

Supporting Information

Experimental

Materials. Cadmium perchlorate ($\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 99.99%), silver nitrate (AgNO_3 , 99.5%), sodium borohydride (NaBH_4 , 99%), iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%), sodium nitrite (NaNO_2 , 97%), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt. % in water), potassium hydroxide (KOH), potassium persulfate (KPS, 99%), sodium dodecyl sulfate (SDS, 99%), N, N'-methylenebisacrylamide (BIS, 99%), acrylic acid (AA, 99%), and 2-hydroxyethyl acrylate (HEA, 96%) were purchased from Aldrich Canada and used as received. N-isopropyl acrylamide (NIPAM, 99%) was purchased from Scientific Polymer Inc. (Ontario, NY). The deionized water had a conductivity of $18.2 \text{ S} \cdot \text{cm}^{-1}$ (Millipore Milli-Q water purification system).

Microgel Polymerization. Polymer particles with dimensions from 165 to 710 nm (at 25 °C and pH = 4.2) were prepared by copolymerization of NIPAM, AA and HEA in an aqueous medium.^{1,2} Polymerization was carried out in a three-neck round-bottom flask equipped with a stirrer, reflux condenser, thermometer and nitrogen outlet. In a typical procedure: 1.0g of NIPAM, AA and HEA (in different molar ratios), a crosslinking agent BIS, and 0.03g of SDS were dissolved in 95 ml of water. Nitrogen gas was purged through the solution for 30 min. Then, 0.02g KPS in water (5 ml) were added and the solution was heated for 4 h at 70 °C under stirring. The dispersion was then

purified from the low-molecular weight species by dialysis against the deionized water.

Synthesis of inorganic NPs.

To synthesize CdS NPs, poly(NIPAM-AA-HEA) dispersion (20ml) was diluted to $[\text{COOH}] = 3.0 \text{ mM}$ and pH was adjusted to a required value by a 1.0 M aqueous KOH solution. The details of pH adjustment are given below in *Results and Discussion*. Then, 0.1M aqueous solution of $\text{Cd}(\text{ClO}_4)_2$ was added to the microgel dispersion, causing increase in turbidity of the system. The dispersion was stirred overnight to allow for ion-exchange between K^+ and Cd^{2+} -ions, the system was then dialyzed to remove free ions from the dispersion. Following this stage, a 0.1M Na_2S solution was slowly introduced into the system yielding a yellow transparent dispersion.

The introduction of Ag^+ -ions into the microgel particles was similar to that used for Cd^{2+} -ions. A 0.1 M solution of AgNO_3 was added to the microgel dispersion; the dispersion was stirred overnight and then dialyzed against the deionized water. Then, Ag^+ -cations in the interior of microgel particles were reduced to Ag NPs at 0°C with 0.1 M NaBH_4 solution.

Magnetic Fe_3O_4 NPs were prepared using a co-precipitation technique.³ A 1.0 M aqueous KOH solution was added to 200 ml of poly(NIPAM-AA-HEA) microgel dispersion ($[\text{COOH}] = 3.0 \text{ mM}$) to achieve $\text{pH} = 6.3 \pm 0.3$. The system was purged with N_2 , mixed with 1.05 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and then stirred overnight. After dialyzing the dispersion under a N_2 atmosphere, 0.104 g of NaNO_2 were added under stirring. Then, 12.5 mL of 28 wt % ammonia solution were quickly introduced into the system under vigorous stirring. The color of the dispersion became green and after ca. 2 h turned to

black. The resulting dispersion was dialyzed against the deionized water under a N₂ atmosphere.

Microgel Characterization. The concentration of carboxyl groups in microgels was determined by potentiometric titration⁴ using a PH/mV/temperature meter (Model P25, EcoMet Inc, USA). Particle hydrodynamic diameter and polydispersity were measured at room temperature by photon correlation spectroscopy (Zetasizer 3000HS_A, Malvern Instruments, U.K.). Transmission electron microscopy (TEM) experiments were carried out on a JEOL 1210 electron microscope operating at 75 kV. The samples were prepared by placing an aliquot of a dispersion or hybrid particles onto carbon-coated copper grids (400 mesh, Electron Microscopy Sciences, Fort Washington, PA) and allowing to dry.

