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Template Synthesis of Ternary Hybrid Nanocrystals of $CoS/Ag_2S-Fe_2O_3$ with Near-infrared Photoluminescence

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Hybrid nanocrystals, such as Fe_3O_4/Au, Fe_2O_3/Ag and Fe_2O_3/Ag_2S, obtain multiple functions and properties from their individual components [1]. Besides, intimate solid-state interfaces within these hybrid nanocrystals promote direct electronic and magnetic transport among components. However, these hybrids are mainly binary systems, and there are still few reports on the construction of ternary or higher-order hybrid nanocrystals [2]. With the development of synthesis and preparation technologies, the template method has gradually become an effective method for preparing complex multi-order nanocomposites. For instance, the Pearson hard-soft acid based (HSAB) principle has been employed to synthesize anisotropic nanoparticles [3-4]. The perception that anisotropic shape and interactions through chemical "patchiness" are powerful tools for engineering the assembly of specific targeted structures has fueled the discovery of new chemical, physical, and biosynthetic methods for the synthesis of anisotropic nanoparticles and colloidal building blocks.

Herein, Ag-$CoFe_2O_4$ nanocomposites with core-shell and heteromeric nanostructures were synthesized and utilized as templates for sulfidation reactions with 1-Dodecanethiol at 100 °C for 2 h. Morphology transformation along with the sulfidation was recorded and the photoluminescence property of the consequently produced $CoS/Ag_2S-Fe_2O_3$ was characterized. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images were taken by JEM-2100 and Tecnai G2 F20 electron microscopes equipped with x-ray energy dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a VG ESCALAB MK. Photoluminescence (PL) spectrum was recorded with a fluorescence spectrophotometer (Horiba NanoLog) at room temperature.

As shown in Figure 1a-b, Ag-$CoFe_2O_4$ core-shell templates transform to CoS/Ag_2S-hollow-Fe_2O_3 trimers. Interestingly, the formed solid CoS tends to form on Ag_2S nanocrystals, and the hollow Fe_2O_3 shell structure remains in the process of vulcanization. The observed lattice fringes marked in the HRTEM image are 2.0 Å and 2.6 Å, corresponding to the (102) interplane spacing of CoS and the (-121) plane of Ag_2S, respectively. According to the HSAB principle, 1-Dodecanethiol as a soft alkali is easy to combine with soft acid Ag0 and boundary acid Co^{2+}, but difficult to combine with hard acid Fe^{3+}, reasonably explaining the formation of CoS/Ag_2S-hollow-Fe_2O_3 trimer. Also, the HSAB principle can explain morphology transformation with the sulfidation of Ag-$CoFe_2O_4$ heteromeric nanostructures to $CoS/Ag_2S-Fe_2O_3$ trimers in Figure 1c-d. Meanwhile, STEM-EDS line scan shows elemental distribution of Ag, Co, Fe and S along a CoS/Ag_2S-hollow-Fe_2O_3 heterotrimer in Figure 1e-f. The S signals co-exist along with Co and Ag, but Fe separates from Ag, Co, and S, clearly suggesting the formation of CoS/Ag_2S-hollow-Fe_2O_3 structure. The XPS and PL spectra of the CoS/Ag_2S-hollow-Fe_2O_3 heterotrimer are given in Figure 1g-h. With an excitation wavelength of 960 nm, there are two major emission peaks at around 980 nm and 1280 nm, attributed to the size-dependent near-infrared (NIR) fluorescence of Ag_2S nanoparticles [5].

