@iitm.ac.in

Materials

Synthesis of poly(N-isopropyl acrylamide) (PNIPAm) microgels: PNIPAm microgels were made by precipitation polymerization following the literature procedure.¹ The monomer, N-isopropyl acrylamide (1.4 mg) and the crosslinking agent, N,N'-methylene bisacrylamide (30 mg) were dissolved in 100 mL distilled water. The solution was purged with argon to remove dissolved oxygen. Then the free radical initiator, ammonium persulfate (50 mg) was added. The temperature was raised to 70°C, well above the phase transition temperature of the gels which resulted in microgels with 500 nm average diameter. The unreacted persulfate was removed by filtering the solution through cellulose nitrate filter with a pore size 450 nm. The residue was redispersible in distilled water.

Synthesis of gold nanorods: The gold nanorod samples were synthesized following the well-known seed mediated growth approach reported by Murphy et al.² To prepare the seed particles, 10 mL of 100 mM cetyltrimethylammonium bromide (CTAB) was mixed with 250 µL of 10 mM HAuCl₄ solution and to this, 600 µL of freshly prepared ice cold solution of 10 mM NaBH₄ was added in a single stretch. The resulting solution was stirred for 10 minutes. This method gives seed particles with 5 nm average diameter. Growth solution was made by mixing the reagents in a plastic tube in the following order: 40 mL of 100 mM CTAB, 1.7 mL of 10 mM HAuCl₄.3H₂O, 250 µL

of 10 mM AgNO_3 and 270 μL of 100 mM ascorbic acid. This growth solution was mixed with 420 μL seed solution which resulted in nanorods of aspect ratio 3.18 after 3 h (the typical dimensions are: 11 nm diameter, 35 nm length).

Instrumentation: UV-visible spectra were recorded using a Perkin Elmer Lambda 25 spectrometer with 1 cm quartz cells. Images were taken using a JEOL 3010 High Resolution Transmission Electron Microscope (HRTEM) operating at 300 keV. Specimens for the measurements were prepared by spreading a small drop of a dilute dispersion of the materials on a 200 mesh carbon coated copper grid.

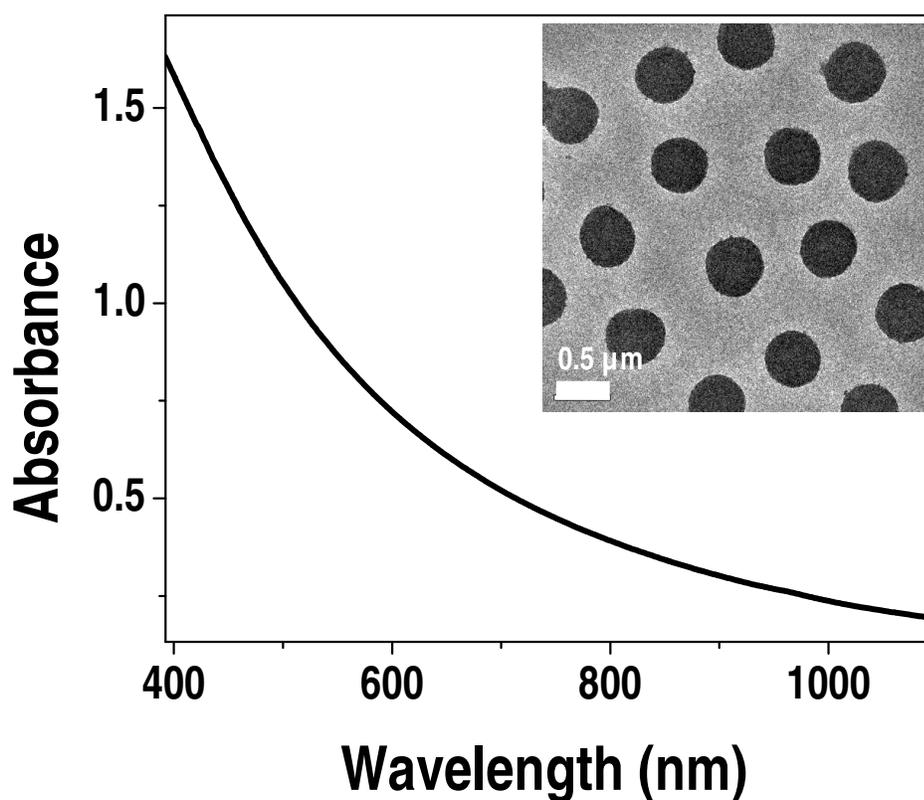


Figure S1. UV/vis spectrum of purified microgel particles. The figure in the inset shows the TEM image of the purified poly(N-isopropyl acryl amide) microgel particles.