Nanoparticle Characterization. NP concentration in microgels was determined by atomic absorption spectroscopy (Perkin-Elmer Analyst 100 inductively coupled plasma spectrophotometer). UV-vis absorption spectra of NPs were taken on a Varian-Cary 5000 scanning spectrophotometer operating at a slit width of 1.0 nm. The dimensions of NPs were determined by image analysis of TEM images. The size of CdS NPs was also calculated from their spectral absorption edge.^{5,6} Photoluminescence spectra of CdS NPs were acquired on a Spex FluoroMax spectrometer ($\lambda = 380$ nm). The structure of CdS and Fe₃O₄ NPs was characterized using X-ray powder diffraction (X'Pert Philips Materials Research Diffractometer) using Cu K _{α} radiation ($\lambda = 1.54178$ Å) at 40 kV and 50 mA at a scanning speed of 0.02° s⁻¹ in the 2 θ range 5-75°. Measurements of magnetic properties of Fe₃O₄ NPs were carried out on a Quantum Design, Inc. Model PPMS-9 superconducting quantum interference device (SQUID) susceptometer at 300K.

Stability of hybrid microgels after long-time storage

We examined stability of hybrid microgels during long-time storage in two ways: by examining the properties of nanoparticles in the interior of microgels and by studying the response of hybrid microgels to temperature variation. Nanoparticle properties were studied for CdS NPs, since their properties show the strongest size dependence. We compared TEM images, XRD spectra and fluorescence properties for the freshly synthesized CdS NPs and for the same samples after four month storage. **Figure S1a** shows identical XRD spectra of CdS NPs before and after storage, which indicates that nanoparticle structure did not change. In **Figure S1b** after four month storage, a PL spectrum of CdS NPs featured a moderate change but the wavelength and intensity of the emission peak does not change.

Finally, in **Figure S1c** a TEM image of a hybrid microgel particle shows that no notable size change or aggregation of CdS NPs occurred after long-time storage of hybrid microgels (compared to the TEM image given in **Figure 5a**). Similar TEM and XRD results were obtained for Fe₃O₄ nanoparticles.

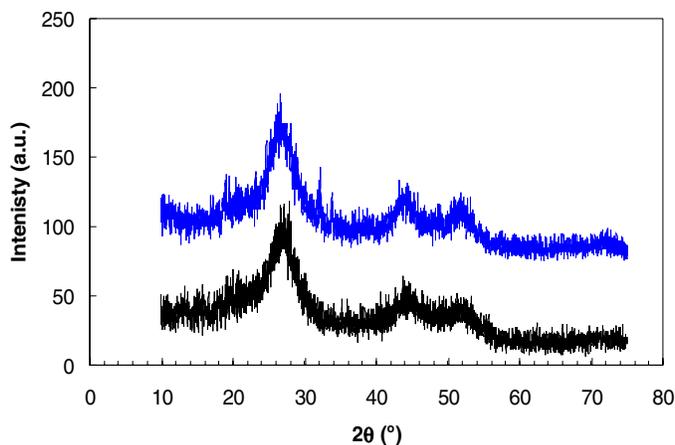


Figure S1a. XRD spectra of CdS NPs synthesized in the interior of microgels taken immediately after NPs synthesis (top spectrum) and after four month storage (bottom spectrum). Preparation conditions: [AA]/[HEA]/ [NIPAM]= 0.36/0.13/1, [BIS] = 4 mol %; [COOH]/[Cd²⁺]/[S²⁻] = 1/0.5/0.5; CdS concentration in microgel is 0.054 g/g polymer.

