Fabrication of Magnetic Luminescent Nanocomposites via Adsorption–Precipitation of Metal Ions on Sulfonated Iron Oxide Nanoparticles

Sou-Yee Mak[2] and Dong-Hwang Chen*[1]
[1]*Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 701*
[2]*Department of Chemical Engineering, Wu-Feng Institute of Technology, Ming-Hsiung, Chia-Yi, Taiwan 621*

(Received June 26, 2006; CL-060719; E-mail: chendh@mail.ncku.edu.tw)

A novel magnetic luminescent nanocomposite has been fabricated by the adsorption of Cd^{II} ions on the sulfonated Fe_3O_4 nanoparticles and the subsequent precipitation with sodium sulfide. The adsorption isotherm of Cd^{II} ions on the sulfonated Fe_3O_4 nanoparticles was investigated, and the product was characterized by TEM, HRTEM, EDX, XRD, UV–vis, and PL.

Semiconductor nanocrystals show remarkable size-dependent optical properties owing to the quantum confinement effect and hence can be widely used in optoelectronics[1] and biolabeling.[2] Iron oxide nanoparticles have various applications in the field of high-density data storage, ferrofluids, magnetic resonance imaging (MRI), enzyme immobilization, bioseparation, drug delivery, immunoassays, and biosensors because of their biocompatibility and superparamagnetism.[3] Combining semiconductor nanocrystals and iron oxide magnetic nanoparticles in a single entity can make use of both advantages and may lead to new applications. Several luminescent/magnetic nanocomposite particles have been fabricated through the binding of a single layer of CdSe/ZnS nanocrystals on the surface of thiol-modified superparamagnetic Fe_2O_3 beads,[4] the simultaneous encapsulation of both CdTe nanocrystals and Fe_3O_4 nanoparticles in polymer microcapsules,[5] the surface-initiated atom-transfer radical polymerization (ATRP) of cadmium dimethacrylate on the surface of Fe_3O_4 nanoparticles and the thermal decomposition of thioacetamide,[6] and the layer-by-layer self assembly of CdTe nanocrystals and polyelectrolytes on the surface of Fe_3O_4 nanoparticles.[7]

Recently, we have developed a magnetic nanoadsorbent using Fe_3O_4 nanoparticles as the cores and poly(acrylic acid)-(PAA) as the ion-exchange group.[8] It possessed a high ion-exchange capacity and could recover positively charged enzymes and basic dyes quite fast and effectively.[8,9] After chemical modification with sulfanilic acid, the sulfonated magnetic nanoadsorbent exhibited a significantly improved ability to adsorb mono-, di-, and trivalent metal cations.[10] Herein, we proposed a novel approach to fabricate Fe_3O_4/CdS magnetic luiminescent nanocomposites by the adsorption of Cd^{II} ions and the subsequent precipitation with sodium sulfide on the surface of sulfonated magnetic nanoadsorbent, as schematically illustrated in Figure 1.

The sulfonated magnetic nanoadsorbent was prepared according to our previous work.[10] At first, Fe_3O_4 nanoparticles were prepared by coprecipitation method. Then, PAA (degree of polymerization = 2000–3000) was bound and sulfonated with sulfanilic acid on the surface of Fe_3O_4 nanoparticles via carbodiimide activation. The resultant nanoparticles were superparamagnetic and have a mean core diameter of 13.5 nm and an isoelectric point of 2.45. Detailed information could be obtained

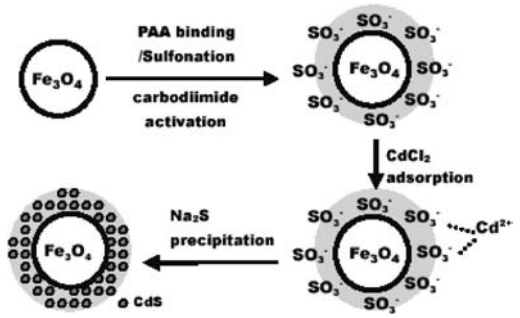

Figure 1. A scheme for the fabrication of magnetic luminescent nanocomposites.

elsewhere.[10] The equilibrium isotherm for the adsorption of Cd^{II} ions was obtained by contacting the sulfonated magnetic nanoparticles (23.6 mg/mL) with aqueous $CdCl_2$ solutions (8.9–78 mM) at pH 5 and 30 °C. The equilibrium was reached within several minutes. For the fabrication of magnetic luminescent nanocomposites, sulfonated magnetic nanoparticles (23.6 mg/mL) was contacted with 5 mL of $CdCl_2$ solution (0.1 M) at first. After equilibrium, the aqueous solution was removed by holding the Cd^{II} ion-adsorbed nanoparticles using a permanent magnet. Then, 3.5 mL of Na_2S solution (0.1 M) was added to lead to the precipitation of CdS nanocrystals on the sulfonated magnetic nanoparticles. To obtain a significant CdS amount, the adsorption–precipitation process was repeated five times.

