Facile One-Pot Synthesis of Bifunctional Heterodimers of Nanoparticles: A Conjugate of Quantum Dot and Magnetic Nanoparticles

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This communication reports a simple chemical synthetic route for producing heterodimers of nanoparticles that have sizes of around 7 nm and are composed of magnetic nanoparticles and semiconductor colloids (quantum dots). In the rapidly advancing field of materials science, colloidal nanocrystals, especially quantum dots[1,2] and magnetic nanoparticles,[3,4] have attracted broad attention and promise new applications because their mechanical, optical, electrical, magnetic, or chemical properties distinguish them from the corresponding bulk solid or liquid. The successful applications of nanoparticles require the ability to tune their properties. Besides the control of the size and composition of the spherical nanoparticles, their special properties are influenced by their shapes or long-range orders, which remain an important research goal under development.[5,6] One of the simple strategies to generate nonspherical nanoparticles is to form asymmetrical dimers or heterodimers of two nanoparticles of different kinds. This has been achieved on the submicrometer scale via self-assembly and assistance through surface dewetting.[6] The direct chemical synthesis of such dimers composed of distinct parts on the nanoscale (e.g., ∼10 nm) has yet to be developed.

In this work, we report on a one-pot chemical synthesis method for generating heterodimers of nanoparticles by taking advantage of lattice mismatching and selective annealing at a relatively low temperature. In particular, we deposited amorphous CdS on the surface of FePt nanoparticles to form a metastable core–shell structure, in which the CdS transformed into a crystalline state upon heating. Because of the incompatibility of the lattices of FePt and CdS and the surface tension when they are dispersed in solution, the FePt@CdS core–shell nanoparticles evolve into heterodimers of CdS and FePt nanocrystals, which have sizes less than 10 nm and exhibit both superparamagnetism and fluorescence. This procedure offers a simple and easy method for creating various types of heterostructures on the nanodimension, for increasing the complexity and integrating multiple functions in a nanoparticle, and for initiating new technological applications of nanomaterials.

Scheme 1 illustrates the typical synthetic route. By using the procedure reported by Sun et al.,[4] the thermolysis of $Fe(CO)_5$ and the reduction of $Pt(acac)_2$ by hexadecane-1,2-diol produces FePt magnetic nanoparticles (**1**) in dioctyl ether in the presence of oleylamine and oleic acid. Without separation or purification, the addition of suitable amounts of elemental sulfur to the dioctyl ether solution at 100 °C allows the sulfur to be deposited on the surface of FePt to form **2**.[7] The subsequent addition of trioctylphosphineoxide (TOPO), hexadecane-1,2-diol, and $Cd(acac)_2$ at 100 °C produces **3**, likely a metastable core–shell nanostructure, in which CdS is amorphous.[7] Raising the solution temperature to 280 °C converts CdS from its amorphous to a crystalline state, accompanied by a dewetting process, and results in the heterodimers of CdS and

Scheme 1
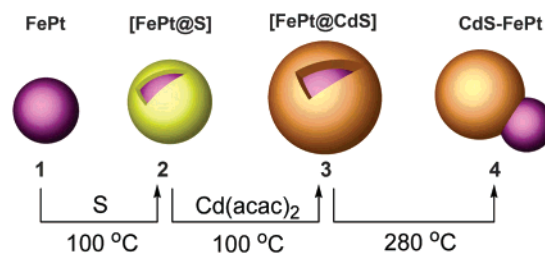
FePt nanoparticles. After the reaction is completed, these heterodimers are purified by ethanol and hexane to give the brown-colored final product (**4**), which is stored under nitrogen.

Figure 1A shows a transmission electron micrograph (TEM) of the as-prepared FePt nanoparticles before adding sulfur, which have an average diameter of 2.5 nm. Selected area electron diffraction (SAED) indicates that **1** has a disordered face-centered cubic (FCC) phase.[7] The attempt to produce large amounts of well-defined FePt@S and FePt@CdS core–shell nanoparticles was unsuccessful, probably because the shell of amorphous S or CdS was impaired during the process of isolating these two intermediates. The TEM analysis, however, reveals residues of S or CdS on the surface of FePt in the particles obtained in the intermediate stages.[7] Figure 1B displays the almost monodispersed **4** after the reaction is completed. The diameters of the FePt parts remain at 2.5 nm, and the CdS parts have diameters of ∼3 to 4 nm. A high-resolution TEM image shows that the CdS parts are crystalline (Figure 1C). The SAED image (Figure 1D) of **4** displays the rings that originate from the zinc blende phase of CdS ({111}, {220}, and {311} planes) and the disordered FCC phase of FePt ({111}, {200}, {220}, and {311} planes). In addition, X-ray fluorescence spectrum (XRF) analysis[7] indicates that the ratio of Fe/Pt/Cd/S is about 1:1:3:3.6, corresponding to FePt/CdS = ∼1:3, which also agrees with the volume ratio between FePt and CdS shown by TEM. The small excess amount of sulfur likely forms the junction between FePt and CdS.

The above data agree well with the process depicted in Scheme 1, in which the key factors are the mismatch of the lattice spacing and the phase transition occurring at a relatively low temperature. The conservation of the composition and structure of each part in **4** implies that the properties of the individual parts should also remain. To confirm this assumption, we measured the magnetic and optical properties of **4**.