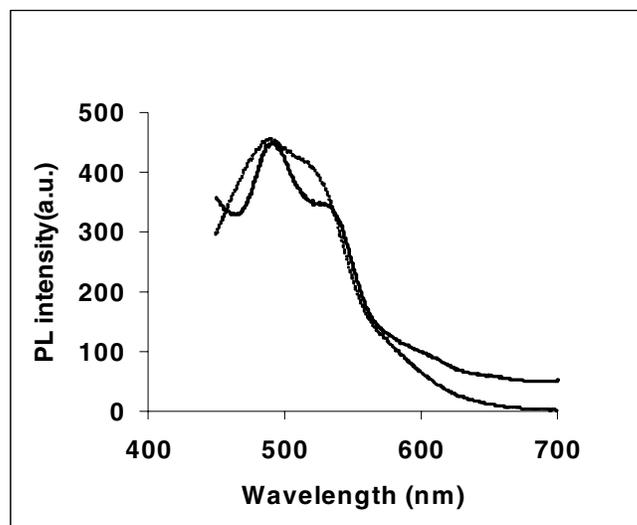


Figure S1b. Photoluminescence of CdS NPs synthesized in the interior of microgels after their preparation (—) and following four month storage (—). Preparation conditions are as in **Figure S1a**.

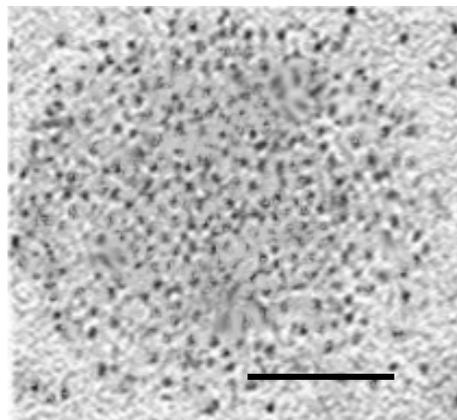


Figure S1c. TEM image of a microgel bead doped with CdS NPs after four month storage. Scale bar is 50 nm. Preparation conditions as in **Figure S1a**.

Response of CdS NP-doped microgels to the variation in temperature (that is, microgel volume change upon heating) before and after long-time storage is shown in **Figure S2** as the variation in V/V_0 versus temperature, where V_0 and V are the volumes

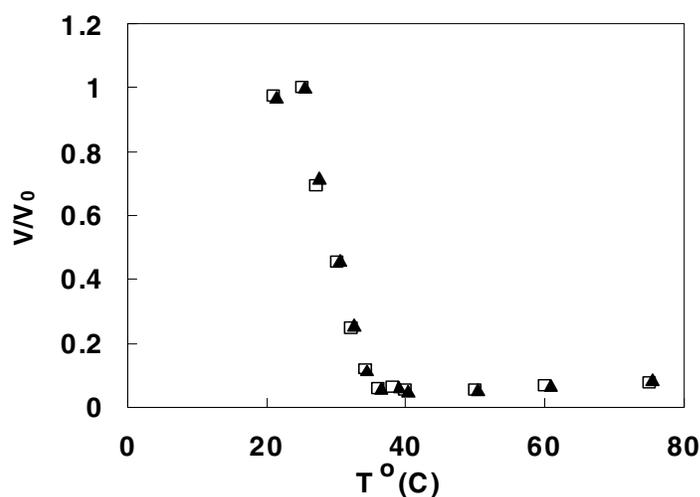


Figure S2. Variation in volume change of microgels doped with CdS NPs as a function of temperature for the freshly prepared CdS-doped microgels (□) and following their 6 month storage (▲). pH = 4.2.

of hybrid particles at the temperature of interest and at 25 °C, respectively. In the temperature range from 25 to 35 °C microgel volume reduces due to deswelling of

poly(NIPAM) at its lower critical solution temperature. We note that this temperature range was lower than for pure poly(NIPAM) particles because of the hydrophobic nature of PAA at pH=4.2. More important, the relative volume change of hybrid microgels did not change after 6 month storage.

References

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