The equilibrium isotherm for the adsorption of Cd^{II} ions on the sulfonated magnetic nanoparticles was shown in Figure 2, in which q_e was the adsorption capacity (mmol/g) and C_e was the equilibrium concentration (mmol/L) in solution. The plot of C_e/q_e vs. C_e as shown in the inset yielded a straight line, revealing that the adsorption of Cd^{II} ions on the sulfonated magnetic

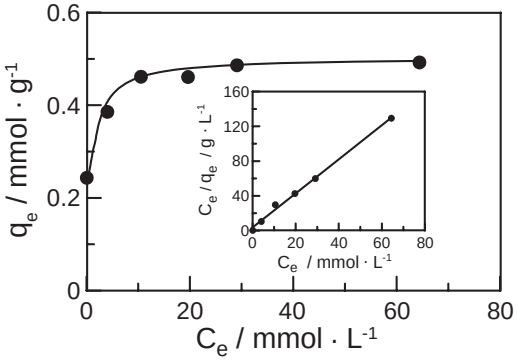

Figure 2. Adsorption isotherm of Cd^{II} ions on sulfonated magnetic nanoparticles at pH 5 and 30 °C. The inset is the Langmuir plot.

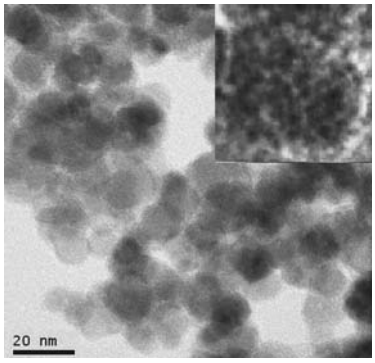

Figure 3. TEM micrograph of magnetic luminescent nanocomposites. The inset indicates the high-resolution image.

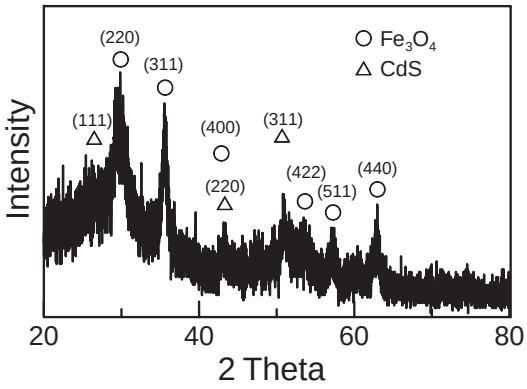

Figure 4. XRD pattern of magnetic luminescent nanocomposites.

nanoparticles obeyed the Langmuir adsorption isotherm. From the slope and intercept, the maximum adsorption capacity and Langmuir adsorption equilibrium constant could be estimated as 0.503 mmol/g and 1.05 L/mmol, respectively.[9]

Figure 3 is the typical transmission electron microscope (TEM) image for magnetic luminescent nanocomposites. Their morphologies were essentially similar to that before the adsorption–precipitation of Cd^{II} ions.[10] However, the high resolution TEM image (shown in the inset) indicated that the CdS nanocrystals of about 1 nm were formed on a sulfonated magnetic nanoparticle of about 14 nm. In addition, the analysis of energy dispersive X-ray (EDX) spectrum revealed the presence of Cd and S on the particle surface. Also, except those for Fe_3O_4, the X-ray diffraction (XRD) pattern (Figure 4) showed three characteristic peaks of CdS at $2\theta = 26.6$, 43.7, and 51.5°, which related to the (111), (220), and (311) crystalline planes, respectively. Both analyses confirmed the formation of magnetic luminescent nanocomposites.

The UV–vis absorption and photoluminescence (PL) spectra of magnetic luminescent nanocomposites were shown in Figure 5. The broad absorption essentially was resulted by iron oxides as observed previously.[6,11] The shoulder peak centered at 372 nm corresponded with the absorption spectra of CdS nanocrystals reported in the literature.[12] The band gap energy, calculated as 3.34 eV, was higher than the bulk value (2.53 eV)[1] because of the small size. According to the Brus equation,[13] the particle size could be estimated to be 1.48 nm. This was in agreement with that observed from the HRTEM image. The

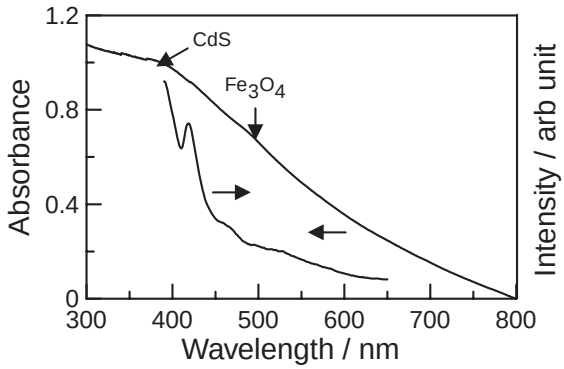

Figure 5. Absorption and photoluminescence spectra of magnetic luminescent nanocomposites in ethanol.

fluorescent spectrum shows an emission maximum at 419 nm owing to the band-edge emission, consistent with the literature value of CdS nanocrystals[14] and confirming the formation of CdS nanocrystals. The quantum yield of the nanocomposite was about 0.6% determined by using Rhodamine B/ethanol solution (QY0.95 in ethanol) as a comparative standard.[15]

In summary, we have demonstrated the fabrication of Fe_3O_4/CdS magnetic luminescent nanocomposites by the adsorption–precipitation of Cd^{II} ions on the sulfonated iron oxide nanoparticles. This novel approach could be extended to other semiconductor nanocrystals by using different metal cations and precipitation agents.

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