Electronic Supporting Information for the Article

Ag_2S-hollow Fe_2O_3 nanocomposites with NIR photoluminescence

Yingjie Chen,[a] Lifeng Dong,*[a,b] Mei Zhao[a] and Hongzhou Dong[a]

[a]*College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China. Fax/Tel: 86-532-84022869; E-mail: DongLifeng@qust.edu.cn*

[b]*Department of Physics, Astronomy, and Materials Science, Missouri State University, Springfield, MO 65897, USA. Fax: 1-4178366226; Tel: 1-4178363755; E-mail: LifengDong@MissouriState.edu*

Materials

Oleic acid, oleylamine (OA, 80%), 1-dodecanol, octadecene (ODE, 90%), silver acetate (Ag(ac), 99.5%), ferric acetylacetonate ($Fe(acac)_3$, 99.0%), and indocyanine green (ICG) were purchased from Sigma-Aldrich. 1-dodecanethiol (DDT, 98%) was purchased from Aladdin reagent company. All these reagents were used without any further purification.

Experimental Methods

Synthesis of Ag-Fe_2O_3 core-shell nanoparticles

Firstly, 50 mg of Ag(ac) was hot-injected into a mixture containing 0.5 mL of oleic acid, 0.5 mL of OA and 5 mL of 1-dodecanol at 220 °C under nitrogen with stirring. After half an hour, the solution was naturally cooled down to 160 °C, and 150 mg $Fe(acac)_3$ was added and reacted for two hours. After cooling down to room temperature, the final product was washed several times by ethanol and dispersed in 2 mL of n-hexane for later use.

Sulfidation of Ag-Fe_2O_3 core-shell nanoparticles by DDT

Above-mentioned 2 mL of Ag-Fe_2O_3 core-shell nanoparticles in n-hexane was mixed with 10 mL of ODE, and 1 mL of DDT was added dropwise into the solution under stirring. This solution was heated to 80 °C at a ramping rate of 5 °C/min and reacted at this temperature for hours. The obtained nanoparticles were isolated from reaction solution by precipitation and centrifugation with ethanol, and re-dispersed in chloroform. After washing for several times by ethanol, the final product was dried or dispersed in n-hexane for further analyses.

Characterization of nanoparticles

Transmission electron microscopy (TEM) and STEM images were taken by JEM-2100 and Tecnai G2 F20 electron microscope respectively at an accelerating voltage of 200 kV. TEM samples were prepared by drop-casting 1 to 2 drops of the nanoparticle hexane solution onto a carbon-coated Cu grid. Optical absorption spectra were recorded on a Perkin Elmer/Lambda 25 UV-Vis-NIR spectrometer (USA), and photoluminescence (PL) spectra were recorded with a fluorescence spectrophotometer (Horiba NanoLog) at room temperature. The magnetic properties were studied with a vibrate sample magnetometer (VSM, 9600, BOJ Electronics) at room temperature. X-Ray diffraction (XRD) analyses were performed using a Rigaku D/Max-3B diffractometer, using Cu Kα radiation at 0.15418 nm. Fourier transform infrared spectroscopy (FTIR) spectra were obtained by a Nicolet 360 spectrometer with the pressed KBr pellet technique. Regarding the preparation of FTIR samples, 1 to 2 drops of DDT were casted onto a KBr pellet, while 1 to 3 mg of dried nanoparticles after several times washing by ethanol was pressed into a KBr pellet. These obtained KBr pellets were vacuum dried prior to the FTIR analysis by a Nicolet 360 spectrometer.

