

# Lanthanide-Doped Nanocrystals: Synthesis, Optical-Magnetic Properties, and Applications

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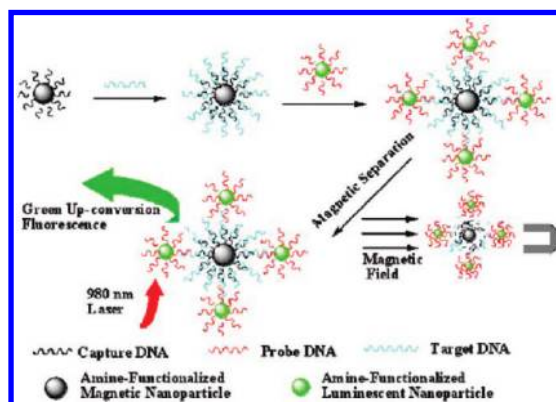
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## CONSPECTUS

**B**ecause of the potential applications of lanthanide-doped nanocrystals in display devices, optical communication, solid-state lasers, catalysis, and biological labeling, the controlled synthesis of these new nanomaterials has sparked considerable interest. Nanosized phosphorescent or optoelectronic devices usually exhibit novel properties, depending on their structures, shapes, and sizes, such as tunable wavelengths, rapid responses, and high efficiencies. Thus, the development of facile synthetic methods towards high-quality lanthanide-doped nanocrystals with uniform size and shape appears to be of key importance both for the exploration of their materials properties and for potential applications.

This Account focuses on the recent development in our laboratory of the synthesis and applications of lanthanide-doped nanocrystals. Since 2005, when we proposed a general strategy for nanocrystal synthesis via a liquid–solid–solution process, a range of monodisperse and colloidal lanthanide-doped fluoride, oxide, hydroxide, orthovanadate, thiooxide, borate, and phosphate nanocrystals have been successfully prepared. By rationally tuning the reaction conditions, we have readily synthesized nanostructures, such as hollow microspheres, nanorods, nanowires, hexagonal nanoplates, and nanobelts. By adjusting the different colloidal nanocrystal mixtures, we fabricated unique binary nanostructures with novel dual-mode luminescence properties through a facile ultrasonic method.

By tridoping with lanthanide ions that had different electronic structures, we successfully achieved  $\beta$ - $\text{NaYF}_4$  nanorods that were paramagnetic with tuned upconversion luminescence. We have also used  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  combined with magnetite nanoparticles as a sensitive detection system for DNA:  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  and  $\text{Fe}_3\text{O}_4$  nanoparticles were modified with two different DNA sequences. Then, the modified  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  nanoparticles were conjugated to the modified  $\text{Fe}_3\text{O}_4$  nanoparticles. These binary nanoparticles can be hybridized with a third DNA (target DNA) molecule and separated with the assistance of a magnetic field. In addition, a novel fluorescence resonance energy transfer (FRET) method for nonenzymatic glucose determination has been developed by using the glucose-modified  $\text{LaF}_3:\text{Ce}^{3+}/\text{Tb}^{3+}$  nanocrystals. By using bioconjugated  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  nanoparticles as the energy donor and bioconjugated gold nanoparticles as the energy acceptor, we successfully developed a simple and sensitive fluorescence resonance energy transfer (FRET) biosensor for avidin. Meanwhile, we also carried out preliminary studies to investigate possible applications of lanthanide-doped nanocrystals in catalysis and in dye-sensitized solar cells.



## 1. Introduction

In recent years, great effort has been devoted to the controllable synthesis of rare earth (RE)-doped nanoparticles driven primarily by the fact that doped nanocrystalline phosphors yielded high luminescence efficiencies.<sup>1</sup> With rapidly shrinking size, nanomaterials display novel shape- and size-dependent properties for their extremely small size and relatively large specific surface areas.<sup>2–6</sup> Based on these unique properties, RE-doped nanocrystalline materials

may play an outstanding role in display devices, optical telecommunication, solid-state lasers, and so on.<sup>7</sup> Therefore, the development of a facile synthetic method toward high-quality RE nanocrystals with uniform size and shape appears to be of key importance for the exploration of new research and application fields.<sup>8–12</sup>

RE-doped nanoparticles have been suggested as a promising new class of fluorescent probes. In comparison to organic dyes and semiconductor quantum dots, RE-doped

**TABLE 1.** The Crystal Structures, Morphologies, and Applications of Typical Ln-Doped Nanocrystals

|                                    | samples                                                                                                                                                             | crystal structure | morphology               | application             |
|------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|--------------------------|-------------------------|
| core@shell<br>hydroxides<br>oxides | CeO <sub>2</sub> @Ce <sub>1-x</sub> Zr <sub>x</sub> O <sub>2</sub>                                                                                                  | cubic             | hollow                   | catalysis               |
|                                    | Ln(OH) <sub>3</sub> , (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Tb, Ho, and Tm)                                                                                          | hexagonal         | nanowires                |                         |
|                                    | Ln <sub>2</sub> O <sub>3</sub> , (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Tb, Ho, and Tm)                                                                               | cubic             | nanowires<br>nanoflowers |                         |
| fluorides                          | CeO <sub>2</sub>                                                                                                                                                    |                   |                          | biology                 |
|                                    | NaYF <sub>4</sub> :Ln <sup>3+</sup> (Ln = Eu, Yb <sup>3+</sup> , Ho <sup>3+</sup> , Er <sup>3+</sup> , Tm <sup>3+</sup> , Gd <sup>3+</sup> , and Ce <sup>3+</sup> ) | hexagonal         | nanorods                 |                         |
|                                    |                                                                                                                                                                     | cubic             | nanoparticles            |                         |
|                                    | LaF <sub>3</sub> , CeF <sub>3</sub> , PrF <sub>3</sub> , and NdF <sub>3</sub>                                                                                       | hexagonal         | nanoparticles            |                         |
|                                    | SmF <sub>3</sub> and EuF <sub>3</sub>                                                                                                                               |                   | microparticles           |                         |
|                                    | GdF <sub>3</sub>                                                                                                                                                    | orthorhombic      | microparticles           |                         |
|                                    | YF <sub>3</sub>                                                                                                                                                     |                   | nanorices                |                         |
|                                    | CaF <sub>2</sub> :Yb <sup>3+</sup> /Er <sup>3+</sup>                                                                                                                | cubic             | nanoparticles            |                         |
|                                    | BaF <sub>2</sub> :Eu <sup>3+</sup>                                                                                                                                  | cubic             | nanoparticles            |                         |
|                                    |                                                                                                                                                                     | orthorhombic      | nanorods                 |                         |
| orthophosphate                     | LaPO <sub>4</sub>                                                                                                                                                   | monoclinic        | nanowires                | lasers and biology      |
|                                    |                                                                                                                                                                     | hexagonal         | nanorods                 |                         |
|                                    | YPO <sub>4</sub>                                                                                                                                                    | hexagonal         | nanorods                 |                         |
|                                    |                                                                                                                                                                     | tetragonal        | nanoparticles            |                         |
|                                    | CePO <sub>4</sub>                                                                                                                                                   | monoclinic        | nanowires                |                         |
|                                    | NdPO <sub>4</sub>                                                                                                                                                   |                   | nanorods                 |                         |
|                                    | PrPO <sub>4</sub> , EuPO <sub>4</sub> , and TbPO <sub>4</sub>                                                                                                       | hexagonal         | nanorods                 |                         |
|                                    | SmPO <sub>4</sub> and GdPO <sub>4</sub>                                                                                                                             |                   | nanowires                |                         |
|                                    | DyPO <sub>4</sub> and LuPO <sub>4</sub>                                                                                                                             | tetragonal        | nanoparticles            |                         |
|                                    | LnVO <sub>4</sub> (Ln = Y and lanthanides)                                                                                                                          | tetragonal        | nanosheets               |                         |
| orthovanadates                     |                                                                                                                                                                     |                   |                          | solar cells and biology |

