Highly Luminescent YVO_4 - Eu^{3+} Nanocrystals Coating on Wirelike $Y(OH)_3$ - Eu^{3+} and Y_2O_3 - Eu^{3+} Microcrystals by Chemical Corrosion

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Highly luminescent YVO_4-Eu^{3+} nanocrystals (NCs) coating on wirelike $Y(OH)_3-Eu^{3+}$ and $Y_2O_3-Eu^{3+}$ microcrystals were synthesized by a chemical corrosion method, that is, first preparation of $Y(OH)_3-Eu^{3+}$ wirelike microcrystals by a hydrothermal method, and subsequently chemical corrosion with NaVO₄ solutions through a second hydrothermal treatment. The crystal structure, morphology, and optical properties of the composites were characterized and compared with those of the general nanoparticles (NPs) obtained by a one-step hydrothermal process. The results indicate that chemical corrosion method yields high-quality $YVO_4 Eu^{3+}$ NCs in the composite grown from exterior to interior, compared with the directly hydrothermal NPs grown from interior to exterior. In addition, luminescent intensity for YVO_4-Eu^{3+} in the composite was remarkably increased compared with that of NPs, due to more efficient energy transfer from VO_4^{3-} to Eu^{3+} ions, and was further increased up to level of the the bulk materials after being annealed at 500 °C for 2 h. The local environment surrounding Eu^{3+} in the composite is more complex due to the presence of corrosive interface.

I. Introduction

Rare earth (RE) doped oxide materials, extensively used in the field of lighting, lasers, and displays,¹ were studied in the nanometer range over the past decade due to established technologies and new applications including luminescent fillers in transparent matrices (e.g., glass or plastic) as well as biomedical applications (e.g., biolabeling, optical imaging, or phototherapy) and so $on.^{2-5}$ For practical application, high brightness and luminescent quantum yield are expected in nanosized phosphors. However, a variety of body and surface defects, surface-adsorbed groups in NCs resulting from the small size and lower synthesis temperature, usually serve as nonradiative relaxation channels to dramatically quench luminescence during the energy transfer or emission process. As a result, large amounts of excitation energy loss in NCs enable their luminescence quantum efficiency (QE) to be much lower than that of corresponding bulk materials.^{5,6} A core-shell structure strategy was proved to be particularly favorable to improve QE and was well developed on the semiconductor and RE-doped insulator NCs by chemically modifying the particle surface or by epitaxially growing a shell to passivate the surface.⁶⁻¹¹ Whereas surface modification usually requires additional step and various surfactants are involved as stabilizers, the complicated and time-consuming processes and residual toxic macromolecules limit potential technical applications.¹² Developing facile routes of directly synthesizing high-quality luminescent NCs are therefore necessary and challenging. More recently,

Bühler and Feldmann¹² synthesized top-quality LaPO₄–Ce and -Tb NCs by a microwave-assisted technique in ionic liquid.¹²

Yttrium orthovanadate (YVO₄) as a promising oxide has been extensively applied as an excellent polarizer and laser host material (YVO₄- Er³⁺ or -Nd³⁺ or -Yb³⁺) in larger singlecrystal form and as a highly efficient red phosphor (YVO₄- Eu^{3+}) in powder form. YVO_4-Eu^{3+} NCs have been prepared and investigated in detail;^{5,6,13-17} however, the luminescent QE was usually much lower even if a core-shell strategy was employed.^{5,6} Herein, we present a novel and facile synthesis of highly luminescent YVO₄-Eu³⁺ NCs coating the Y(OH)₃-Eu³⁺ wirelike microcrystals [Y(OH)₃-Eu³⁺/YVO₄-Eu³⁺ composite labeled as S1] by a chemical corrosion method through a twostep hydrothermal process, that is, first preparation of Y(OH)₃-Eu³⁺ microcrystals and subsequently chemical corrosion by Na₃VO₄ solution. The composite was characterized in detail by various experimental techniques. The results indicate that crystallinity of $YVO_4{-}Eu^{3+}$ NCs in the composites was improved more than in the general NPs obtained by a one-step hydrothermal process. More efficient energy transfer from VO_4^{3-} to Eu³⁺ ions and the reduction of quenching centers in the composite remarkably enhanced luminescence.

