

Supplementary Information

Fabrication of Well-Defined Water-Soluble Core/Shell Heteronanostructures through the SiO₂ Spacer

Minghai Chen, Lian Gao,^{*} Songwang Yang and Jing Sun

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, P. R. China

Experimental details

Preparation of Fe₃O₄ spheres

Fe₃O₄ spheres were synthesized by a polyol media solvothermal method according to reference 9 with some modifications. Briefly, 2.7 g of FeCl₃ and 2 g PEG-1500 were dissolved in 80 mL of EG in a warm-water bath at 60 °C, and then 7.2 g of NaAc was added into the mixture under vigorous stirring. The as-formed viscous slurry was transferred into a Teflon-lined autoclave of 80 mL capacity, and maintained at 200 °C for 8 h. After cooling to room temperature, the black precipitates were collected after being washed with distilled water and absolute alcohol repeatedly, and kept in alcohol solution.

Coating silica spacers on Fe₃O₄ spheres

A certain amount of Fe₃O₄ spheres were dispersed in a mixture of 70 mL isopropanol, 3.8 mL water and 2.1 mL aqueous ammonia in a round bottom flask by ultrasonic. After 15 min, the mixture was transferred into an oil bath, and then 0.3 g of PVP was added under gentle stirring. Finally, 0.2 mL of TEOS was added to the mixture. The temperature of the oil bath was set at 40 °C and kept for 15 h. The products were magnetically collected, washed three times with alcohol and dried in vacuum at 60 °C for 4 h.

Coating the magnetic core with CdS

A certain amount of silica coated Fe₃O₄ spheres were dispersed in 300 mL of distilled water by ultrasonic, and then 0.5 mL of triethanolamine (TEA), 20 mL trisodium citrate solution (0.1 M), 10 mL of CdCl₂ solution (0.1 M), and 20 mL of thiourea solution (0.1 M) were added. The pH value was adjusted to 11 by aqueous ammonia. After 15 min, the mixture was transferred to a water bath and kept at 60 °C under vigorous stirring. 2 h later, the mixture was quickly cooled by diluting some water. The Fe₃O₄@CdS nanocomposite was magnetically collected and washed with distilled water and alcohol repeatedly to remove the excess CdS nanoparticles. The as-prepared sample was dried in vacuum at 60 °C for 4 h and kept in a desiccator for later characterization. In order to gain a protective layer over CdS, another thin silica layer was coated on the Fe₃O₄@CdS core/shell nanostructure by repeating the second step with 0.1

mL of TEOS added.

Characterizations

Powder X-ray diffraction (XRD) was carried out in a Japan Rigaku D/max 2550V X-ray diffractometer using Cu K α ($\lambda=0.15406$ nm) radiation at 40 kV and 60 mA. TEM images were collected using a JEOL-2100F electron microscope with an accelerating voltage of 200 kV. FE-SEM images were collected on a JSM 6700F field-emission scanning electron microscope. EDS was recorded on an OXFORD ISIS spectroscope, which was attached to the JEOL-2100F electron microscope. UV-Vis absorption spectrum analysis was performed on a Lambda 950 UV-Vis spectrophotometer. PL (Photoluminescence) spectrum characterization was carried out in a LS55 luminescence spectrometer with a Xe lamp as the excitation source at room temperature. Magnetic characterization was conducted on a vibrating sample magnetometer (EG&G VSM Model 155).

