Self-limiting adsorption of Eu^{3+} on the surface of rod-shape anatase TiO_2 nanocrystals and post-synthetic sensitization of the europium-based emission

Choumini Balasanthiran, Bo Zhao, Cuikun Lin, P.S. May,* Mary T. Berry,* James D. Hoefelmeyer*

Department of Chemistry, University of South Dakota, 414 E. Clark St., Vermillion, SD 57069

Corresponding author email: mberry@usd.edu; smay@usd.edu; jhoefelm@usd.edu

Abstract

The surface of oleic acid stabilized rod-shape anatase TiO_2 nanocrystals was modified by adsorption of Eu^{3+} ions. The Eu^{3+} attachment showed Langmuir adsorption behavior, thus the loading of Eu^{3+} could be controlled precisely up to surface saturation coverage. The Eu^{3+} - TiO_2 nanorods show weak Eu^{3+} based luminescence. However, addition of thenoyltrifluoroacetone (TTFA) leads to coordination of the ligand to the Eu^{3+} centers and the TTFA- Eu^{3+} - TiO_2 materials exhibit strong Eu^{3+} fluorescence sensitized by the TTFA ligand.

Introduction

Nanostructured materials possess multiple tunable features that allow careful optimization for a wide variety of applications, including the possibility to select composition, size, shape, and surface termination.¹⁻⁶ While the size and shape of the nanocrystal implicate electronic structure and surface reactivity, selection of the surface termination can impart additional functionality. Examples of functional surface termination include dye sensitization of nanocrystals,⁷ conjugation of biomolecules to nanocrystals,^{8,9} direct attachment of other nanocrystals (such as quantum dot sensitization or metal-semiconductor hybrid nanocrystals),¹⁰⁻¹⁵ and shell growth.^{16,17} The possibilities for synthetic modification of a nanocrystal surface are obviously enormous, and already span organic and inorganic synthetic methodologies to add the respective surface components.

Despite the tremendous gains in this area, there is room for new innovation. In particular, core-shell nanoparticles are especially attractive for a growing range of applications. Precise understanding of fundamental processes that occur in core-shell nanoparticles and their deployment in applications require careful control of the structure, including shell uniformity and thickness. Multi-shell nanocrystals, which find use as quantum well and inverse-quantum well systems¹⁸⁻²⁰ or in catalysis²¹⁻²⁴ are even more challenging since structural precision is required at several interfaces and compositions. The “successive