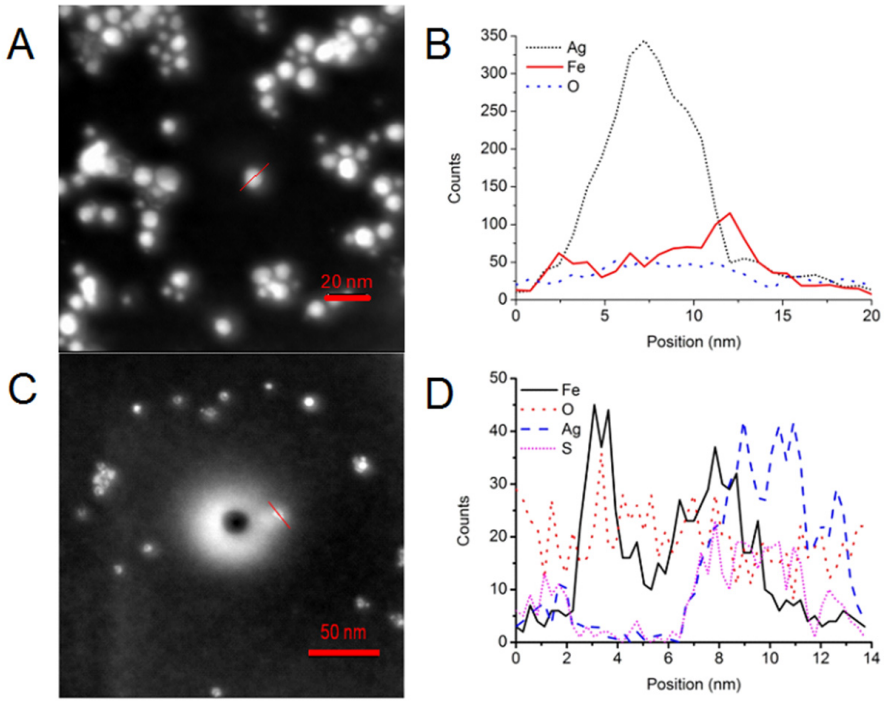

Fig. S1 STEM-EDS line scan for (A) Ag-Fe_2O_3 core-shell, (B) showing the presence of Ag, Fe and O, and (C) Ag_2S-hollow Fe_2O_3 nanocomposites, (D) showing the presence of Ag, Fe, O and S. It further revealed the diffusion of Ag from the core to the outer surface of Fe-O containing shell.

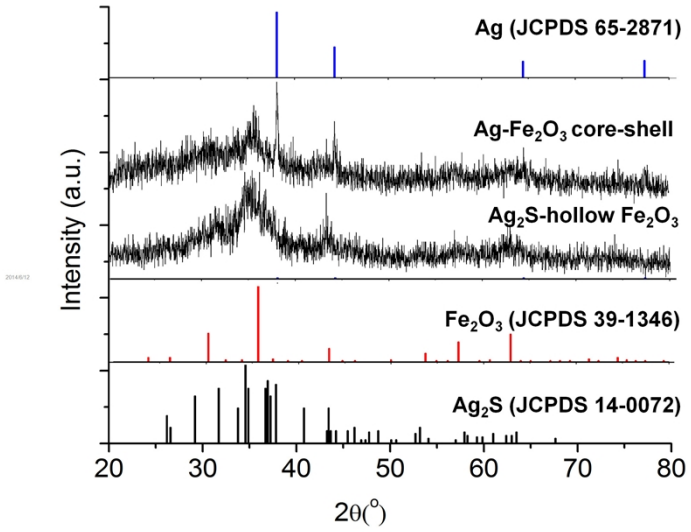

Fig. S2 XRD patterns of as-prepared Ag-Fe_2O_3 core-shell and Ag_2S-hollow Fe_2O_3 nanoparticles.

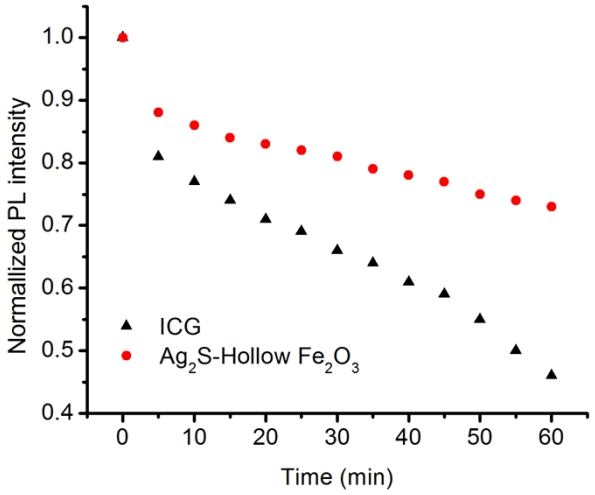

Fig. S3 PL intensities of ICG dispersed in DMSO and Ag_2S-hollow Fe_2O_3 nanoparticles dispersed in n-hexane after continuous illumination with mercury lamp.