nanocrystals show superior chemical and optical properties, including low toxicity, large effective Stokes shifts, sharp emissions, long fluorescence lifetimes, and high resistance to photobleaching.<sup>13–23</sup> In addition, these nanoparticles can enable time-resolved fluorescence imaging for quantitative detection of antigens as well as tissue-specific transcripts and genes. More importantly, the RE nanoparticles have the potential to be used for noninvasive, nondestructive, and real-time in vivo diagnosis of various diseases, including atherosclerotic plaques, which can lead to stroke and heart disease.<sup>24</sup>

Multimodal bioimaging is a new frontier in biology and medicine, which combines more than one imaging modality, such as optical, ultrasound, nuclear, and magnetic resonance imaging (MRI).<sup>25,26</sup> It is well-known that Gd<sup>3+</sup> complexes usually have paramagnetic properties at room temperature due to the 4f<sup>7</sup> electronic configuration of Gd<sup>3+</sup>. These paramagnetic Gd<sup>3+</sup> complexes are widely used as contrast agents in MRI owing to their enhancement of the relaxation of the neighboring protons.<sup>27</sup> And thus, by co-doping of Gd<sup>3+</sup> and other RE ions in nanocrystals, a novel material possessing the advantages of fluorescent and magnetic properties could be achievable.<sup>28</sup>

Our interest in the chemistry of RE-doped nanocrystals started in the early 2000s, when we proposed a general strategy (liquid–solid–solution process) for nanocrystal synthesis.<sup>29</sup> Since then, a range of monodisperse and colloidal RE-doped fluoride, oxide, hydroxide, oxyhydroxide, orthovanadate, thiooxide, borate, and phosphate nanocrystals have been successfully prepared.<sup>30–65</sup> Subsequently, the applications of RE nanocrystals in biology,

catalysis, and dye-sensitized solar cells were also studied preliminarily.<sup>66–74</sup>

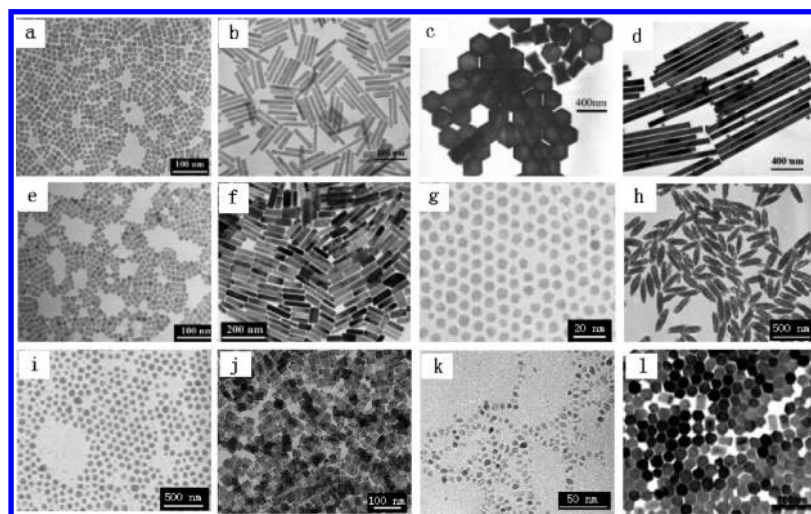
In this Account, we summarize the progress that we have made over the past decade in the study of this unique class of RE-doped nanocrystals. The crystal structure, morphology, and application of typical Ln-doped nanocrystals have been summarized in Table 1.

## 2. Synthetic Studies

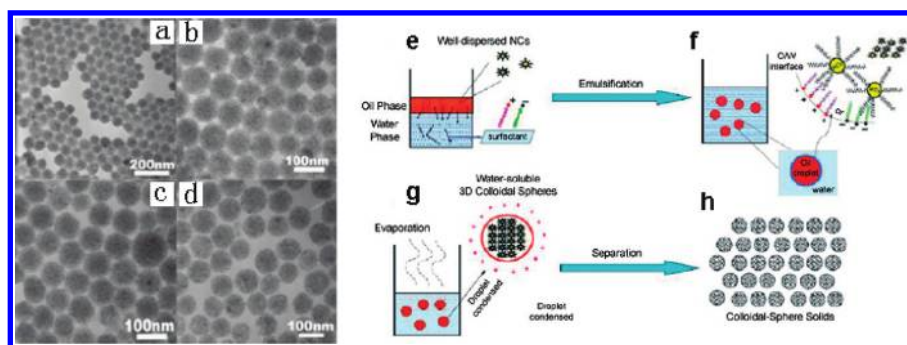
### 2.1. Liquid–Solid–Solution (LSS) Process for the Synthesis of Monodisperse RE Fluorescent Nanocrystals.

Over the past decade, monodisperse nanocrystals, which exhibit many interesting shape- and size-dependent phenomena and properties, have been extensively investigated for both their scientific and their technological applications.<sup>29–45</sup> Our group has reported a unified approach, the LSS process,<sup>29</sup> to the synthesis of a large variety of nearly monodisperse RE fluorescent nanocrystals with narrow size distribution (Figure 1). Detailed explanations of the LSS process can be found in ref 29. By tuning the synthetic conditions, such as dopant concentration, solvothermal temperature, and time, we have successfully prepared nanocrystals with different shapes. It is noted that the nanocrystals synthesized by the LSS process are hydrophobic. These hydrophobic nanocrystals could be further rendered hydrophilic by oxidizing oleic acid ligands on the surface of nanocrystals with Lemieux–von Rudloff reagent.<sup>13</sup>

**2.2. Synthesis of 3D Colloidal Spheres.** Using these dispersible RE nanocrystals mentioned above as building



**FIGURE 1.** Typical TEM images of (a)  $\text{NaYF}_4\text{:Tb}$ , (b,c)  $\text{NaYF}_4\text{:Eu}$ , (d–f)  $\text{NaYF}_4\text{:Yb-Er}$ , (g)  $\text{LaF}_3$ , (h)  $\text{YF}_3$ , (i)  $\text{YbF}_3$ , (j)  $\text{LaVO}_4\text{:Eu}$ , (k)  $\text{YBO}_3\text{:Eu}$ , and (l)  $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}$  nanocrystals.