II. Experimental Section

To synthesize core-shell-based composites that may create many new functions, many routes have been developed, including seeded growth,^{18,19} microemulsion,^{20,21} ion irradiation,²² sol-gel process,^{13,23} layer-by-layer technique (LBL),^{24,25} plus laser deposition (PLD),²⁶ chemical vapor deposition (CVD),²⁷ and so on. In this work, chemical corrosion, based on chemical dynamics and thermodynamics, was applied to prepare the composite, which was actually an in situ surface

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chemical reaction that occurred on the surface of crystalline Y(OH)₃-Eu³⁺ wirelike microcrystals by slowly substituting the OH⁻ with VO₄³⁻ groups [Y(OH)₃-Eu³⁺ + VO₄³⁻ \rightarrow Y(OH)₃- Eu³⁺/YVO₄-Eu³⁺ + OH⁻). Similar methods have been employed to prepare core-shell composite in the previous work.^{28,29} Annealing of Y(OH)₃-Eu³⁺/YVO₄-Eu³⁺ composite at 500 °C for 2 h in air yielded Y₂O₃-Eu³⁺/YVO₄-Eu³⁺ composite (labeled as S2). Annealing at such a relatively low temperature will not lead to terrible aggregation of nanomaterials and remarkable variations of morphology.⁹ For comparison, pure phase YVO₄-Eu³⁺ NCs were prepared by etching the Y(OH)₃- Eu^{3+}/YVO_4-Eu^{3+} composite with dilute hydrochloric acid (pH =1.5) to dissolve the internal $Y(OH)_3 - Eu^{3+} [Y(OH)_3 - Eu^{3+}/$ $YVO_4 - Eu^{3+} + H^+ \rightarrow YVO_4 - Eu^{3+} + Y^{3+} + Eu^{3+} + H_2O)$ and by a direct hydrothermal process $(Y^{3+} + Eu^{3+} + VO_4^{3-} \rightarrow$ YVO_4 -Eu³⁺). These samples were labeled as S3 and S4, respectively.

Preparation of Y(OH)₃-2 mol % Eu³⁺ and Y₂O₃-2 mol % Eu3+ Wirelike Microcrystals. In a typical synthetic procedure, Y(OH)₃-Eu³⁺ powder was first synthesized by a hydrothermal method. Briefly, an appropriate amount of Y(NO₃)₃. $6H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ ($n_Y:n_{Eu} = 98:2$) was dissolved in deionized water and was then precipitated by adding dropwise 2 M NaOH solution. Under vigorous stirring, the final pH value of this suspension was adjusted to be around 13.4. After continuous stirring for 1 h, a given volume of milky colloidal solution was finally transferred into a Teflon bottle held in a stainless steel autoclave and subsequently heated at 170 °C for 12 h. As the autoclave cooled down to room temperature, the resultant product was collected, washed with deionized water, and dried at 60 °C for 24 h in a vacuum oven to obtain Y(OH)₃-Eu³⁺ powders. The Y₂O₃-2 mol % Eu³⁺ wirelike microcrystals were obtained by firing the Y(OH)₃-Eu³⁺ powders at 500 °C for 2 h.

Preparation of Y(OH)₃–2 mol % Eu³⁺/YVO₄–2 mol % Eu³⁺ Composite. One part of as-obtained Y(OH)₃–Eu³⁺ powders was redispersed into deionized water by ultrasonic and vigorous stirring for 2 h; an appropriate amount of Na₃VO₄ solution ($n_{\text{Na}_3\text{VO}_4}$: $n_{\text{Y(OH)}_3\text{-Eu}^{3+}} = 0.4$) was dripped into the dispersion with a final pH value of 12.5 adjusted by 2 M NaOH solution, followed by further stirring for 2 h. Resultant milky suspensions were given another hydrothermal treatment at 170 °C for 12 h. The powders of the Y(OH)₃–Eu³⁺/YVO₄– Eu³⁺ composite were finally obtained after washing with deionized water and alcohol and drying at 60 °C for 24 h in a vacuum oven.

Preparation of YVO₄- **2 mol % Eu³⁺ NPs and Bulk YVO₄**- **2 mol % Eu³⁺.** For comparison, YVO₄- 2 mol % Eu³⁺ NPs were also synthesized by a one-step hydrothermal process at 170 °C for 12 h. The synthetic procedure was similar to that of Y(OH)₃-Eu³⁺ except that a slight excess of Na₃VO₄ solution was used to precipitate the Y(Eu)(NO₃)₃ solution ($n_{\rm Y}$: $n_{\rm Eu} = 98:2$) and the final pH value was adjusted to be around 12.5. Bulk YVO₄-Eu³⁺ was prepared by directly firing YVO₄-Eu³⁺ NPs at 1100 °C for 4 h.