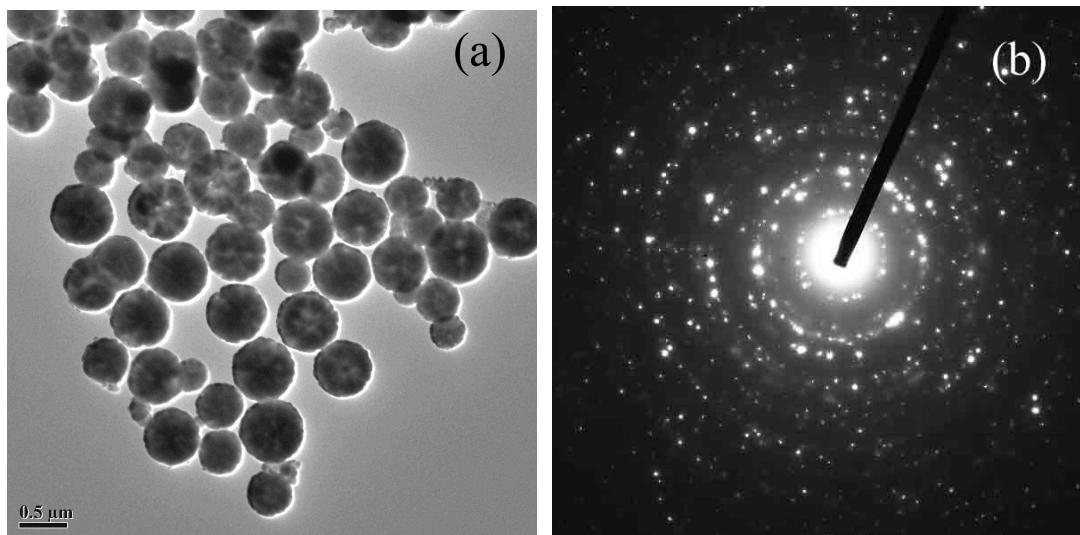


Fig. S1 (a) TEM image and (b) its corresponding polycrystal SAED pattern of Fe_3O_4 spheres prepared by solvothermal method at 200 °C for 8 h.

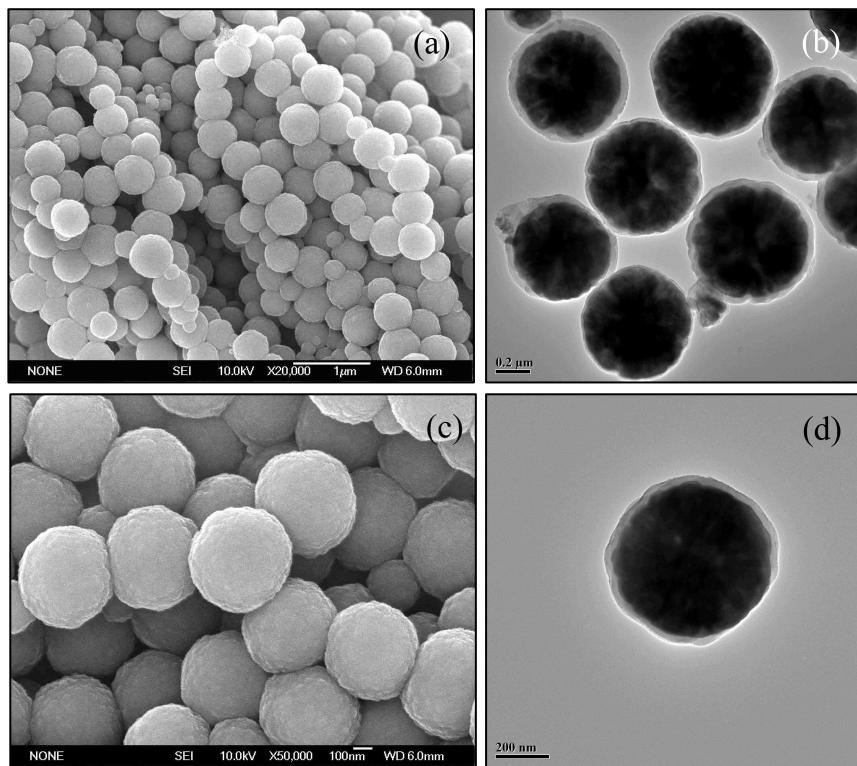


Fig. S2 SEM (a, c) and TEM (b, d) micrographs of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanostructure

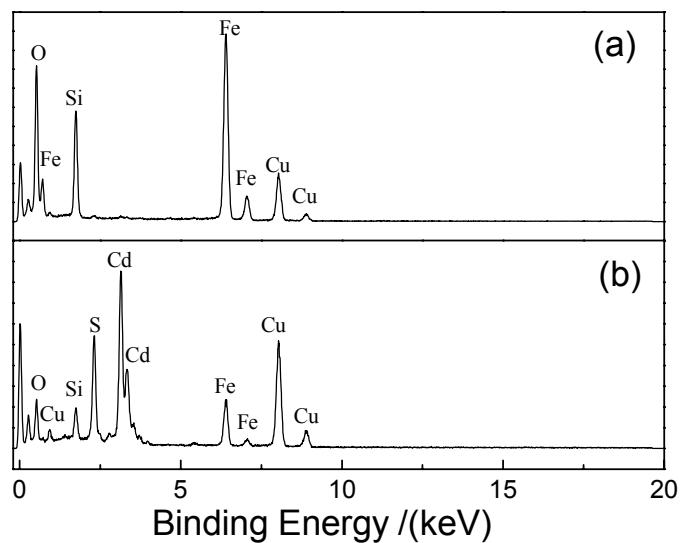


Fig. S3 EDS patterns of the samples: (a) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CdS}$, presenting the direct proof of the layers' composition.