**FIGURE 2.** Typical TEM images of (a)  $\text{LaF}_3\text{:Eu/LaF}_3\text{:Yb-Er}$ , (b)  $\text{NaYF}_4\text{:Tb/NaYF}_4\text{:Yb-Er}$ , (c)  $\text{LaF}_3\text{:Ce-Tb/NaYF}_4\text{:Yb-Er}$ , and (d)  $\text{LaF}_3\text{:Yb-Er}$ . (e–h) Schematic of the EBS method: (e) mixture of oil phase and water phase (nanocrystals capped with ligands, well-dispersed in cyclohexane, are added to an aqueous solution of surfactant); (f) formation of the microemulsion system (oil droplets containing nanocrystals are stabilized by surfactant at the interface); (g) Evaporation of the low-boiling solvent in the oil droplets at a specified temperature, and the assembly process of the nanocrystals in the confined oil droplets into 3D colloidal spheres, which can be well-dispersed in water; (h) separation of the assembled 3D colloidal sphere solids from the solutions.

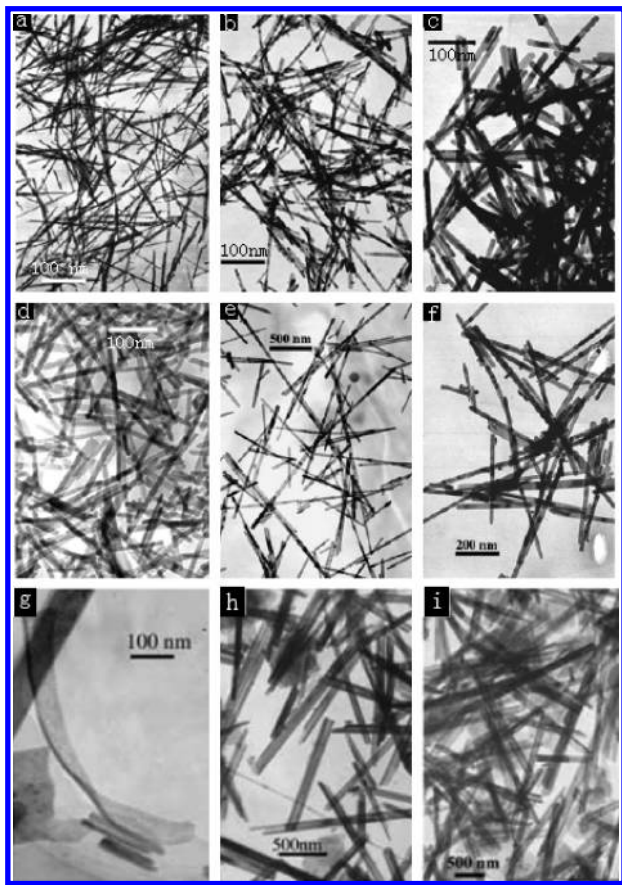
blocks, one can prepare 3D colloidal spheres by a simple microemulsion-based bottom-up self-assembly (EBS) method (Figure 2).<sup>30,35</sup> This method is based on a designed oil-in-water (O/W) microemulsion system. The nanocrystals are gathered, assembled, and fixed together spontaneously during controlled evaporation of a low-boiling oil solvent in the restricted, micrometer-sized 3D space provided by the microemulsion droplets. The composition, size, and surface charge of the colloidal spheres were controlled by rationally designing the experimental conditions.

**2.3. Hydrothermal Synthesis of RE Compound Nanocrystals.** Hydrothermal methods have been shown to be effective in the synthesis of nanowires, nanorods, and nanotubes.<sup>47,51,59,63</sup> Based on the preparation of RE hydroxide (or fluoride) colloidal precipitates at room temperature and the subsequent hydrothermal treatment at designated reaction conditions, a systematic study has been carried out to

investigate the controlled formation of nanowires, nanosheets, and nanotubes.<sup>51</sup> Figure 3a–f shows the TEM images of lanthanide hydroxide nanowires and nanotubes.<sup>47,51</sup> Detailed reaction mechanisms of the hydrothermal method are provided in ref 47.

Recently, our group synthesized lanthanide hydroxide nanocrystals by regularly decomposing RE nitrates in octadecylamine (ODA).<sup>65</sup> The results indicate that the electron configuration, ionic radius, and crystal structure of lanthanide ions are responsible for the morphologies of the nanocrystals. For larger  $\text{RE}^{3+}$  ions ( $\text{RE} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$ , and  $\text{Gd}$ ), the lanthanide hydroxides exhibit plate-like nanostructures. For smaller  $\text{RE}^{3+}$  ions ( $\text{RE} = \text{Y}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ , and  $\text{Yb}$ ), the lanthanide hydroxides exhibit belt-like nanostructures.  $\text{Tb}^{3+}$  is a mid-sized  $\text{RE}^{3+}$  ion, and  $\text{Tb}(\text{OH})_3$  nanocrystals are rod-like. By calcination, the corresponding RE oxides with the same morphologies as their precursors were





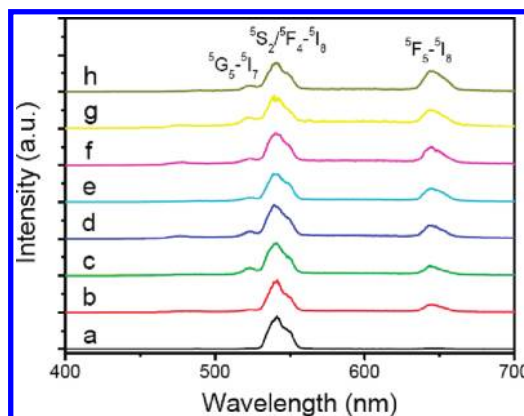
**FIGURE 3.** Typical TEM images of (a)  $\text{La}(\text{OH})_3$ , (b)  $\text{Pr}(\text{OH})_3$ , (c)  $\text{Eu}(\text{OH})_3$ , (d)  $\text{Ho}(\text{OH})_3$ , (e)  $\text{Sm}(\text{OH})_3$ , and (f)  $\text{Gd}(\text{OH})_3$  nanowires, (g)  $\text{Er}(\text{OH})_3$  nanobelts, (h)  $\text{Yb}(\text{OH})_3$  nanotubes, and (i)  $\text{Tm}(\text{OH})_3$  nanotubes.

obtained. It is imperative to point out that flower-like cerium oxide could be obtained directly from the decomposition of the nitrate without further calcination.