Measurements. The structure and morphology of samples were characterized by X-ray diffraction (XRD) (Rigaku D/maxrA powder diffractometer with Cu K α 1.540 78 Å radiation), Fourier-transform infrared spectra (FTIR) (Nexus 670 FT-IR spectrometer), transmission electron microscopy (TEM) (JEM 2010), and high-resolution transmission electron microscopy (HRTEM) (JEM 3010). The element analysis was performed on a Leeman prodigy inductively coupled plasma atomic emission spectrometer (ICP-AES). Fluorescence and excitation



Figure 1. (A) XRD patterns and (B) FTIR spectra of $Y(OH)_3$ -Eu³⁺ and samples S1-S4.

as well as reflection spectra were recorded on a Hitachi F-4500 spectrophotometer equipped with a 150 W Xe-arc lamp at room temperature. For comparison of different samples, the spectra were measured at a fixed band-pass of 0.2 nm with the same instrument parameters. In the measurement of reflection spectra, BaSO₄ was used as a reflection standard. Luminescent decay curves were recorded by an oscillograph (Tektronix, TDS3052, 500 MHz, 5Gs/s), with a 266-nm light as excitation source. It was generated from the fourth harmonic generator pumped by the pulsed Nd- YAG laser, with a line width of 1.0 cm^{-1} , pulse duration of 10 ns, and repetition frequency of 10 Hz. Wavelengthselective experiments were performed at liquid nitrogen temperature (77 K), with a rhodamine 6G dye pumped by the YAG- Nd laser as excitation source. The spectra were recorded by a Spex-1403 spectrometer, a photomultiplier, and a boxcar integrator and processed by a computer.

III. Results and Discussion

3.1. Crystal Structure and Morphology. 3.1.1. X-ray Diffraction. Figure 1A shows the XRD patterns of all samples discussed in this paper. It is clear that crystalline Y(OH)₃-Eu³⁺ powders are obtained, in which all of the diffraction peaks can be index as pure hexagonal phase (JCPDS 83-2042) with the unit cell parameters $a_0 = b_0 = 6.261$ Å and $c_0 = 3.544$ Å. For sample S1, the appearance of some peaks deriving from tetrahedral phase YVO₄ (JCPDS 17-0341) of the zircon structure with lattice constants $a_0 = b_0 = 7.119$ Å and $c_0 = 6.289$ Å indicates that corrosion of the Na₃VO₄ solution is very effective. The annealing of sample S1 enables $Y(OH)_3$ phase to convert into cubic phase Y₂O₃ (JCPDS 79-1257), while the YVO₄ phase is maintained and no unassigned peaks appear, so $Y_2O_3 - Eu^{3+}/$ YVO_4 -Eu³⁺ composite (sample S2) was finally obtained. Etching on sample S1 successfully removed the internal Y(OH)₃ phase so that only diffraction peaks of YVO₄ phase can be detected in sample S3. Sample S4 also crystallized into tetrahedral phase YVO₄, but each diffraction peak slightly



Figure 2. TEM, SAED, and HRTEM images of $Y(OH)_3-Eu^{3+}$ and samples S1-S4. (A) TEM image of $Y(OH)_3-Eu^{3+}$ microcrystals and SAED pattern of single MWs. (B, C) Low and high magnification TEM image of sample S1. (D, E) Typical TEM image of core-shell structure in sample S1 and SAED pattern of shell layer. (F) TEM image of sample S4 and SAED pattern of single NPs. (G) HRTEM image of sample S1.

broadens in contrast with that of sample **S3**, implying a smaller crystallite size in sample **S4**. The results of element content analysis by ICP-AES are Y, 40.3 wt %; Eu, 1.3 wt %; and V, 26.9 wt % for sample **S1** and Y, 52.9 wt %; Eu, 2.0 wt %; and V, 15.0 wt % for sample **S4**, which indicate almost the same Eu content (2.1 mol % for sample **S1** and 1.8 mol % for sample **S4**) and 48.4 mol % YVO_4 - Eu³⁺ in the composite, higher than the value calculated according to the starting materials due to experimental errors.

3.1.2. Fourier Transfer Infrared Spectroscopy. The chemical component of each sample is further confirmed by FTIR spectra, as shown in Figure 1B. In Y(OH)₃-Eu³⁺, besides the stretching vibration of physically adsorbed H₂O (2800-3700 cm⁻¹), absorption bands of the Y(Eu)-O (736 cm⁻¹) bond and the structural O-H (3617 cm⁻¹) bond could be clearly observed. For sample S1, in addition to the above vibration bands present in $Y(OH)_3$ -Eu³⁺, the characteristic vibration bands of the V-O bond in vanadate species (700-1100 cm⁻¹) emerge,¹³ which coincide well with the results of XRD. After etching, the vibration bands of Y(OH)₃-Eu³⁺ phase disappear, indicating that the internal Y(OH)₃-Eu³⁺ phase was completely removed and sample S3 was pure YVO₄-Eu³⁺ phase. The vibration bands of the V-O bond were also observed in the direct hydrothermal YVO_4 -Eu³⁺ (sample **S4**); however, they differ from those in the sample synthesized by chemical corrosion (samples S1-S3). In the corroded sample, the V-O vibration bands $(700-1000 \text{ cm}^{-1})$ can be obviously divided into three components peaking at 790, 815, and 896 cm⁻¹, while in sample S4 the band at 790 cm^{-1} does not clearly appear. More splitting modes in the corroded sample may strongly correlate with its high crystallinity or specific structure as described in the next section. Vibration bands of the Y(Eu)-O bond originating from Y_2O_3 -Eu³⁺ in sample S2 (at 569 cm⁻¹) and YVO_4 -Eu³⁺ in samples S1-S4 (at 453 cm⁻¹) are also observed.^{13,30}