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4 ionic layer adsorption and reaction” (SILAR) method has been utilized to prepare core-
5 shell nanoparticles.^{17,25-28} However, the reactions are not self-limiting, the method
6 requires careful stoichiometric control, and can lead to additional nucleation events. One
7 possibility to achieve precise control of shell growth is atomic layer deposition; however
8 this has remained an elusive challenge for colloidal materials. Very recently, a colloidal
9 atomic layer deposition technique (cALD) was developed for CdSe nanocrystals in which
10 self-limiting alternating adsorption steps for Cd²⁺ and Se²⁻ led to precise control of shell
11 growth on quantum dots.²⁹ The technique was confirmed for PbSe nanocrystals shortly
12 after.³⁰ The cALD technique is so far limited to II-VI semiconductor nanocrystals, and it
13 would be highly desirable to expand this methodology more broadly.
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18 Recently, we found a method to deposit Co²⁺ ions on the surface of rod shape *brookite*
19 TiO₂ nanocrystals.³¹ This finding led us to develop a systematic approach for the
20 deposition of transition metal ions on the surface of rod shape *anatase* TiO₂
21 nanocrystals.³² Briefly, the method utilizes inexpensive metal chloride hydrates of the
22 first-row transition metals. A surfactant solubilizes the metal ions and allows adsorption
23 onto the nanocrystal surface. The reactions are tunable and self-limiting, which was
24 demonstrated by surface titrations that exhibited Langmuir adsorption behavior. The
25 adsorption of transition metal ions occurred with no change in the oxidation states of the
26 metals; however, it was noted that exposure to air was sufficient for oxidation of surface
27 Fe²⁺ and Mn²⁺ to the +3 oxidation state.³³ In order to expand the scope of the self-
28 limiting metal adsorption reactions, we hypothesized that lanthanide ions (Ln³⁺) would
29 show similar behavior.
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34 The unique luminescent properties of Ln³⁺ ions provide significant opportunities for
35 exploiting Ln³⁺ surface functionalization. The most relevant of these to the present study
36 is that Ln³⁺ emission can be dramatically sensitized by chelation to select organic ligands
37 via the so-called “antenna effect”.³⁴⁻³⁹ Excitation into strong ligand absorbance bands in
38 the UV can result in Ln³⁺ emission thousands of times brighter than achieved via direct
39 excitation into the 4f→4f metal-ion transitions. Lanthanide chelates have been used in
40 numerous sensing and imaging technologies. For example, the anthrax biomarker,
41 dipicolinate (DPA), can be detected with high sensitivity by its binding to, and
42 sensitization of, Tb³⁺ and Eu³⁺ emission.⁴⁰⁻⁴³ The vast majority of such studies and
43 applications, however, are based on free Ln³⁺ complexes in solution. Only recently have
44 workers begun to realize the potential of sensitization of the Ln³⁺ surface sites on
45 nanostructures.^{34,36,41,42,44} Nanostructures are better adapted for applications in complex
46 solution environments, and can be separated from the analyte solution following testing.
47 Moreover, non-interfering ratiometric markers can be incorporated into the
48 nanostructures to serve as an internal calibration of the binding signal.⁴¹ Nanostructures
49 also offer the opportunity for simultaneous multi-modal detection, e.g., optical and
50 electrochemical.⁴² Herein, we report self-limiting adsorption of the Eu³⁺ ion (and
51 supporting data as evidence that the phenomenon is broadly applicable to the lanthanide
52 ions in general) and show that the ligand environment can be modified specifically to
53 sensitize the luminescence of the Eu³⁺ ion. We demonstrate that an important sensitizing
54 ligand, thenoyltrifluoroacetone (TTFA), binds to the Eu³⁺ ions on the surface of the TiO₂
55 nanorods and effectively sensitizes luminescence from these ions. The Eu³⁺-TiO₂ surface
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offers unique opportunities for sensitization schemes, because the Eu^{3+} ions occur only at the surface, and the extent of surface coverage can be precisely controlled, independent of the other properties of the nanorods. In most cases of sensitization of nanostructures, the surface coverage of Ln^{3+} ions is determined either by the bulk doping levels of the nanostructure,^{34,36,44-57} which ties the surface properties to the bulk properties, or covalent linkage of Ln^{3+} chelates to the surface, which is difficult to characterize and quantitatively control.^{41,42,58}

Experimental

General considerations. All preparations were carried out under an atmosphere of N_2 by using both Schlenk line techniques and an inert atmosphere glove box unless otherwise noted. Europium(III) chloride hexahydrate, oleic acid (97%, Fisher Catalog # A195-500), oleylamine (OLAM; manufactured by TCI, 50+%, Fisher Catalog # 50-014-43281), octadecene (ODE; 90%, technical grade, Fisher Catalog # AC12931-0025), isopropanol, and hexanes were purchased from Fischer and used without purification. Titanium(IV) isopropoxide (TTIP) 98+%, was manufactured by Acros Organics. Thenoyltrifluoroacetone was purchased from Aldrich. All syntheses in which TiO_2 nanorods were a reactant require precise knowledge of the mass of TiO_2 . This was determined by taking an aliquot of known volume from a stock solution of dispersed TiO_2 nanorods with known volume. The solvent in the aliquot was allowed to evaporate and the remaining residue was calcined at 450°C in air for 6 hours to remove organic material. The remaining inorganic TiO_2 powder was carefully weighed, and then the mass of TiO_2 in the stock solution could be calculated.