### 3. Optical and Magnetic Property Studies

**3.1. Tunable Upconversion (UC) Luminescence.** Considerable interest has been centered on the frequency UC from infrared radiation to shorter wavelengths by using laser diodes as pump sources and RE materials as active emissive media.<sup>6,7,10</sup> In particular, the ability to manipulate UC color output opens the door to more complex, multiplexed labeling. Utilization of varied dopant–host combinations is one of the most straightforward approaches to obtain multicolor UC luminescence.<sup>10</sup>

We have taken  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Ce}^{3+}$  nanorods as an example to obtain the multicolor UC luminescence of RE-doped nanocrystals (Figure 4).<sup>34</sup> The results indicated that the relative intensity of  $^5\text{F}_5 \rightarrow ^5\text{I}_8$  to  $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$  rises with increasing  $\text{Ce}^{3+}$  concentration, which can be attributed to the efficient energy transfers of  $^5\text{I}_6(\text{Ho}) + ^2\text{F}_{5/2}(\text{Ce}) \rightarrow ^5\text{I}_7(\text{Ho}) +$



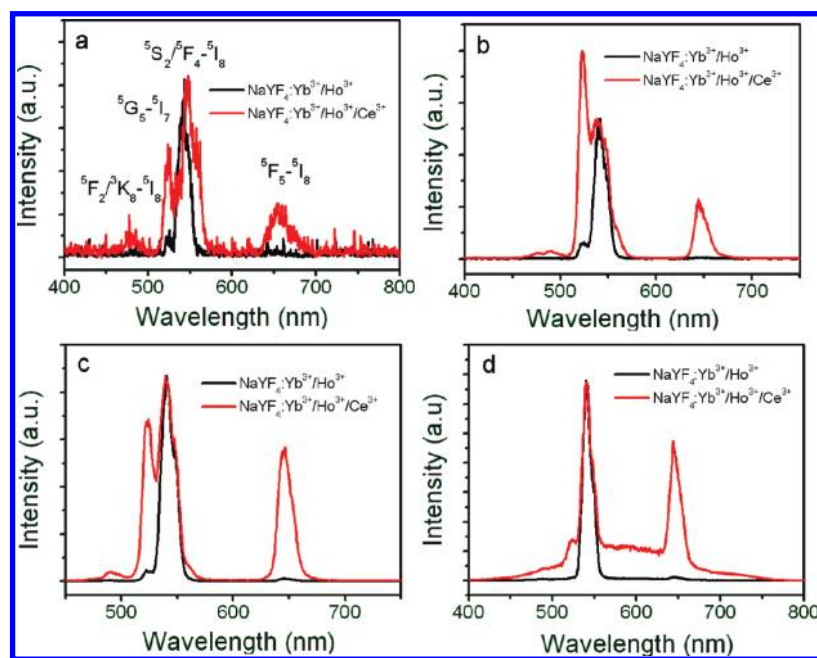
**FIGURE 4.** Dependence of UC luminescence spectra (normalized to  $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$  transitions) on  $\text{Ce}^{3+}$  concentration (20%  $\text{Yb}^{3+}$  and 2%  $\text{Ho}^{3+}$ ): (a) 0%; (b) 2%; (c) 3%; (d) 5%; (e) 10%; (f) 15%; (g) 20%; (h) 30%.

$^2\text{F}_{7/2}(\text{Ce})$  and  $^5\text{S}_2/^5\text{F}_4(\text{Ho}) + ^2\text{F}_{5/2}(\text{Ce}) \rightarrow ^5\text{F}_5(\text{Ho}) + ^2\text{F}_{7/2}(\text{Ce})$ . In addition, the  $^5\text{G}_5 \rightarrow ^5\text{I}_7$  and  $^5\text{F}_2/^3\text{K}_8 \rightarrow ^5\text{I}_8$  transitions of  $\text{Ho}^{3+}$  ions under infrared excitation were observed for the first time. With increasing  $\text{Ce}^{3+}$  concentration, the emission intensity of the  $^5\text{F}_5 \rightarrow ^5\text{I}_8$  gradually increased and that of the  $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$  gradually decreased.

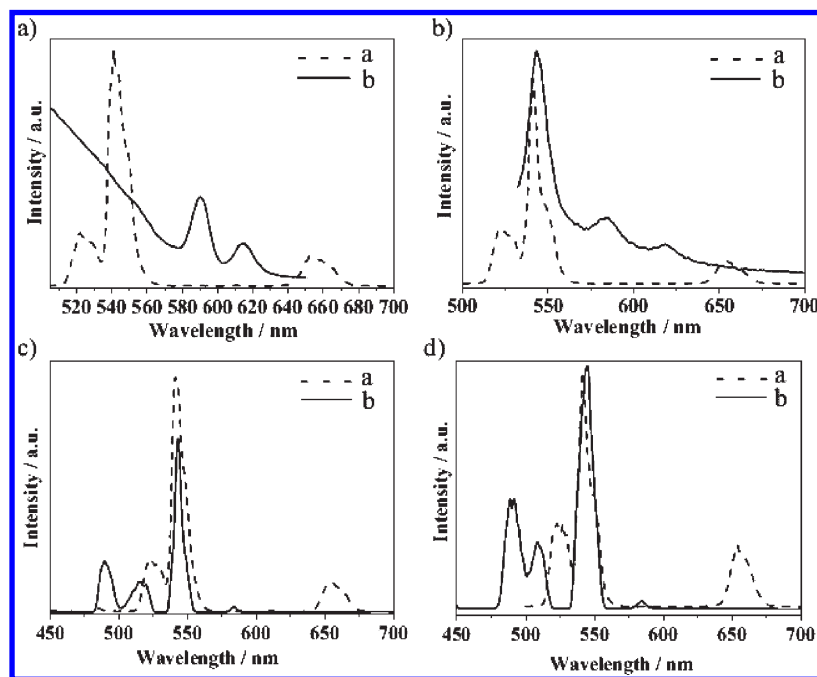
Another most important spectral feature of  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Ce}^{3+}$  nanorods is the dependence of UC luminescence upon the pump power (Figure 5). It is surprising to observe that the intensity ratio of  $^5\text{G}_5 \rightarrow ^5\text{I}_7$  to  $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$  of  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Ce}^{3+}$  nanorods fluctuates with increasing pump power density. However, the luminescence of  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Ho}^{3+}$  nanorods is always dominated by the  $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$ .