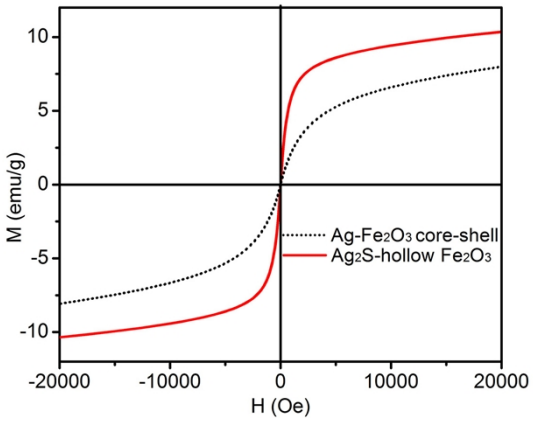

Fig. S4 Magnetization curves of Ag-Fe_2O_3 core-shell and Ag_2S-hollow Fe_2O_3 nanoparticles at room temperature.

In addition, high reaction temperature accelerated the sulfidation process. The color of solution containing Ag-Fe_2O_3 core-shell nanoparticles and DDT changed from brown red to dark brown within an hour at 120 °C. As shown in Fig. S5, the reaction product contains Ag_2S-hollow Fe_2O_3 and separated Ag_2S nanocrystals. On the other hand, the presence of too much DDT can competitively capture Ag^+ ions into solution and help the formation of hollow Fe_2O_3 NPs. As to the reaction of 2 mL Ag-Fe_2O_3 core-shell in n-hexane mixed with 10 mL of ODE and 4 mL of DDT at 80 °C for 1 h, a mixture of hollow and yolk-shell nanostructures was obtained (Fig. S6).

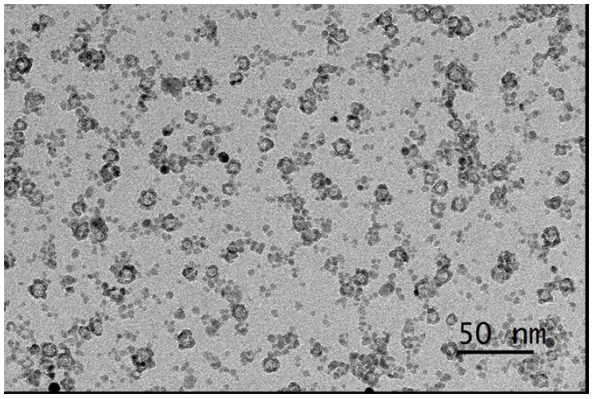

Fig. S5 TEM image shows the coexistence of Ag_2S-hollow Fe_2O_3 and separated Ag_2S nanocrystals in the product, which was obtained by the reaction of 2 mL of Ag-Fe_2O_3 core-shell nanoparticles in n-hexane mixed with 10 mL of ODE and 2 mL of DDT at 120 °C for 1 h.

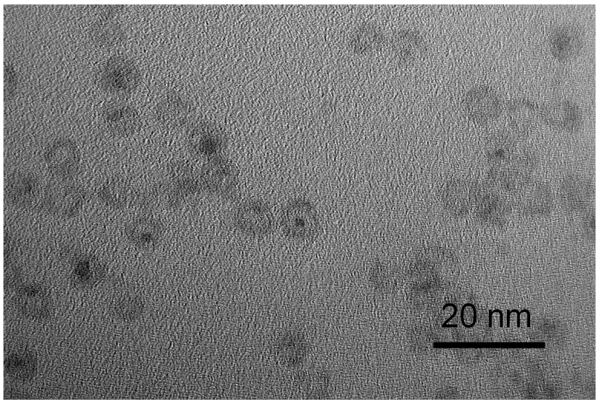

Fig. S6 TEM image shows a mixture of hollow and yolk-shell nanostructures in the product, which was obtained by the reaction of 2 mL of Ag-Fe_2O_3 core-shell nanoparticles in n-hexane mixed with 10 mL of ODE and 4 mL of DDT at 80 °C for 1 h.