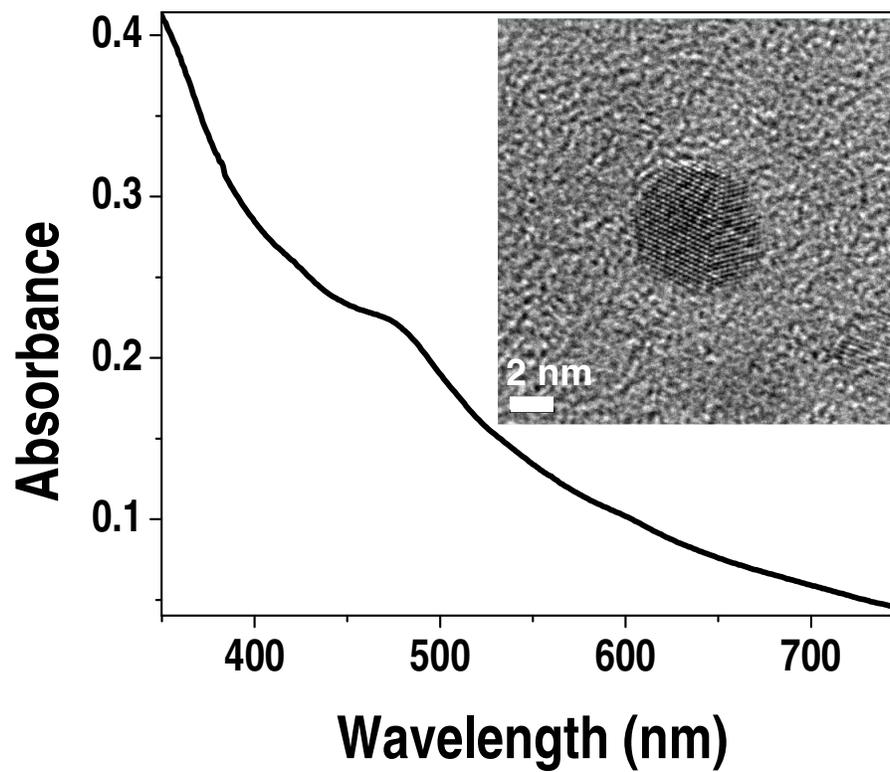


Figure S2. UV-vis spectrum of CTAB coated gold nanoparticles. The figure in the inset shows an HRTEM image of a CTAB coated gold nanoparticle.

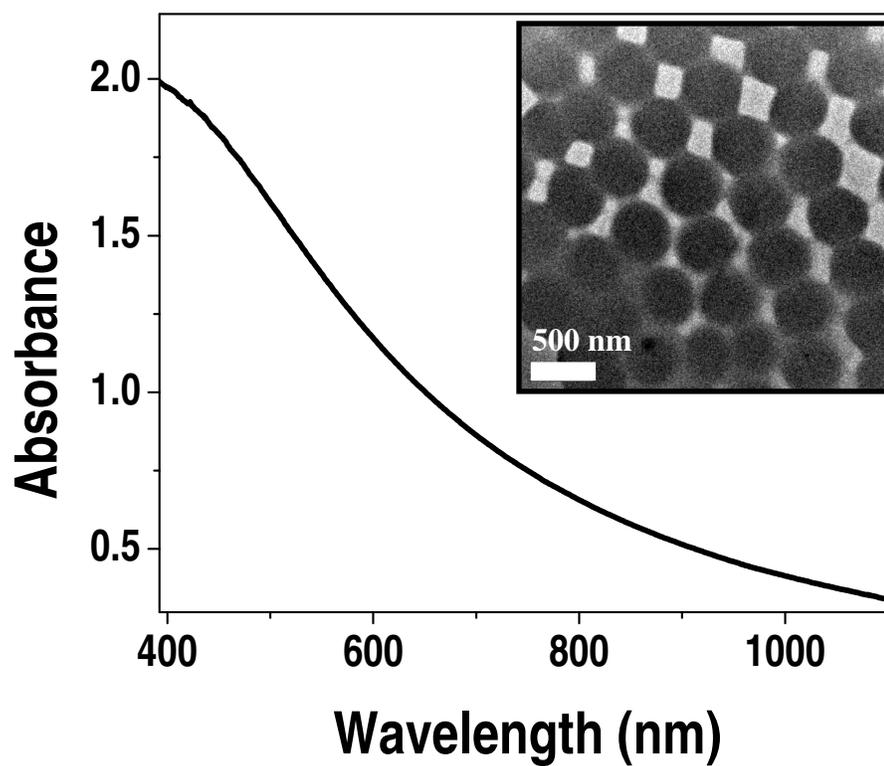


Figure S3. UV-vis spectrum of gold nanoparticle adsorbed microgel dispersion in water. The rectangle indicates the region of the microgel spectrum modified due to the adsorption of gold nanoparticles. The figure in the inset shows the TEM images of CTAB coated Au nanoparticles-loaded microgel particles after fusion.