Characterization. UV-Visible absorption spectra were recorded with Cary 50-Bio UV-Visible spectro photometer. Fluorescence spectra were recorded with a Fluoromax 4 spectrofluorometer. Transmission electron microscopy (TEM) data was obtained using a Technai Spirit G² Twin (FEI Company) transmission electron microscope fitted with LaB_6 filament operated at 120kV. Samples were dispersed in hexanes, and then drop cast onto carbon film (20-30 nm) on 200 mesh copper grid (Electron Microscopy Sciences) and allowed to dry in the air. Electron micrographs were obtained by projection onto a Gatan US1000 or Orius SC200 CCD Digital Camera and recorded with Digital Micrograph software. The phases present in the powdered samples were characterized by using Rigaku Ultima IV powder X-ray diffractometer. The X-ray tube produced Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), and the generator was set to 40 kV and 44 mA during data collection. Data was collected from $20-80^\circ$ (2θ). Dry TiO_2 nanorod powders and Eu^{3+} - TiO_2 nanorod powders were prepared by evacuating the solvent under vacuum at room temperature. Elemental analyses were performed at Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of Eu^{3+} - TiO_2 nanorods. Oleic acid stabilized rod shaped anatase TiO_2 nanocrystals were prepared according to a procedure described in the literature.⁵⁹ As an illustrative example, we describe the synthetic procedure for 0.05:1 Eu^{3+} - TiO_2 mole ratio. A dispersion of oleic acid stabilized TiO_2 nanorods (1 mmol) in hexane, OLAM (46 μL , 0.13 mmol) and ODE (3.77g to bring total volume 5 mL) were combined in a 100 mL

three neck flask and evacuated at 120°C for 30 minutes to remove volatiles. The flask was allowed to cool to room temperature and filled with N₂. To this mixture, EuCl₃·6H₂O (17.2 mg, 0.05 mmol) was added under N₂ atmosphere with magnetic stirring. The flask was connected with a reflux condenser and thermocouple-temperature controller relay. Under N₂ blanket, the mixture was heated to 250°C with a heating rate of 10°C/min, kept at this temperature for 3 hours, and then allowed cool to room temperature. On addition of approximately 15 mL isopropanol to the mixture, a white precipitate was observed. The white precipitate was separated by centrifugation at 3500 rpm for 8 minutes. The precipitate was redispersed in non-polar solvents such as hexane to give a transparent dispersion.

Coordination of Eu³⁺-TiO₂ nanorods with thenoyltrifluoroacetone (TTFA). In air, a flask was charged with 100 mg Eu³⁺-TiO₂ nanorods (5 mol% Eu; 0.06 mmol Eu) in 5 mL hexane. To this solution was added 0.444 g of TTFA (2 mmol) followed by stirring for 5 hours. The resulting nanoparticles precipitated out from the hexane solution. The solid was washed with pure hexane three times, and subsequently dispersed in pyridine to give a transparent dispersion.

Results and Discussion

Preparation of Eu³⁺-TiO₂ nanocrystals.

In previous work, we showed tunable and self-limiting adsorption of first-row transition metal ions on the surface of oleic acid-stabilized-rod-shaped *anatase* TiO₂ nanocrystals. The TiO₂ nanocrystals are readily prepared in multigram scale, can be reproducibly made, and are obtained from a simple synthesis with only two reagents.⁵⁹ The sample is phase-pure *anatase* TiO₂ in anisotropic rod shape (diameter = 3.3 ± 0.4 nm; length = 43.3 ± 7.6 nm) with growth along the *c*-axis (powder X-ray diffraction and TEM data are shown in the supporting information). The surfaces are dominated by the {101} facets and are oleic acid terminated, allowing dispersion in non-polar solvents.

To test the hypothesis that lanthanide (Ln³⁺) ions can adsorb on the TiO₂ nanocrystal surface, we use a similar methodology as was used for the first-row transition metal ions.³² Namely, to a dispersion of TiO₂ nanorods in 1-octadecene was added a precise amount of oleylamine and LnCl₃·*n*H₂O. We focus the remaining discussion on the results obtained with Eu³⁺ while data and results for adsorption of other lanthanide ions are presented in the supporting information. It is important to note that for each of the lanthanide ions, there is a specific temperature, determined empirically, at which adsorption efficiency (Ln³⁺ adsorbed to TiO₂ / total Ln³⁺) below saturation is greatest. For example, the temperature was optimized for Eu³⁺ loading on the TiO₂ surface at a Eu:Ti ratio of 0.03 based on the emission spectra of the products (Figure 1). The data indicate the optimum temperature for Eu³⁺ loading was 250°C. Above this temperature, the nanocrystals became unstable and lost solubility.

Figure 1. Emission of Eu^{3+} - TiO_2 samples prepared at theoretical $\text{Eu}:\text{Ti} = 0.03$ at various temperature. The emission intensity of the resultant sample increased with higher reaction temperature.