Magnetic measurements of **4** were performed immediately after the synthesis. Standard zero-field cooling (ZFC) and field cooling measurements (Figure 2A) give an estimated blocking temperature of ∼11 K. The well-defined sharp peak indicates the uniform sizes of FePt parts in **4** and rather weak magnetic dipolar interactions between the FePt parts in the sample, further proved by the fact that the extrapolation of the plot of 1/m vs T passes the origin
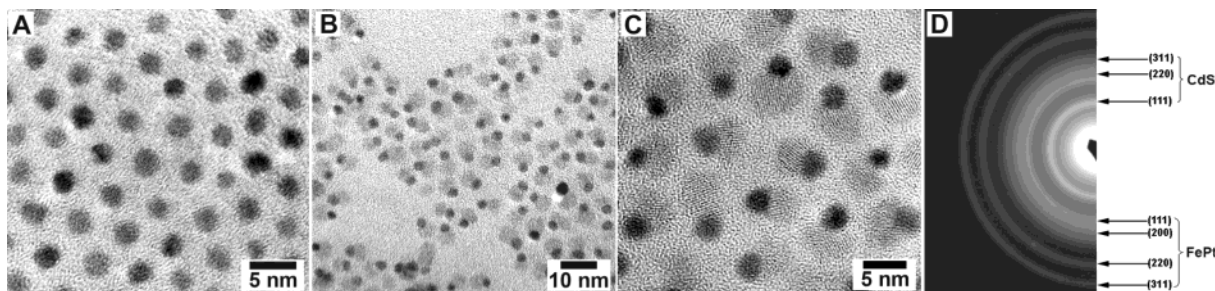
Figure 1. (A) A TEM image of **1** before being converted to **4**, (B) a TEM image and (C) a high-resolution TEM image of **4**, and (D) EDP of **4**.
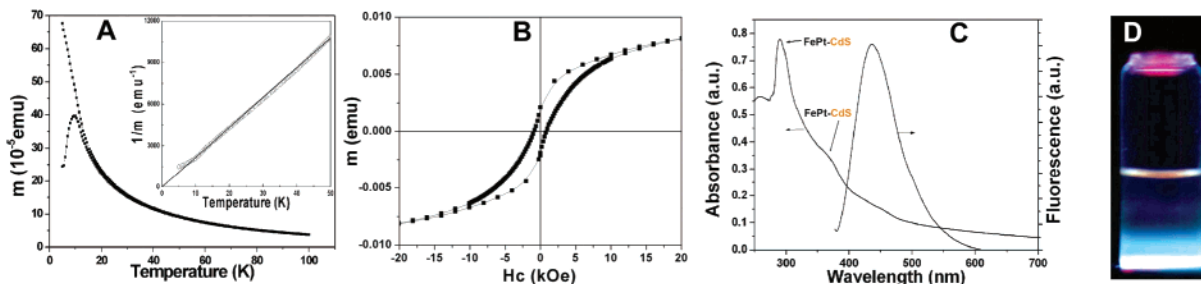

Figure 2. (A) Temperature-dependent magnetization (ZFC/FC) measured with a magnetic field of 100 Oe (inset: FC, 1/m vs T), (B) the hysteresis loop obtained at 5 K of **4**, (C) the UV−vis and fluorescent spectra (λ_{ex} = 365 nm) of **4** in hexane, and (D) a fluorescent image of the hexane solution of **4**.

(Figure 2A, inset). Using the average diameter of the FePt parts (~2.5 nm) observed by TEM and the relation of $t_{mes} = \tau_0 \exp(K_u V/k_B T_B)$, where t_{mes} = 30 s and $\tau_0 \approx 10^{-10}$ second, the estimate of the magnetic anisotropy constant, K_u, is ~2.4 × 10^6 erg/cm^3, which is the same as that of the as-prepared FePt nanoparticles[7] and comparable with literature values.[8] The field-dependent magnetization measured at 5 K displays hysteretic behavior and gives a coercivity (H_c) of ~0.85 kOe (Figure 2B). As indicated by the M−T and M−H curves, the magnetic properties of FePt in **4** are conserved. Figure 2C displays the UV−vis and fluorescent spectra of **4**. The absorption at 293 nm originates from the FePt parts, which agrees with the spectra of **1**[7] and previous observations.[9] The shoulder centered at 369 nm corresponds with the absorption spectra of CdS quantum dots reported in the literature.[1] The fluorescent spectrum of **4** shows an emission maxima at 438 nm (with quantum yield of 3.2%),[7] which is also consistent with the value in the literature of corresponding CdS nanocrystals.[10] Upon illumination of a hand-held UV lamp, the CdS parts of **4** give off blue emission (Figure 2D), which further confirms that the properties of CdS are preserved.

In summary, we have shown that a heterodimer of two nanocrystals with discrete properties can be made easily by sequential chemical synthesis of two components having different lattice spacings and phase transition temperatures. Since lattice spacing and phase transition temperature are fundamental properties associated with each material, this process should allow the production of large quantities of various types of heterostructures on the nanoscale. It is also possible to decorate each part of the dimer with a different surface chemistry. Although we demonstrated the formation of bifunctional dimers in this work, the generation of other multifunctional dimers or oligomers should be possible.

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