**3.2. Dual-Mode Luminescence from Hydrophilic RE Fluoride Colloidal Spheres.** In order to advance the applications of RE nanocrystals in multiplexed and highly sensitive bioassays, we fabricated hydrophilic dual-mode luminescent colloidal spheres that were composed of two distinct units, one offering down-converting luminescence under UV excitation and the other providing up-converting luminescence excited with a 980 nm laser.<sup>35</sup> Figure 6a shows the luminescence spectra of  $\text{LaF}_3:\text{Eu}/\text{LaF}_3:\text{Yb}-\text{Er}$  nanospheres. Under the excitation of 980 nm light, three emissions were observed, which are assigned to the  $^2\text{H}_{1/2} \rightarrow ^4\text{I}_{5/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{5/2}$ , and  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{5/2}$  transitions of  $\text{Er}^{3+}$  ions. When excited at 396 nm, the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$  were observed.

Figure 6b–d shows the luminescence spectra of  $\text{NaYF}_4:\text{Tb}/\text{NaYF}_4:\text{Yb}-\text{Er}$ ,  $\text{LaF}_3:\text{Ce}-\text{Tb}/\text{NaYF}_4:\text{Yb}-\text{Er}$ , and  $\text{LaF}_3:\text{Ce}-\text{Tb}/\text{LaF}_3:\text{Yb}-\text{Er}$  nanospheres. Similar to  $\text{LaF}_3:\text{Eu}/\text{LaF}_3:\text{Yb}-\text{Er}$  nanospheres, under 980 nm excitation, the emissions of  $\text{Er}^{3+}$  were observed. Under UV excitation, there are four emission peaks of  $\text{Tb}^{3+}$  at  $\sim 489$ ,  $\sim 543$ ,  $\sim 587$ , and



**FIGURE 5.** UC luminescence spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Ho<sup>3+</sup> (20/2) and NaYF<sub>4</sub>:Yb<sup>3+</sup>/Ho<sup>3+</sup>/Ce<sup>3+</sup> (20/2/30) nanorods under different excitation power density: (a) 140; (b) 300; (c) 450; (d) 680 W/cm<sup>2</sup>.

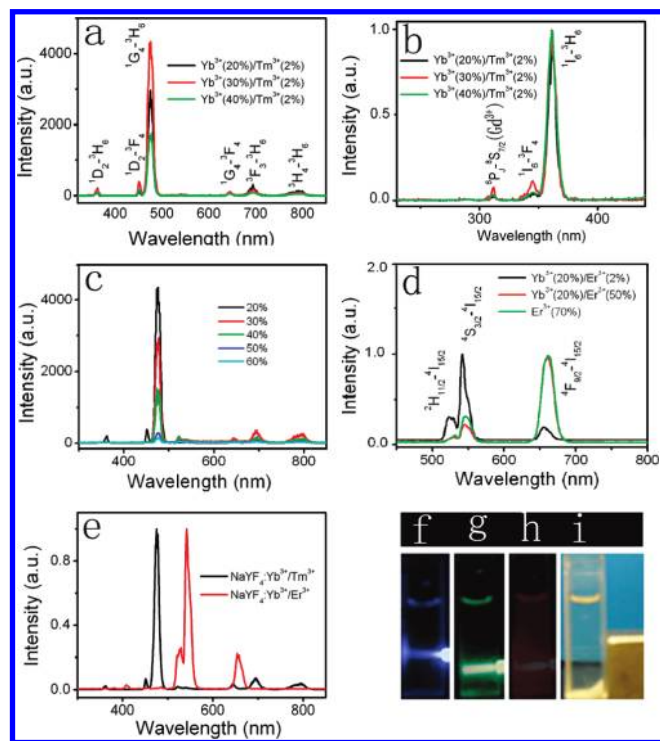


**FIGURE 6.** Down- and up-converting luminescence spectra of the as-obtained nanospheres: (a) LaF<sub>3</sub>:Eu/LaF<sub>3</sub>:Yb–Er; (b) NaYF<sub>4</sub>:Tb/NaYF<sub>4</sub>:Yb–Er; (c) LaF<sub>3</sub>:Ce–Tb/NaYF<sub>4</sub>:Yb–Er; (d) LaF<sub>3</sub>:Ce–Tb/LaF<sub>3</sub>:Yb–Er (---, a, downconverting luminescence spectra; —, b, upconverting luminescence spectra).

~618 nm, attributed to the  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$ ,  $^5D_4 \rightarrow ^7F_4$ , and  $^5D_4 \rightarrow ^7F_3$  transitions, respectively. This strategy may provide new routes to rationally assemble nanometer-scale building blocks into multifunctional superstructures.

**3.3. Bifunctional Optical–Magnetic Nanorods:  $\beta$ -NaYF<sub>4</sub>:Ln<sup>3+</sup>.** As mentioned above, optical and magnetic

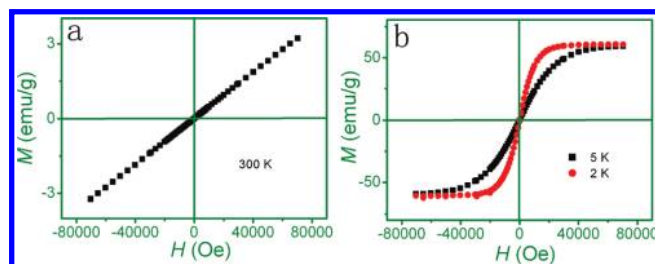
materials have attracted much attention due to their importance in the fields of chemistry, biology, medical sciences, and biotechnology. We successfully prepared bifunctional  $\beta$ -NaYF<sub>4</sub>:Ln<sup>3+</sup> (Ln = Yb/Gd/Tm and Yb/Gd/Er) nanorods according to our reported LSS strategy.<sup>34</sup> The obtained nanorods not only can exhibit paramagnetic behavior at room



**FIGURE 7.** UC luminescence spectra of (a,b) NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup> (x/30/2), (c) NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup> (30/x/2), and (d) NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Er<sup>3+</sup> (x/20/x) nanorods in cyclohexane. For comparison, the UC luminescence spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> and NaYF<sub>4</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup> nanorods are also shown panel e. Compiled luminescent photos showing corresponding colloidal solutions of (f) NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup> (30/20/2), (g) NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Er<sup>3+</sup> (30/20/2), (h) NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Er<sup>3+</sup> (20/70), and (i) the photo of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup> colloidal solution in the presence of a magnet.

temperature but also can emit fine-tuning UC emissions spanning from the UV to the near-infrared under 980 nm excitation.