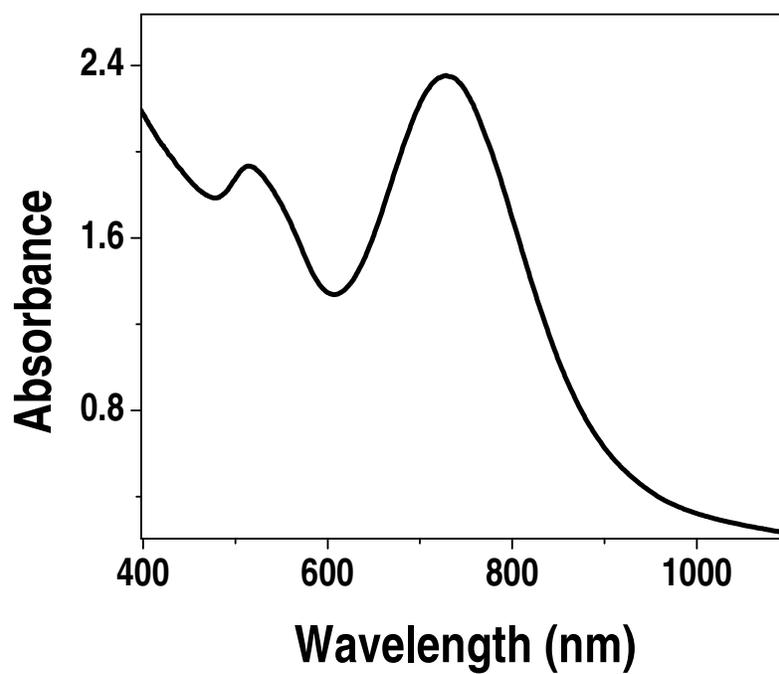


Figure S4. UV-vis spectrum of the microgel particles after gold nanorod growth.

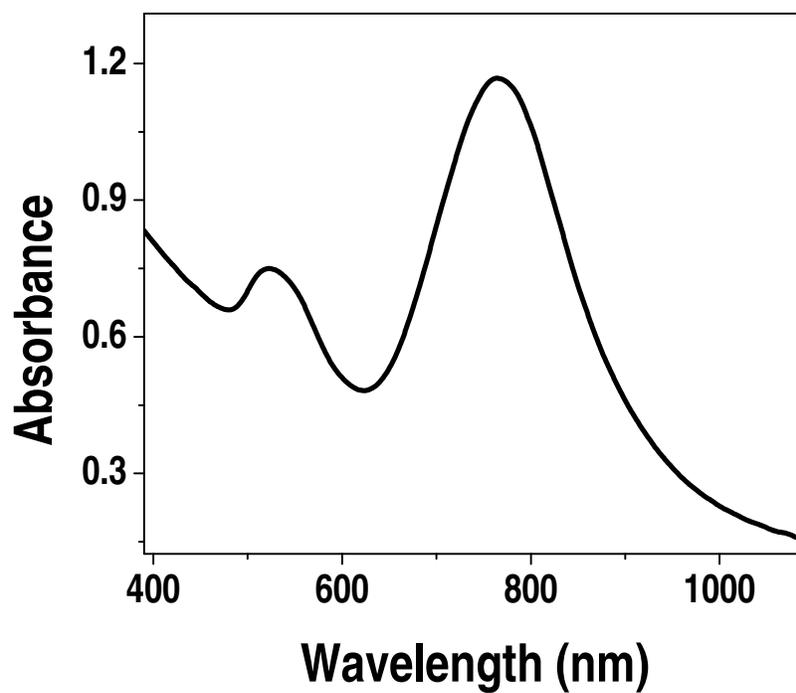


Figure S5. UV-vis spectrum of the hexagonally fused gold nanorod-PNIPAm composite.

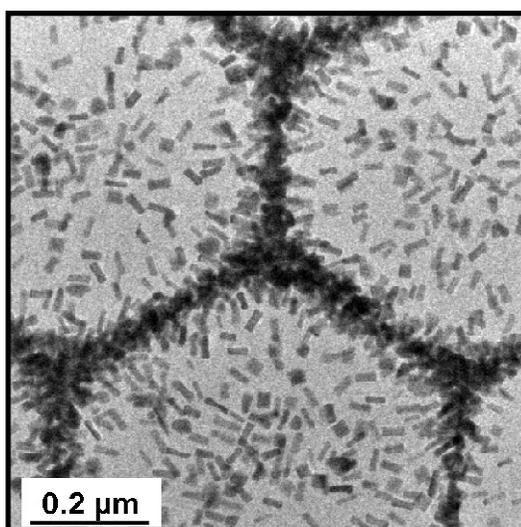


Figure S6. A large area TEM image of gold nanorod-PNIPAm composite. The image shows the interpenetration of nanorods.