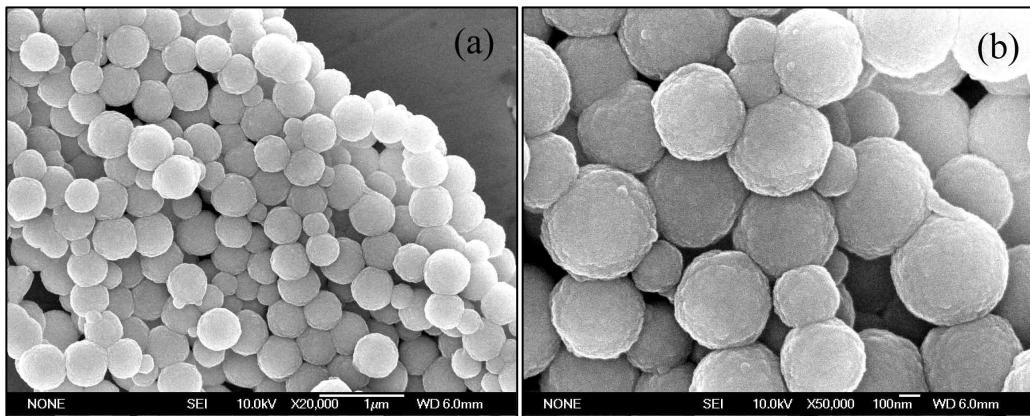


Fig. S4 SEM micrographs of $\text{Fe}_3\text{O}_4 @\text{SiO}_2@\text{CdS}$ nanostructure

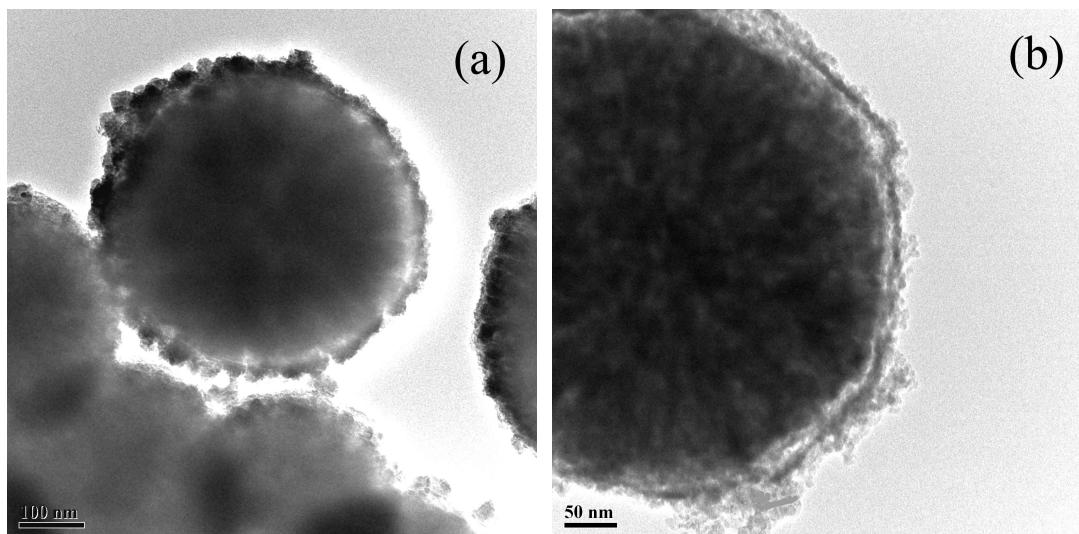


Fig. S5 TEM micrographs of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{CdS}$ samples prepared at short holding time (30 min) and low reactant concentration (2 mL of CdCl_2 solution was added).

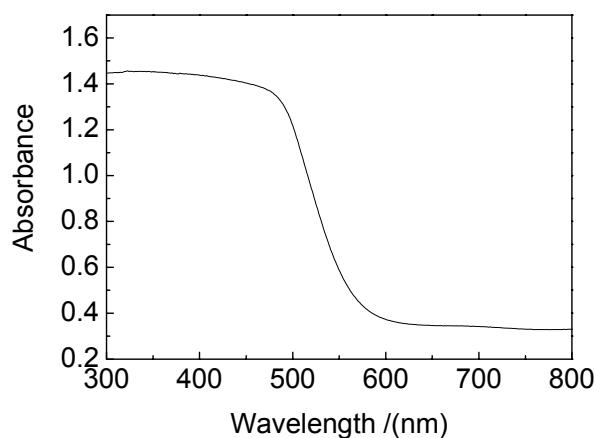


Fig. S6 UV-Vis absorption spectrum of CdS nanocrystals prepared under the same conditions with the core/shell heteronanostructures