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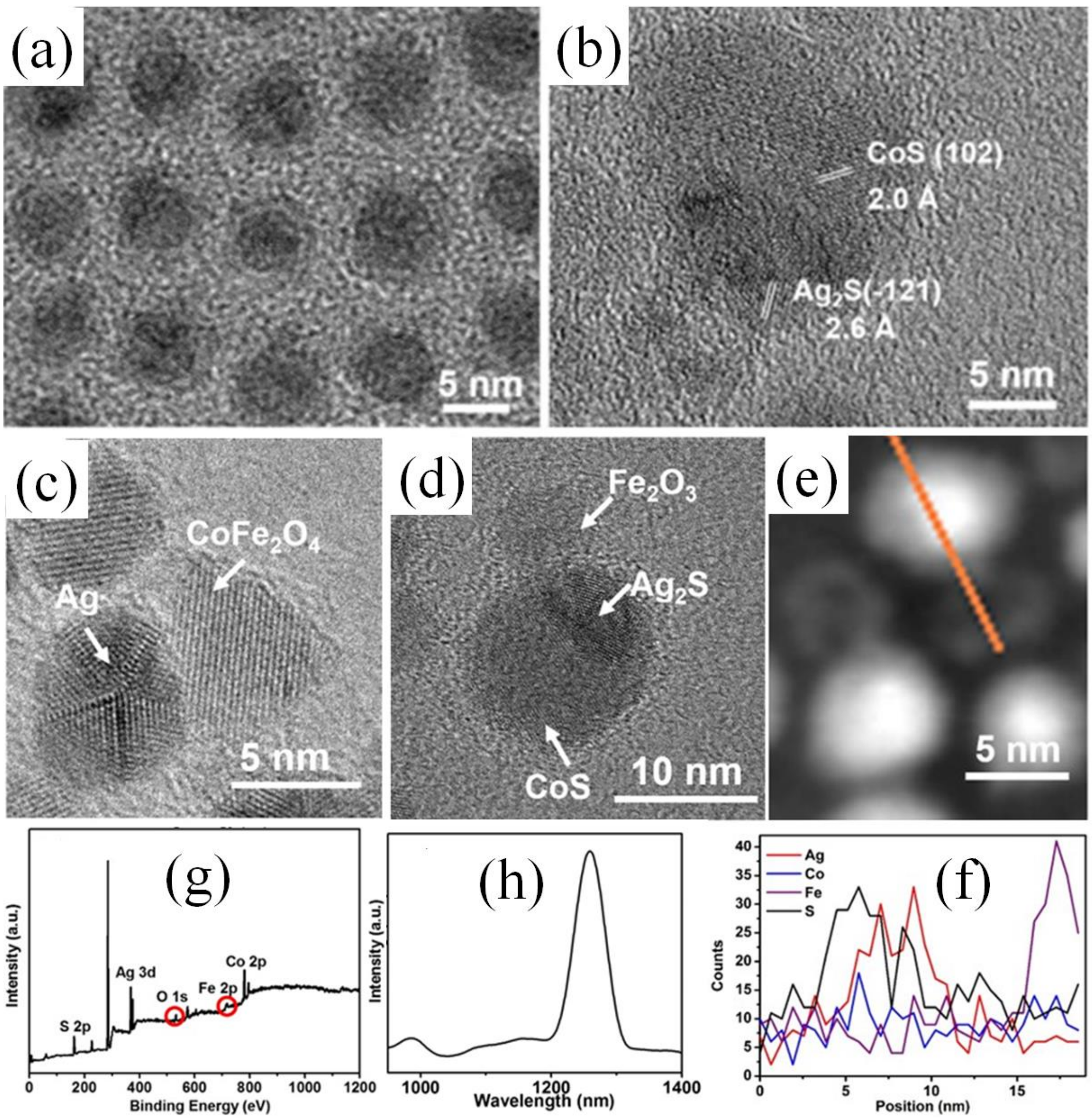

Figure 1. HRTEM images of Ag-$CoFe_2O_4$ nanocomposites before and after sulfidation: (a) Ag-$CoFe_2O_4$ core-shell templates vs. (b) Ag_2S/CoS-hollow-Fe_2O_3, (c) Ag-$CoFe_2O_4$ heteromeric templates vs. (d) Ag_2S/CoS-Fe_2O_3. (e) STEM-EDS elemental line scan of Ag, Co, Fe, and S along an Ag_2S/CoS-hollow-Fe_2O_3 (f-g). (g) XPS and (h) NIR fluorescence emission spectrum of CoS/Ag_2S-hollow-Fe_2O_3.