Oleylamine served as a transporting agent to solubilize the metal salts in the non-polar reaction medium. To understand the effect of the oleylamine concentration on the adsorption of Eu^{3+} on the nanorod surface, a series of experiments were carried out with constant $\text{Eu}:\text{Ti} = 0.05$ while varying the concentration of oleylamine as shown in Table 1. We use emission intensity of the Eu^{3+} - TiO_2 product as proxy for adsorption efficiency, and the data is shown in Figure 2. As the amount of oleylamine in the mixture was increased the europium ion loading increases until oleylamine: $\text{Eu} = 3$. There was a noticeable drop in the emission intensity at greater oleylamine concentration. This could be due to a chemical equilibrium between europium ion on the TiO_2 surface and in solution for which the equilibrium shifts towards solution as the concentration of surfactant is increased.

TiO_2 NRs (g)	OLAM (μL)	$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (mg)	ODE (g)	OLAM:Eu
0.10	21	23.5	3.93	1
0.10	63	23.5	3.91	3
0.10	106	23.5	3.90	5
0.10	148	23.5	3.88	7
0.10	232	23.5	3.87	11
0.10	317	23.5	3.85	15

Table 1. The parameters used for the determination of optimum oleylamine:Eu ratio for Eu^{3+} adsorption on the TiO_2 nanocrystal surface.

Figure 2. (Left) Emission spectra of Eu³⁺-TiO₂ samples prepared at theoretical ratio Eu:Ti = 0.05 and at varying oleylamine:Eu ratio. (Right) Emission intensity (λ = 615 nm) versus oleylamine:Eu mole ratio.

With the optimum conditions for Eu³⁺ adsorption established, we prepared a series of adsorption experiments in which the theoretical Eu:Ti ratio was varied from 0.01 to 1. The product from the reaction was isolated after five cycles of precipitation/redispersion. A portion of each product was calcined in air at 450°C for 6 hours to remove organic material before the samples were submitted for Eu analysis. Thus, each adsorption experiment is an *ex-situ* analysis of the Eu³⁺-TiO₂ sample along different points of the Eu:Ti ratio. The experimental Eu:Ti ratio could be plotted against theoretical Eu:Ti ratio to establish an adsorption isotherm (figure 3). The europium ion loading on the nanorod increased as europium chloride was added until the TiO₂ NR surface was saturated. The maximum average mass fraction of Eu in the calcined samples at the saturation limit was 0.178 ± 0.011 , corresponding to a Eu:TiO₂ mole ratio of 0.20. Further increases in the concentration of europium ion led to no additional Eu on the surface. This is due to the saturation of surface sites on the TiO₂ nanocrystals by the europium ions. It is noteworthy that the results are in close agreement to the theoretical mole ratio of M:TiO₂ = 0.22 for bidentate binding geometry at the surface.³² The Langmuir adsorption behavior indicates that the incorporation of the Eu³⁺ is specific to the surface of the nanocrystal and that the reaction is self-limiting, *i.e.* that multilayers or separately-seeded particles do not form.

Figure 3. Actual (from elemental analysis) versus theoretical $\text{Eu}:\text{TiO}_2$ mass ratio. Inset is the linear fit of the $\text{Eu}:\text{TiO}_2$ data below the surface saturation limit.

Characterization of $\text{Eu}^{3+}\text{-TiO}_2$ nanocrystals.

The powder X-ray diffraction patterns of TiO_2 nanorods and 5 mol% $\text{Eu}^{3+}\text{-TiO}_2$ are shown in Figure 4 with *anatase* as reference (JCPDS file 21-1272). The patterns exclusively resembled the *anatase* phase without any indication of europium oxide. TEM images for 5 mol% $\text{Eu}^{3+}\text{-TiO}_2$ are shown in Figure 5. From the data, we observe that the products consisted of crystalline uniform nanorods without any agglomeration. In addition, there was no evidence of additional nanosized metal or metal oxides in the TEM images. Powder patterns and TEM images of samples prepared across a range of Eu loadings similarly show no change in nanocrystal phase, morphology, nor the formation of additional phases or nanoparticles (see supporting information).

Figure 4. Powder X-ray diffraction for TiO_2 and $\text{Eu}^{3+}\text{-TiO}_2$ with JCPDS file 21-1272 (anatase) shown for comparison. Note for black and white reproduction: upper trace is the TiO_2 nanorod sample, lower trace is the $\text{Eu}^{3+}\text{-TiO}_2$ sample.