3.1.3. Standard and High-Resolution Transmission Electron Microscopy. The morphology and size of the samples were examined by transmission electron microscopy and highresolution transmission electron microscopy, as shown in Figure 2. Y(OH)₃-Eu³⁺ powder consists of microwires (MWs) and microtubes (MTs) with diameter of 100–150 nm and length of several micrometers (see Figure 2A). Both MWs and MTs depict Pan et al.

a smooth surface and well-defined framework. A selected area electron diffraction (SAED) pattern taken on single MWs comprises regular diffraction spots aligned in parallel lines (see inset of Figure 2A), implying its almost single crystallinity. After corrosion (sample S1), the wirelike morphology still remains but with a very rough surface and irregular lattice fringes (see Figure 2B), which suggests that the YVO_4 -Eu³⁺ coating layer is polycrystalline and inhomogeneously yields along the surface of wirelike microcrystals (for MTs, corrosion occurs in both interior and outer surfaces). A high-magnification TEM image (Figure 2C) further shows the surface features of composite. It could also be observed that the YVO₄-Eu³⁺coating layer is not a homogeneous entity but mainly comprises many NCs over a wide size range. Similar results have been observed in the in situ hydrothermal synthesis of YVO₄-Eu³⁺ nanorods and MTs with (NH₄)_{0.5}V₂O₅ as template.³¹ The nonuniform environment of Y(OH)₃-Eu³⁺substrates along the surface and the complicated corrosion process, as well as a larger lattice mismatch between $Y(OH)_3$ and YVO_4 phases, should be primarily responsible for the above corroded results. An image (see Figure 2D) exhibits a typical core-sheath structure with outer sheath thickness of ~20 nm, identified by different electron penetrability between core and sheath. However, this obvious structure with homogeneous sheath and smooth surface was less observed in the composite over extensive TEM examination. The SAED pattern (see Figure 2E) recorded on the shell shows a regular rhombus, indicating almost single crystalline structure of high quality. Etching on the above sample removes the Y(OH)₃-Eu³⁺ phase and leaves the almost hollow structure of pure YVO_4 -Eu³⁺ (S3) (see Supporting Information, Figure S1). While sample S4 consists of tetragonlike NPs with grain size of 20-40 nm (see Figure 2F), the SAED pattern taken on a single nanoparticle (see inset of Figure 2F) is composed of some discrete spots, which illustrate that it is polycrystalline and consists of many smaller crystallites. This is in good agreement with the recent results by Sun et al.³² using the same synthetic method.

A representative HRTEM image was performed on the corrosion interface, as clearly illustrated by the crystallinity of the interior [Y(OH)₃-Eu³⁺ phase] and exterior (YVO₄-Eu³⁺ phase) in Figure 2G. The left side, corresponding to highly crystalline YVO₄-Eu³⁺ phase, consists of only one set of well-defined (002) crystalline planes with interplanar spacing of 0.29 nm,³² while on the right side the image is faint and inhomogeneous. Two sets of crystalline planes cross each other: one is the extension from the outer YVO₄-Eu³⁺ phase, and the other should correspond to the (101) lattice plane of internal Y(OH)₃-Eu³⁺ microcrystals. The nonuniform crystallinity of Y(OH)₃-Eu³⁺ wirelike microcrystals accounts for the inhomogeneous growth of YVO₄-Eu³⁺ phase because preferential corrosion may initiate at the locale with weaker crystallinity.

3.2. Enhanced Photoluminescent Properties in Y(OH)₃– **Eu**³⁺/**YVO**₄–**Eu**³⁺ **Composite.** Figure 3 shows the excitation (left-hand side) and emission (right-hand side) spectra of samples **S1**, **S2**, and **S4** and bulk materials. A broad band in the range of 200–350 nm is observed in the excitation spectra, corresponding to vanadate band resulting from charge transfer from oxygen ligands to the central vanadium atom inside VO₄^{3–} ions,^{5,6,13–16} and strong red-emitting ${}^{5}D_{0}-{}^{7}F_{J}$ (J = 1, 2) transitions of Eu³⁺ dominate the emission spectra, which confirm that the luminescence is a host-sensitized energy transfer process from excited vanadate to europium ions.^{6,15,17} A major difference in different samples is that emission in the composite **S1** is stronger than in the pure NPs (**S4**) by a factor of about 3. For



Figure 3. Excitation ($\lambda_{em} = 618$ nm) and emission spectra ($\lambda_{ex} = 280$ nm) of sample **S1**, **S2**, **S4**, and bulk materials.