The UC luminescent spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup>-(Er<sup>3+</sup>) nanorods are shown in Figure 7. Upon excitation at 980 nm, the NaYF<sub>4</sub> nanorods doped with Yb/Gd/Tm exhibit characteristic sharp emission peaks, which can be attributed to the <sup>6</sup>P<sub>5/2</sub> → <sup>8</sup>S<sub>7/2</sub> and <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transitions of Gd<sup>3+</sup> and the <sup>1</sup>I<sub>6</sub> → <sup>3</sup>F<sub>4</sub>, <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>6</sub>, <sup>1</sup>D<sub>2</sub> → <sup>3</sup>F<sub>4</sub>, <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub>, <sup>1</sup>G<sub>4</sub> → <sup>3</sup>F<sub>4</sub>, <sup>3</sup>F<sub>3</sub> → <sup>3</sup>H<sub>6</sub>, and <sup>3</sup>H<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transitions of Tm<sup>3+</sup>. The optimum concentrations of Yb<sup>3+</sup> and Gd<sup>3+</sup> ions are 30% and 20%, respectively. Here, the Ln<sup>3+</sup> concentrations refer to the initial dopant concentrations of reactants. The UC emission spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Er<sup>3+</sup> nanorods are shown in Figure 7d. These emission peaks can be attributed to the <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub>, and <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions of Er<sup>3+</sup> ions. It is noted that upon doping with increased concentrations of Yb<sup>3+</sup> and Er<sup>3+</sup>, one can precisely manipulate the relative emission intensities of the two constituent



**FIGURE 8.** Magnetization curves of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup> nanorods.

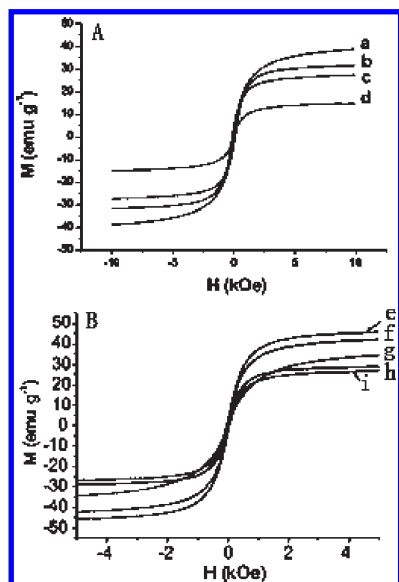
colors, thus resulting in tunable color output of the nanorods from green to red.

Apart from the aforementioned luminescence properties, the NaYF<sub>4</sub>:Yb<sup>3+</sup>(30%)/Gd<sup>3+</sup>(40%)/Tm<sup>3+</sup>(2%) nanorods are paramagnetic at room temperature (Figure 8). At 2 or 5 K, the nanorods are superparamagnetic with saturation magnetization value of about 60 emu g<sup>-1</sup>. It is well-known that the magnetic behavior is highly size dependent. When the size of the ferromagnetic particles is reduced to a critical value, the magnetic property is no longer ferromagnetic but superparamagnetic. Usually, Gd<sup>3+</sup> complexes have paramagnetic properties beyond magnetic ordering temperature and exhibit magnetic order below the magnetic ordering temperature. In this work, the average diameter of nanorods is ~50 nm, and thus, it is not surprising to observe that NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup> nanorods are superparamagnetic at 2 or 5 K. These UC luminescent and paramagnetic properties of the nanorods underscore their potential as robust UC luminescence and magnetic resonance dual-mode fluorescent labels for bioimaging applications. It is noted that the magnetic susceptibility of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Gd<sup>3+</sup>/Tm<sup>3+</sup> increased with increasing Gd<sup>3+</sup> concentration.

**3.4. Tunable Magnetic Properties of Magnetite by RE Doping.** Nanometer-sized iron oxides and oxyhydroxide compounds are of great industrial and scientific importance. For example, nanoparticulate magnetite has been widely applied in catalysis, energy storage, magnetic data storage, and ferrofluids for its unique electric and magnetic properties. Doped iron oxides, especially the spinel-structured MFe<sub>2</sub>O<sub>4</sub>, have shown tunable magnetic properties and attracted research interest for magnetic storage and catalysis.<sup>67</sup>

Five kinds of RE ions (Gd, Sm, Nd, Y, and Lu) were selected to be doped into magnetite to investigate the influence of RE doping on the magnetic properties of magnetite.<sup>67</sup> Here, the concentrations of the RE ions are 50%. The results indicate that lanthanide ions have a great effect on the magnetic properties of magnetite (Figure 9e–i). For comparison, the magnetization curves of undoped magnetite nanoparticles with different sizes are shown in Figure 9a–d. Magnetite





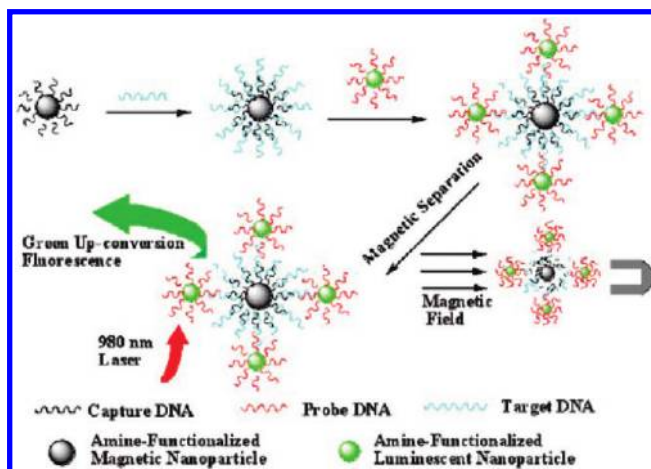
**FIGURE 9.** (A) Magnetization curves for undoped magnetite nanoparticles with different sizes: (a) 15.8, (b) 14.5, (c) 6.4, and (d) 4.7 nm. (B) Magnetization curves for magnetite doped with different kinds of lanthanides: (e) Gd, (f) Sm, (g) Lu, (h) Y, and (i) Nd.

samples doped with  $\text{Gd}^{3+}$  have the highest saturation magnetization of  $45.9 \text{ emu g}^{-1}$ . In contrast, the sample doped with  $\text{Nd}^{3+}$  has the smallest saturation magnetization of  $26.8 \text{ emu g}^{-1}$ . It can also be seen from the magnetization curves that the powders doped with Sm, Lu, and Gd are superparamagnetic with zero coercivity in contrast to the samples doped with Nd and Y, which exhibit a small hysteresis loop.