Figure 5. Transmission electron microscopy images of 5 mol% $\text{Eu}^{3+}\text{-TiO}_2$. Bar scale = 100 nm (left) and 10 nm (right).

The UV-Vis spectra of TiO_2 and 5 mol% $\text{Eu}^{3+}\text{-TiO}_2$ samples were obtained (figure 6). Strong absorbance features below ~ 310 nm are due to $\text{O}_{2p} \rightarrow \text{Ti}_{3d}$ LMCT bands. The samples show very little absorbance in the visible region, and only on close inspection of concentrated samples do we observe a very slight red-shift of the primary absorbance feature in the $\text{Eu}^{3+}\text{-TiO}_2$ material. No specific f-f absorbance features were found in the spectrum. Absorbance spectra of Eu^{3+} in metaphosphate glasses show sharp transitions at 394 nm ($^7F_0 \rightarrow ^5L_6$) and 464 nm ($^7F_0 \rightarrow ^5D_2$).⁶⁰ In contrast, absorbance spectra of Eu^{3+} -modified mesoporous titania thin film showed no specific f-f transitions.⁶¹ Lanthanide f-f transitions, in general, exhibit low extinction coefficients. The difference in detection limits for the various reported materials may be attributable to differences in inhomogeneous spectral broadening, different doping concentrations, or different background scattering characteristics of the samples.

Figure 6. UV-Vis spectra of Eu-TiO₂ (5%) and TiO₂ in hexane dispersion.

The emission spectra of TiO₂ nanorods and a 5 mol% Eu³⁺-TiO₂ sample were recorded with excitation wavelength of 250 nm (figure 7). At this excitation energy, LMCT (O_{2p} → Ti_{3d} and O_{2p} → Eu) transitions can be excited. The emission spectrum from 550-725 nm showed no appreciable emission from the TiO₂ nanorod sample; however the Eu³⁺-TiO₂ sample gave rise to emission features centered at 592, 614, 653 and 700 nm, assigned to ⁵D₀ → ⁷F_J transitions (*J* = 1, 2, 3, 4).⁶² The emission bands are broadened due to low symmetry and a disordered environment that is consistent with surface Eu³⁺ species.

It is well known that UV excitation of TiO₂ can sensitize Eu³⁺ luminescence based on a non-radiative energy transfer mechanism, which has been described previously for Eu³⁺-doped TiO₂ materials.^{45-57,61} Also, it has been shown that amorphous Eu₂O₃ exhibits similar luminescence (⁵D₀ → ⁷F_J transitions, relative intensities, and line-broadening) upon irradiation at 325 nm.^{63,64} Nanocrystalline Eu₂O₃ nanotubes give rise to a similar emission fingerprint when excited at 254 nm.⁶⁵ Therefore Eu-based luminescence could arise from TiO₂ excitation and energy transfer to Eu³⁺ or from direct excitation of the O → Eu LMCT band.

Figure 7. Emission spectra of 5 mol% Eu^{3+} - TiO_2 nanorods and TiO_2 nanorods ($\lambda_{\text{ex}} = 250$ nm).

Sensitization of Eu based luminescence on the Eu^{3+} - TiO_2 nanorods using thenoyltrifluoroacetone

The use of organic ligands to sensitize $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_J$ luminescence via the so-called ‘antennae effect’ is well-established.³⁴⁻³⁹ In particular, thenoyltrifluoroacetone (TTFA) has been shown to dramatically improve external fluorescence quantum yields and has a long excitation wavelength (350 nm) relative to most organic sensitizing ligands.^{34,35,66} In our investigation, we performed post-synthetic modification of the Eu^{3+} - TiO_2 nanorods by adding TTFA in order to coordinate the ligand to the surface bound Eu^{3+} centers. A large excess of the TTFA was used in the coordination step. Upon coordination of TTFA to the Eu^{3+} centers (presumably with displacement of oleic acid/oleylamine ligands), the nanocrystals precipitated from the hexanes solution, strongly indicating functionalization of the nanocrystal surface. The product was washed several times with hexanes to remove uncoordinated ligands and then redispersed in pyridine. The dramatic change in solubility properties seems to indicate the displacement of a significant portion of