Figure 4. Reflection spectra of samples S1, S3, S4, and $Y(OH)_3$ -Eu³⁺.

 $Y(OH)_3$ -Eu³⁺ phase, it hardly emits under UV excitation due to the strong luminescence quenching of OH⁻ groups. As a result, after etching, the optical properties of sample **S3** are nearly same as those of sample **S1** (see Supporting Information, Figure S2). In practice, the highly doped samples (5 mol %) are also fabricated through the same procedure described in the Experimental Section, as shown in Supporting Information Figure S3; the emission intensity in composite is also about 2.5 times larger than in the NPs, which is close to that of the bulk materials prepared by ourselves and is ~80% of the corresponding commercial phosphors.

The whole excitation process of $YVO_4{-}Eu^{3+}$ under UV radiation should comprise three major steps.⁶ The first is absorption of UV radiation by vanadate groups; the excited energy is subsequently transferred to Eu³⁺ ions via a thermally activated energy migration through the vanadate sublattice, which is well-known as the subject of many investigations; and the final one is the deexcitation process of excited Eu³⁺ ions, producing strong red emissions. Any of the three steps may significantly influence the final emission intensity. As shown in Figure 4, the reflection spectra of sample S3 and S4 almost fit well with each other, indicating nearly the same absorption efficiency for vanadate species in composite S1 and NPs S4. Light scattering processes closely related to the particle size and surface morphology of phosphors may influence the total reflectance. As illustrated in Figure 2, the surface is rougher in sample S1 than in sample S4; however, here the differences of the scattering effects between the two samples can nearly be neglected. Although the reflectance for sample S1 exhibits some enhancement relative to sample S3, it should mainly result from the much lower absorption efficiency for internal Y(OH)₃-Eu³⁺ phase in UV region, which may be partly radiated due to the surface nonuniformity. The room-temperature luminescent decay



Figure 5. Room-temperature luminescent decay cures of ${}^5D_0 - {}^7F_2$ transitions at 619.4 nm for Eu³⁺ ions in composite S1 and sample S4.

curves of ${}^{5}D_{0}-{}^{7}F_{2}$ transitions at 619.4 nm in composite S1 and NPs S4 are displayed in Figure 5 and were well fitted into a biexponential function. There are two delay processes, a faster and a slower one. These values together with the average lifetimes are listed in the figure. In fact, the biexponential delay behavior is frequently observed in the energy transfer-induced luminescence route.^{13,33,34} Similar processing on YVO₄-Eu³⁺ has been predicted and carried out in previous reports.^{13,17} The results listed in the figure indicate the Eu³⁺ ions in both samples almost have the same room-temperature luminescent lifetimes for the ${}^{5}D_{0}$ level (i.e., nearly the same electron transition rates). Herein, it can be concluded that the energy transfer process in samples S1 and S4 should be responsible for the difference of emission intensity between the two samples. It is suggested that more efficient energy transfer to Eu³⁺ ions occurred in sample **S1**. In other words, more excited energy of vanadate groups was quenched by body defects and/or surface states during thermal migration in sample S4.

For bulk YVO_4 -Eu³⁺ phosphors, very efficient energy transfer through adjacent vanadate species has been observed to dominantly contribute to its high QE. The average migration distance among vanadate sublattices is as far as $\sim 9 \text{ nm}$,⁶ until the excitation energy reaches one Eu³⁺ ion. Besides, the absorption coefficient (α) for YVO₄ (at 272 nm) was as high as $\sim 200\ 000\ \mathrm{cm}^{-1}$,^{14,15} so that the effective excitation depth of UV light may be on the order of tens of nanometers. This means the photoluminescence QE is significantly dominated by the Eu³⁺ ions in the surface layers around tens of nanometers. In NCs with high defect densities (including body and surface defects), most of the excited-state energy will be trapped by defect states in the process of $VO_4^{3-} - VO_4^{3-}$ energy migration, and less energy can be transferred to Eu³⁺ ions. As a consequence, the photoluminescence QE will be lower. On the contrary, in NCs with better crystallinity, the energy transfer from VO_4^{3-} to Eu^{3+} ions will be more efficient.

High crystallinity of YVO_4 - Eu^{3+} in the composite is assigned to the quite different growth process of chemical corrosion compared with the general precipitation and hydrothermal method. The latter case is a typical nucleus and growth mechanism. Numerous terribly agglomerated nuclei are rapidly formed by precipitation of Y^{3+} and Eu^{3+} with VO_4^{3-} ions, and subsequently these grow at the expense of surrounding amorphous precursors under a hydrothermal environment. It is a layer-by-layer process from interior to outer, where ion (Y^{3+} and Eu^{3+}) and group (VO_4^{3-}) species regularly realign on the outermost lattice plane of nuclei. It could be considered that the starting materials were not rich enough for the final stage growth of surface layer of NCs so that many defects may be induced. However, a different process presents in the chemical



Figure 6. (Left) Excitation and (right) emission spectra of sample S2 and Y_2O_3 -Eu³⁺.

corrosion. First, the growth, that is, substitution of structural OH⁻ groups in Y(OH)₃–Eu³⁺ with VO₄³⁻ species in solution, is much slower, as occurs on a crystalline surface with certain periodic structure and rigidity. Second, it grows from exterior to interior of Y(OH)₃–Eu³⁺ wirelike microcrystals; the surface layer has more sufficient starting materials (VO₄³⁻ species) and time to perfect the lattice, because it is always exposed to and touches VO₄³⁻ species over the whole corrosion process.