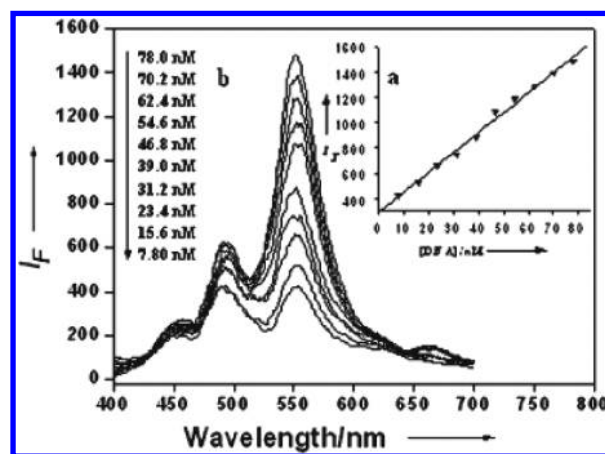
## 4. Application Exploration

**4.1. Biological Applications.** Optical and magnetic materials have attracted much attention due to their importance in the fields of chemistry, biology, medical sciences, and biotechnology. By combination of magnetic-field-assisted biochemical separation and concentration technology, novel composite materials of  $\text{Fe}_3\text{O}_4$  and  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  have been applied to the sensitive detection of DNA (Figure 10).<sup>69</sup> The luminescent nanoparticles we chose were water-soluble  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  with a mean size of about 50 nm. Under 980 nm excitation, these nanoparticles can emit strong green UC fluorescence. The magnetic nanoparticles applied here were  $\text{Fe}_3\text{O}_4$ . These magnetic nanoparticles have an average size of about 150 nm with a smooth surface. The measurements of magnetic properties reveal that these magnetite nanoparticles have excellent saturation magnetization up to  $83.1 \text{ emu g}^{-1}$ .

Both the magnetic and luminescent nanoparticles were functionalized with polyelectrolyte using layer-by-layer (LbL) technology to introduce an amino group that could be



**FIGURE 10.** Scheme of the DNA assay method combining UC fluorescence with magnetic separation.



**FIGURE 11.** Fluorescence spectra of binary nanocomposite in the presence of different concentrations of target DNA (b) and the linear relationship (a) between luminescence intensity and target DNA content according to panel b.

attached to nucleic acids (Figure 10). In a typical experiment for DNA detection, magnetic nanoparticles were modified with capture DNA (39-AAT-TGA-GGA-GAA-AGA-A<sub>10</sub>-(CH<sub>2</sub>)<sub>3</sub>-SH) and phosphor nanoparticles were modified with probe DNA (59-TCC-ATG-CAA-CTC-TAA-A<sub>10</sub>-(CH<sub>2</sub>)<sub>3</sub>-SH), respectively. These capture DNA modified magnetite nanoparticles can be hybridized with target DNA (59-TTA-GAG-TTG-CAT-GGA-TTA-ACT-CCT-CTT-TCT-39) and separated with an assistant magnetic field. Then, the probe DNA modified luminescent nanoparticles were conjugated to the magnetic nanoparticles through the hybridization with the overhanging region of the target sequences. The binary nanoparticles were purified with magnetic separation and detected with UC fluorescence technology. As shown in Figure 11, the concentration of the target DNA in the range

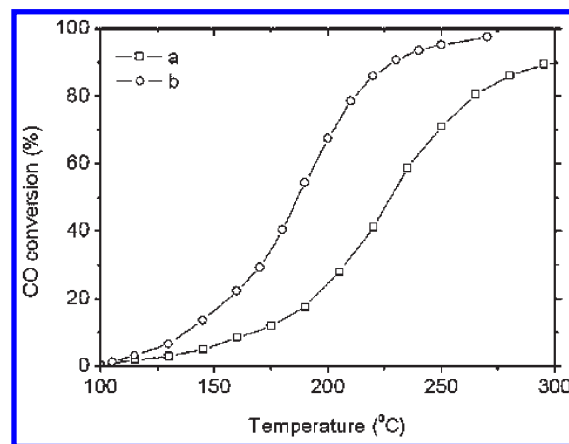
of 7.8–78.0 nM is linear to the UC luminescence intensities. The linear calibration equation,  $F_{UC} = 292.4 + 15.7C$  of the detection was obtained according to the general detection procedure.  $F_{UC}$  and  $C$  represented the intensity of luminescence and the concentration of the target DNA, respectively.

In addition, by use of bioconjugated  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  nanoparticles as energy donor and bioconjugated gold nanoparticles as energy acceptor, a simple and sensitive fluorescence resonance energy transfer (FRET) biosensor for avidin has been successfully developed.<sup>68</sup> Based on FRET between nonenzymatic glucose modified  $\text{LaF}_3:\text{Ce}^{3+}/\text{Tb}^{3+}$  nanocrystals and the 3-aminophenylboronic acid modified rhodamine B isothiocyanate, we have also demonstrated a novel biosensor for the detection of glucose.

**4.2. Catalytic Applications.** Nanosized RE compounds present great promise and opportunities for a new generation of catalysts. It is known that the reactivity depends on the crystal plane of the catalyst for structure-sensitive reactions.<sup>72,76–78</sup> Therefore, a desirable goal for catalyst design and synthesis would be to decrease the area of the less reactive crystal planes and increase that of the more reactive ones so as to optimize the desired structure of the active sites. Shape-controlled synthesis of nanostructured materials may present an opportunity for the synthesis of catalytic materials with such desirable features because these novel materials nucleate and grow in an epitaxial manner, exposing defined crystal planes.

Here, we take  $\text{CeO}_2$  as an example to study the crystal plane effect of RE nanocrystals in catalysis application.<sup>72</sup> There are three low-index planes in the ceria fluorite cubic structure, namely, the very stable and neutral  $\{111\}$  plane, the less stable  $\{110\}$  plane, and the higher-energy  $\{001\}$  plane. Yang et al. have found that there are different adsorption features for CO on  $\{111\}$  and  $\{110\}$  planes. There are only weak adsorptions on the  $\{111\}$  plane,<sup>75</sup> whereas both weak and strong adsorptions are found on the  $\{110\}$  plane. If exposed planes with higher surface energy could be generated and stabilized, they could provide active sites for catalytic reactions.

$\text{CeO}_2$  nanorods and nanoparticles were synthesized via a hydrothermal method and a direct precipitation method, respectively. The HRTEM results reveal that  $\text{CeO}_2$  nanorods predominantly expose the well-defined and less stable  $\{001\}$  and  $\{110\}$  planes, whereas in the  $\text{CeO}_2$  nanoparticles, the most stable  $\{111\}$  planes are predominantly exposed. Measurements were made of the catalytic activity of CO oxidation (Figure 12). Obviously,  $\text{CeO}_2$  nanorods were more active than  $\text{CeO}_2$  nanoparticles. At 190 °C, the percentage CO



**FIGURE 12.** Percentage conversion versus temperature plots for the oxidation of CO over (a)  $\text{CeO}_2$  nanoparticles and (b)  $\text{CeO}_2$  nanorods.

