Supplementary Information

Experimental

Materials

N-isopropylacrylamide (NIPAM) (95%, Tokyo Kasei Kogyo Co.) was purified by repeated recrystallization in a mixture of toluene/hexane (60:40, v/v) and dried in vacuum at 40℃. N, N’-methylene bisacrylamide (MBA) (95%, Aldrich) and ammonium persulfate (APS) (99%, Aldrich), were recrystallized from methanol and ethanol, respectively. Acrylic acid (AA) (99.5%, Acros) was utilized after removing inhibitor using acidic aluminum oxide as adsorbent. 3-(trimethoxysilyl)propyl methacrylate (MPS) (99%, Aldrich) and N,N,N,N-tetramethylethylenediamine (TEMED) (99%, Aldrich) were utilized without further purification. Other agents from Shanghai Chemical Reagents Company (Shanghai, China) were of analytical grade and utilized without further purification. Deionized water was produced using a Millipore Direct-Q system.

Preparation and modification of colloidal silica particles

Colloidal silica particles were synthesized in ethanol by via Stöber method (sol-gel method).The ammonia and tetraethyl orthosilicate (TEOS) concentrations were all fixed at 0.2M and the water concentration was chosen as 4M. The coupling agent, 3-(trimethsilyl)propyl methacrylate(MPS), was used for modification of the colloidal silica particles: excessive MPS (40 µmol of MPS per square meter surface area of silica particles, corresponding to five times the silanol surface concentration estimated to be equal to 8 μmol/m^2) was added to above ethanol dispersion of the colloidal silica particles and kept stirring for 48h at room temperature. Residual MPS and ammonia were removed from the dispersion by centrifugation until the absorbancy of MPS in the supernatant at 203.5 nm detected by UV spectroscopy approached zero. The ethanol dispersion of MPS-modified silica particles was transformed into their aqueous dispersion by centrifugation.

Synthesis of SiO_2/PNIPAM core/shell composite particles

A 95 ml of 0.5 wt% aqueous dispersion of the MPS-modified silica particles was used as seed dispersion for the seed precipitation polymerization of NIPAM (0.685g) and N,N'-methylenebisacrylamide (MBA) (0.017g). The solution was heated to 70^{o}C with nitrogen bubbling for about 1h, and potassium persulfate (KPS) (0.017g) dissolved in 5ml deionized water was added to initiate the reaction. The reaction was carried out at 70^{o}C for 4h. The formed particles were cleaned via repetitive centrifugation and redispersion cycles using deionized water.

Synthesis of silica/(PNIPAM/PAA IPN) core/shell composite particles

A 10ml of aqueous dispersion of SiO_2/PNIPAM core/shell composite particles was diluted to 95ml, and then 0.15g AA and 0.03g MBA were added to the solution. The temperature of the solution was kept at 23 ℃ for about 1h, and then 0.04g ammonium persulfate (APS) and 0.04g

N,N,N,N-tetramethylethylenediamine (TEMED) dissolved in 5ml deionized water was added to initiate polymerization of AA and MBA. The reaction was carried out at 23℃ for 30min. The formed particles were cleaned via repetitive centrifugation and redispersion cycles using deionized water. The resulting silica/(PNIPAM/PAA IPN) core/shell composite particles are called as SiO_2/(PNIPAM/PAA IPN)-1 in Table 1 of the paper.

Synthesis of PNIPAM/PAA IPN hollow nanogels

The above formed silica/(PNIPAM/PAA IPN) core/shell composite particles were immersed into 20 wt% HF aqueous solution for 4h at ambient temperature to etch their silica cores completely. The resulting hollow nanogels called as PNIPAM/PAA IPN-H1 were purified by dialysis in deionized water until pH 6 of their aqueous dispersion was achieved.

Characterization

Fourier transformation infrared (FTIR) spectra were recorded with a NEXUS-670 FTIR spectrometer (Nicolet, USA) in the wavenumber range from 500 to 4,000 cm^{-1}. The aqueous dispersion of the particles was coated on KRS-5 salt chip and dried before test.

Transmission electron microscopy (TEM) images were taken with a H-800 transmission electron microscope (Hitachi, Japan) at a voltage of 200kV. Samples were stained by mixing 0.05 ml of the purified particle dispersion with 0.5 ml of 0.75 mM uranyl acetate and agitated for 1 h. The resulting dispersion was dropped onto carbon coated copper grids and dried at room temperature.

The hydrodynamic diameters (D_H) of the particles were measured via BI-200SM dynamic laser light scattering (DLLS) (Brookhaven, USA), which was equipped with a solid laser sourcer (wavelength of 532 nm and output power of 100mW) and a BI-9000AT digital autocorrelator. The scattering light was collected at 90^o, and the CONTIN statistical method was used to convert the measured correlation data into a particle size distribution. The samples temperature was controlled by a thermostated naphthane bath, and the pH values of the dispersion media were adjusted by 0.1 mol/l HCl or 0.1 mol/l NaOH solution. All particle dispersions were highly diluted and then allowed to equilibrate thermally for at least 15 min before each set of measurement.

The ultraviolet-visible (UV-vis) adsorption spectra were obtained from a Lambda 35 UV-vis spectrometer with a temperature controller (Perkin-Elmer, USA). A quartz cell with 1 cm optical path length was used.