3.3. Luminescent Properties of Y₂O₃-Eu³⁺/YVO₄-Eu³⁺ Composite. Sample S2 was obtained through annealing of sample S1 at 500 °C for 2 h, where the $Y(OH)_3$ -Eu³⁺ phase was decomposed into Y2O3-Eu3+ phase. As shown in Figure 3, the emission intensity is further enhanced and nearly equal to that of the bulk materials upon excitation into VO_4^{3-} groups at 280 nm due to the improved crystallinity to some degree. For pure Y_2O_3 – Eu³⁺, it has a stronger charge-transfer (CT) excitation (\sim 250 nm) related to the electronic transition from the 2p orbital of O^{2-} to the 4f orbital of Eu^{3+} , as monitored by the emission of Eu³⁺ at 611 nm. However, upon excitation into the CT band of Y_2O_3 -Eu³⁺ in sample S2, strong YVO₄-Eu³⁺ emissions were observed only, while the Y_2O_3 -Eu³⁺ emissions for which the ${}^{5}D_{0}-{}^{7}F_{2}$ transitions should locate at 611 nm are hardly identified. Actually, the time-resolved spectra experiments were performed with a 266 nm pulsed laser with high power generated from Nd-YAG and did not yet show obvious emissions of Y_2O_3 -Eu³⁺ from 0.005 to 1 ms. The intrinsic excitation corresponding to the f-f transitions into ⁵D₂ level (465 nm) were carried out on sample **S2**, as shown in Figure 6; the emission of Eu^{3+} ions in Y_2O_3 (611 nm) can be observed obviously. Here there exist two possibilities for the quenched Y₂O₃-Eu³⁺ emissions under UV excitation. First, as demonstrated in sections 3.1 and 3.2, the YVO₄ phase with higher absorption coefficient in the UV region nearly coated the surface of Y(OH)₃ phase completely, so the outer YVO₄ phase may shield internal Y₂O₃-Eu³⁺ phase from UV radiation. The absorption cross section for f-f shell transition of Eu³⁺ at 465 nm $({}^{5}D_{2} - {}^{7}F_{0})$ is usually much smaller than the host absorption, so the 465 nm light can penetrate the YVO₄ layer, and as a consequence, some Eu^{3+} ions in the Y_2O_3 phase can be excited. Second, the present composite may have similar optical properties as our previous observations in YVO₄-Eu³⁺/YBO₃-Eu³⁺ composite in which $YVO_4\mbox{--}Eu^{3+}$ phase was located on the partial surface of YBO3-Eu3+ phase;35 there we also observed only YVO₄-Eu³⁺ emissions upon excitation into CT in YBO₃-Eu³⁺ phase and assigned it to energy transfer process on the basis of detailed demonstrations, that is, O²⁻ (in YBO₃ phase) \rightarrow VO₄³⁻ \rightarrow Eu³⁺(in YVO₄ phase). The CT process usually enables Eu³⁺ ions at higher excited levels, where many other excited-state processes, such as resonant energy transfer, may



Figure 7. Site-selective (left) excitation and (right) emission spectra of samples S1, S2, S4, and bulk YVO_4-Eu^{3+} at liquid nitrogen temperature.

occur. However, here there is no more sufficient evidence for the occurrence of energy transfer process. Therefore, the disappeared Y_2O_3 -Eu³⁺ emissions under UV excitation are mainly attributed to the shielding of outer YVO₄-Eu³⁺ shells.