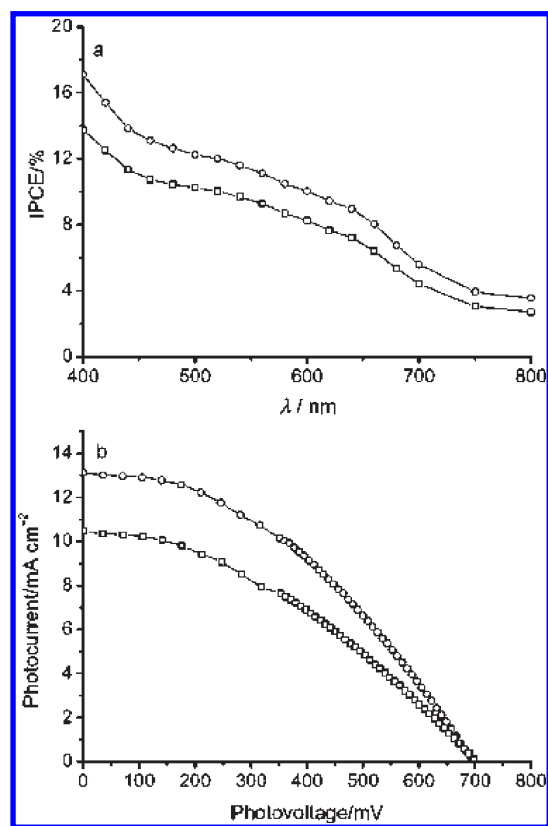
conversion was 40% over the  $\text{CeO}_2$  nanorods and only 17% over the nanoparticles. The rate of conversion of CO over  $\text{CeO}_2$  nanorods was three times higher than that over nanoparticles.

In general, high-surface-area nanocatalytic materials exhibiting numerous crystal faces, edges, and corners, which are conventionally considered active sites for the adsorption of reactants, should generate better catalytic performance. However,  $\text{CeO}_2$  nanoparticles, with higher surface area and smaller particle size, were poorer catalysts, whereas  $\text{CeO}_2$  nanorods, with lower surface area and larger diameter, were more active and demonstrated a stable redox property. These unusual results for these two ceria nanomaterials inspire us to hope that specific crystal planes are indeed a determining factor that will prove useful. Similar phenomena were observed in the study on the catalytic performance of CuO and Ag nanocrystals with different shapes.

Recently, our group selected  $\text{Er}_2\text{O}_3$  nanobelts as catalyst supports and investigated the catalytic activity of Au-nanoparticle-deposited  $\text{Er}_2\text{O}_3$  nanocatalysts for CO oxidation. Although  $\text{Er}_2\text{O}_3$  nanobelts might not be the most excellent support in the case of Au-supported catalysts for CO oxidation, the experiment indicates their potential applications as catalysts or catalyst supports for other important reactions such as selective oxidation of ethane to ethylene.

**4.3. The Application of RE Nanocrystals in Dye-Sensitized Solar Cells.** Dye-sensitized solar cells (DSSCs) have been investigated intensively as a cost-effective alternative to conventional solar cells.<sup>70</sup> In DSSCs,  $\text{TiO}_2$  films have been widely used as the photoanode onto which dye sensitizers were adsorbed. Some researchers have reported that the photoanodes prepared from organized mesoporous  $\text{TiO}_2$  films showed enhanced solar-cell conversion efficiency





**FIGURE 13.** (a) Action spectra and (b) current–voltage cures of DSSCs: (○) = modified; (□) = unmodified.

relative to that of traditional films of the same thickness made from randomly oriented anatase nanocrystals. Therefore, replacing the nanoparticle film with an array of oriented single-crystalline nanowires was investigated. Unfortunately, the efficiency was limited because of the small surface area of the nanowires. Therefore, it is important to modify the titania electrodes for enhancing solar-cell conversion efficiency.

RE ions have unique electronic structures and numerous transition modes, and thus, by introducing RE ions into the photoanode of the DSSCs, some novel properties can be expected. Monodisperse Nd-doped  $\text{TiO}_2$  nanorods ( $20 \text{ nm} \times 2 \text{ nm}$ ) were synthesized by a solvothermal method.<sup>67</sup> These nanorods were easily embedded into the  $\text{TiO}_2$  electrode in DSSCs and did not affect the adsorption amount of dye sensitizer. The result indicates that this incorporation of Nd-doped  $\text{TiO}_2$  nanorods into  $\text{TiO}_2$  electrode remarkably enhanced the short-circuit photocurrent and the fill factor, thus leading to a 33.3% increase in power conversion efficiency (Figure 13).<sup>67</sup> The mechanism is likely to be that Nd ions doped on  $\text{TiO}_2$  nanorods to enhance the injection of excited electrons and decrease the recombination rate of the injected electrons. The introduction of rods not only decreases the total series resistance of a cell but also

accelerates the transport rate of the injected electrons, consequentially improving the collection rate of injected electrons. The incorporation of Nd-doped  $\text{TiO}_2$  nanorods into randomly assembled mesoporous films is a novel strategy to modify the photoanode in DSSCs.

We also prepared transparent  $\text{Dy}^{3+}$ -doped  $\text{LaVO}_4$  film, which was used to coat solar cells. By combination of Dy-doped  $\text{LaVO}_4$  luminescent film onto the back of the solar cell, the lifetime of the solar cell was greatly enhanced.<sup>66</sup> Especially, the downconverted light can be reabsorbed by solar cell and generate current; hence the solar cell with the luminescent film improved energy conversion efficiency by 23.3% relative to the referenced one coated with an undoped  $\text{LaVO}_4$  film.

## 5. Conclusion and Perspectives

This Account summarizes our recent progress on the synthesis, properties, and applications of lanthanide-doped nanocrystals. The growing interest in these doped nanomaterials is primarily due to the interesting structure-, shape-, and size-dependent properties, allowing their use in display devices, optical communication, solid-state lasers, catalysis, biological assays, and medical imaging. Because research on lanthanide-doped nanocrystals is still in its infancy, many of the materials properties and potential uses are yet to be discovered.

It is noted that there are a number of challenges ahead in the path toward practical applications of lanthanide-doped nanocrystals. For example, the luminescent efficiency, water solubility, biologic compatibility, stability, multicolor, and multifunction of nanocrystals are still the most influential factors for the practically biological application that deserve intense research attention, which is not only influenced by the electronic structure and concentration of doping RE ions but also influenced by the structure, shape, size, and synthetic method of nanocrystals. Although great strides have been made in these areas, future advances in controllable synthesis of lanthanide-doped nanocrystals with improved properties are essential before these promises are fulfilled. Our dream is to understand the formation mechanism at the molecular level by chemically controlling the formation process of lanthanide-doped nanocrystals and eventually to replace the empirical strategy by *ab initio* design. Meanwhile, integration of monodisperse lanthanide-doped nanocrystals into complex devices or superstructures is another goal of researchers in nanoscience fields.

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## FOOTNOTES

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