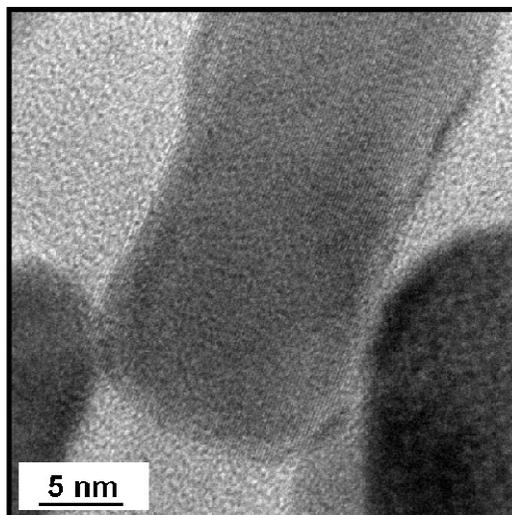


Figure S7. HRTEM image of gold nanorod-PNIPAm composite. The interpenetration of nanorods is clear from the image.

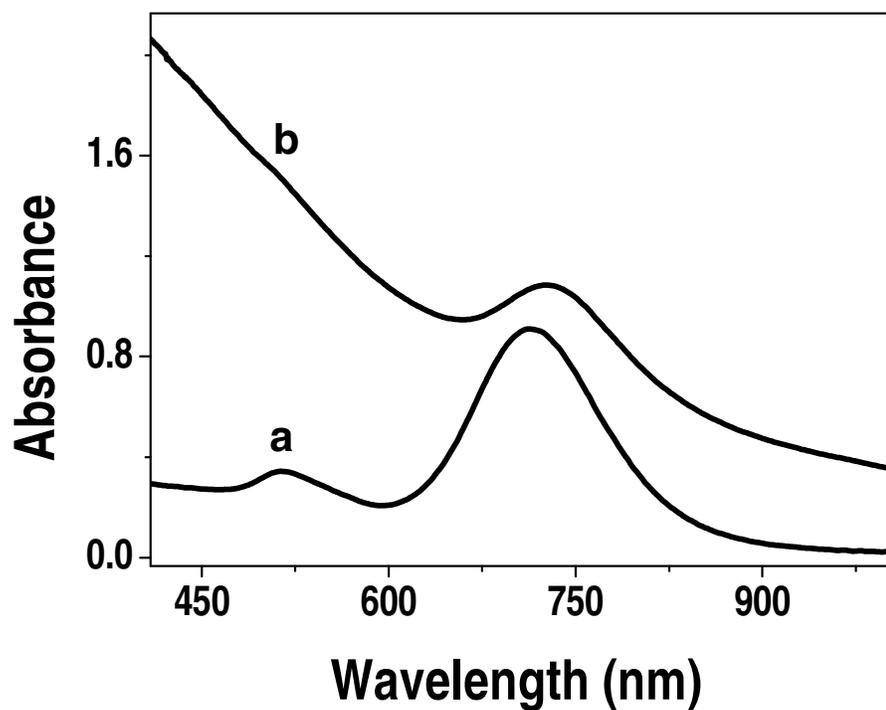


Figure S8. UV-vis spectrum of (a) as prepared gold nanorod dispersion and (b) nanorod coated microgel particles. The inter-particle interaction shows up as a red-shifted LSP.

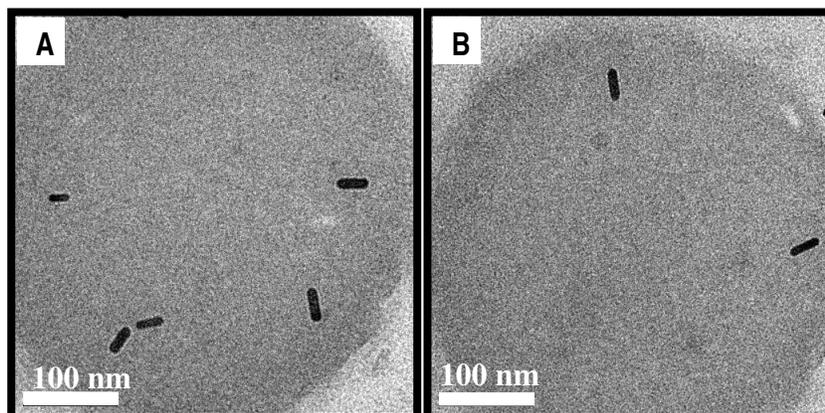


Figure S9. TEM images of nanorod coated microgel particles. Very few nanorods get loaded (compare with Figure 1 of the text).

References

- 1) Debord, S. B.; Lyon, L. A. *J. Phys. Chem. B* **2003**, *107*, 2927.
- 2) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389.