3.4. Local Environment Surrounding Eu³⁺. The site symmetry and local environments surrounding Eu³⁺ in the composite were studied by site-selective excitation experiments of the ${}^{7}F_{0}-{}^{5}D_{0}$ transition. The ${}^{5}D_{0}-{}^{7}F_{0}$ transition has only one emission line when Eu^{3+} occupies one site of C_s , C_n , or C_{nv} (*n* = 2, 3, 4, 6) symmetry, which is ideal as a structural probe to investigate local environment. 36 Note that the $^5D_0-{}^7F_0$ transition is strictly forbidden for Eu³⁺ ions occupying a site of D_{2d} symmetry in the single-crystalline YVO437 but becomes partially permitted in the YVO₄ powders.³⁸ While the Eu³⁺ ions incorporated into Y_2O_3 usually occupy a site of C_2 symmetry, the ${}^{5}D_{0}-{}^{7}F_{0}$ transition could be observed. As shown in Figure 7 (left), a sharp line at 580.64 nm was observed in the bulk and in samples S1, S2 and S4, and it should correspond to the transitions of Eu³⁺ at an intrinsic site, while in the samples S1 and S4 another broad line at the higher-energy side appears and overlaps the above sharp line, which should originate from the transition of Eu³⁺ at or near the surface of NCs. Note that the full width at half-maximum (fwhm) of the sharp line becomes much narrower and the broad line become much weaker in sample S1 than in sample S4, which may relate to its smaller grain size and polycrystallinity of NPs in sample S4 compared to sample S1. In sample S2, as monitored at 616.5 nm, the Eu^{3+} in the interior Y₂O₃-Eu³⁺ phase can be clearly distinguished by the presence of an intense excitation line of 580.60 nm. Note that the broad line still exists and overlaps both sharp lines and further extends toward short wavelengths, which should be derived from transitions of Eu³⁺ at the corrosive interface between the core (Y₂O₃) and shell (YVO₄). Site-selective emission spectra were taken on samples S1 and S2, as shown in Figure 7 (right). Excitation into Eu³⁺ ions at an intrinsic site (581.64 nm) in sample S1 produces only the characteristic emissions of YVO₄-Eu³⁺, like the UV excitation, while for sample S2, other lines appear due to the spectrum overlapping. Stronger Y_2O_3 – Eu³⁺ emissions (611 nm) were observed by excitation into Eu^{3+} ions in Y₂O₃ (580.60 nm). For the broad line, excitation into different locations (579.32 and 581.20 nm) generates different spectral energy distributions contributed by both characteristic Y_2O_3 -Eu³⁺ and YVO_4 -Eu³⁺ emissions, which correspond to the emissions of Eu³⁺ in the interface. In the corrosive interface both Y₂O₃ and YVO₄ phases interact with each other, so the local environments become more complex.

IV. Conclusions

In summary, we synthesize for the first time highly luminescent YVO₄-Eu³⁺ NCs coating on the Y(OH)₃-Eu³⁺ wirelike microcrystals by a chemical corrosion method through a two-step hydrothermal process. With fewer YVO_4 - Eu^{3+} in $Y(OH)_3 - Eu^{3+}/YVO_4 - Eu^{3+}$ composite, the emission intensity upon excitation into vanadate groups increased by a factor of 3 over that of general NPs obtained by the direct hydrothermal method and was further increased up to the level of the bulk materials upon annealing at 500 °C for 2 h. Due to its distinct growth process, the method presented here could be extended to the synthesis of high-quality core-shell NCs by chemical corrosion of a template similar in size and shape to the ones shown in Figure 2F. The disappeared Y_2O_3 -Eu³⁺ emissions in Y_2O_3 -Eu³⁺/YVO₄-Eu³⁺ composite under UV excitation are mainly attributed to the shielding of YVO_4 -Eu³⁺ shells. The local environment surrounding Eu³⁺ in the composite became more complex due to the presence of the corrosive interface.

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Supporting Information Available: TEM image of sample **S3** (Figure S1); excitation and emission spectra as well as site-selective excitation and emission spectra of sample **S3** (Figure S2); and excitation and emission spectra of YVO_4-5 mol % Eu^{3+} NPs, $Y(OH)_3-5$ mol % Eu^{3+}/YVO_4-5 mol % Eu^{3+} composite, bulk YVO_4-5 mol % Eu^{3+} , and commercial $YVO_4 Eu^{3+}$ phosphors, as well as the corresponding element content analysis results (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) *Phosphor Handbook*; Shionoya, S., Yen, W. M., Eds.; CRC: Boca Raton, FL, 1999.

- (2) Dubertret, B.; Skourides, P.; Norris, D. J.; Noireaux, V.; Brivanloue, A. H.; Libchaber, A. *Science* **2002**, *298*, 1759.
- (3) Sivakumar, S.; van Veggel, F. C.; Raudsepp, J. M. J. Am. Chem. Soc. 2005, 127, 12464.
- (4) Lim, S. F.; Riehn, R.; Ryu, W. S.; Khanarian, N.; Tung, C.-k.; Tank, D.; Austin, R. H. *Nano Lett.* **2006**, *6*, 169.

(5) Buissette, V.; Giaume, D.; Gacoin, T.; Boilot, J.-P. J. Mater. Chem. 2006, 16, 529.

- (6) Huignard, A.; Buissette, V.; Franville, A. C.; Gacoin, T.; Boilot, J.-P. J. Phys. Chem. B 2003, 107, 6754.
- (7) Kömpe, K.; Borchert, H.; Storz, J.; Lobo, A.; Adam, S.; Möller, T.; Haase, M. Angew. Chem., Int. Ed. 2003, 42, 5513.
- (8) Buissette, V.; Moreau, M.; Gacoin, T.; Boilot, J.-P. Adv. Funct. Mater. 2006, 16, 351.
- (9) Bai, X.; Song, H.; Pan, G.; Liu, Z.; Lu, S.; Ren, X.; Lei, Y.; Dai, Q.; Fan, L. Appl. Phys. Lett. **2006**, 88, 143104.
- (10) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. J. Am. Chem. Soc. **1997**, 119, 7019.
 - (11) Lin, Y.; Hsieh, M.; Liu, C.; Chang, H. Langmuir 2005, 21, 728.
 - (12) Bühler, G.; Feldmann, C. Angew. Chem., Int. Ed. 2006, 45, 4864.
 - (13) Yu, M.; Lin, J.; Fang, J. Chem. Mater. 2005, 17, 1783.
 - (14) Riwotzki, K.; Haase, M. J. Phys. Chem. B 1998, 102, 10129.
 - (15) Riwotzki, K.; Haase, M. J. Phys. Chem. B 2001, 105, 12709.
- (16) Wu, H.; Xu, H.; Su, Q.; Chen, T.; Wu, M. J. Mater. Chem. 2003, 13, 1223.
 - (17) Venikouas, G. E.; Powell, R. C. J. Lumin. 1978, 16, 29.
 - (18) Jiang, Z.; Liu, C. J. Phys. Chem. B 2003, 107, 1241.
- (19) Penninkhof. J.; Graf, C.; Dillen, T.; Vredenberg, A.; Blaaderen,
- A.; Polman, A. Adv. Mater. 2005, 17, 1484.
 (20) Ma, D.; Li, M.; Patil, A. J.; Mann, S. Adv. Mater. 2004, 16, 1838.
- (21) Yang, Y.; Gao, M. *Adv. Mater.* 2005, *17*, 2354.
 (22) Penninkhof, J. J.; Graf, C.; Dillen, T. V.; Vredenberg, A. M.;
- (22) Penninkhor, J. J.; Grai, C.; Dinen, T. V.; Viedenberg, A. M.; Blaaderen, A. V.; Polman, A. *Adv. Mater.* **2005**, *17*, 1484.
 - (23) Caruso, R. A.; Antonietti, M. Chem. Mater. 2001, 13 3272.
 - (24) Hikmet, R. A. M. Liq. Cryst. 1991, 9, 405.
 - (25) Schuetzand, P.; Caruso, F. Chem. Mater. 2002, 14, 4509.
- (26) He, R.; Law, M.; Fan, R.; Kim, F.; Yang, P. Nano Lett. 2002, 2, 1109.
- (27) Lauhon, L. J.; Gudiksen, M. S.; Wang, D. L.; Lieber, C. M. *Nature* **2002**, *420*, 57.
- (28) Mews, A.; Eychmüller, A.; Giersig, M.; Schooss, D.; Weller, H. J. Phys. Chem. **1994**, *98*, 934.
- (29) Zhang, J.; Huang, Y.; Lin, J.; Ding, X. X.; Huang, Z. X.; Qi, S. R.; Tang, C. C. J. Phys. Chem. B 2005, 109, 13060.
- (30) Zhang, J.; Zhang, Z.; Tang, Z.; Lin, Y.; Zheng, Z. J. Mater. Process. Technol. 2002, 121, 265.
- (31) Wu, X.; Tao, Y.; Mao, C.; Liu, D.; Mao, Y. J. Cryst. Growth 2006, 290, 207.
- (32) Sun, Y.; Liu, H.; Wang, X.; Kong, X.; Zhang, H. Chem. Mater. 2006, 18, 2726.
- (33) Shem, W. Y.; Pang, M. L.; Lin, J.; Fang, J. Y. J. Electrochem. Soc. 2005, 152, H25.
- (34) Fujii, T.; Kodaira, K.; Kawauchi, O.; Tanaka, N.; Yamashita, H.; Anpo, M. J. Phys. Chem. B **1997**, 101, 10631.
- (35) Pan, G.; Song, H.; Bai, X.; Liu, Z.; Yu, H.; Di, W.; Li, S.; Fan, L.; Ren, X.; Lu, S. *Chem. Mater.* **2006**, *18*, 4526.
- (36) Wei, Z.; Sun, L.; Liao, C.; Yin, J.; Jiang, X.; Yan, C. J. Phys. Chem. B 2002, 106, 10610.
- (37) Brecher, C.; Samelson, H.; Lempicki, A.; Riley, R.; Peters, T. *Phys. Rev.* **1967**, *155*, 178.
 - (38) Yan, C.; Sun, L.; Liao, C. Appl. Phys. Lett. 2003, 82, 3511.