aliphatic ligands coordinated to Eu^{3+} in favor of the bidentate chelating TTFA ligand. The solid sample was characterized with FTIR spectroscopy to show the coordination of the TTFA (figure 8). Spectra of sodium oleate, TTFA sodium salt, the oleic acid stabilized TiO_2 nanorods, and the Eu^{3+} - TiO_2 nanorods are shown for comparison. The sodium oleate spectrum shows peaks at 2854 cm^{-1} and 2924 cm^{-1} due to aliphatic C-H stretching modes. These features are also apparent in the TiO_2 nanorods, Eu^{3+} - TiO_2 nanorods, and the TTFA- Eu^{3+} - TiO_2 nanorods indicating retention of the oleic acid on the TiO_2 surface. The TTFA sodium salt shows peaks at 1535 cm^{-1} and 1611 cm^{-1} due to C=C and C=O stretches. These features are also apparent in the TTFA- Eu^{3+} - TiO_2 nanorods and are slightly shifted, likely due to coordination with Eu^{3+} .

Figure 8. FTIR spectra of TiO_2 nanorods, Eu^{3+} - TiO_2 nanorods, TTFA- Eu^{3+} - TiO_2 nanorods, Na-TTFA, and Na oleate.

Spectroscopic studies of the UV-visible absorption and fluorescence properties of the TTFA- Eu^{3+} - TiO_2 nanorods are strongly supportive of TTFA coordination to the Eu^{3+} centers. The UV-vis spectrum shows a new absorbance feature at $\sim 365\text{ nm}$ due to the TTFA ligand (supporting information). Excitation of the sample at 370 nm gives rise to strong $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_J$ emission (figure 9). In this case, ${}^7F_J$ states ($J = 0-4$) were observed. We note that excitation of the Eu^{3+} - TiO_2 sample at 370 nm gives rise to only

very weak emission. Thus the TTFA appears to be sensitizing the Eu^{3+} emission. Visually, there is a dramatic difference in the colors of the fluorescent light emitted from $\text{Eu}^{3+}\text{-TiO}_2$ (dim purple) and $\text{TTFA-Eu}^{3+}\text{-TiO}_2$ (bright red). As further evidence of the sensitized emission, an excitation spectrum was acquired at emission wavelength of 612 nm (the strong $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_2$ emission line). As shown in figure 9 the excitation spectrum shows a peak at ~ 370 nm, which coincides with the absorbance maximum of the TTFA component of the $\text{TTFA-Eu}^{3+}\text{-TiO}_2$ nanorod UV-vis spectrum. Furthermore, we could rule out emission from $\text{Eu}(\text{TTFA})_3$ complexes in solution, which exhibit ${}^5D_0 \rightarrow {}^7F_2: {}^7F_1$ emission intensity ratio of ~ 15 compared to ~ 6 for the complex bound to TiO_2 nanorods.

Figure 9. Emission ($\lambda_{\text{ex}} = 370$ nm) and excitation ($\lambda_{\text{em}} = 612$ nm) spectra of $\text{TTFA-Eu}^{3+}\text{-TiO}_2$ with photograph showing the emission of the $\text{TTFA-Eu}^{3+}\text{-TiO}_2$ dispersion.

Conclusion

To summarize, the surface of oleic acid stabilized rod-shape anatase TiO_2 nanocrystals was modified by adsorption of Eu^{3+} ions. The method utilizes an inexpensive metal chloride hydrate precursor. The Eu^{3+} loading could be varied up to the surface saturation limit. Based on preliminary evidence, the method appears to be generally applicable for the Ln^{3+} ions. Due to the large surface area of the nanocrystals, high loading of Eu^{3+} could be achieved. The $\text{Eu}^{3+}\text{-TiO}_2$ nanorods showed weak Eu^{3+} based emission. However, upon addition of the sensitizing ligand TTFA, there was dramatic enhancement

of the Eu^{3+} emission. We show that the bright emission is due to ligand sensitization of the surface-bound Eu^{3+} . The TTFA- Eu^{3+} - TiO_2 nanorods can be separated and washed, so they are easily processed and recoverable. These features could contribute to potential applications in luminescence sensing.

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References Cited

- ¹ M.C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293.
- ² X. Chen, S.S. Mao, Chem. Rev. 107 (2007) 2891.
- ³ U. Ozgur, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, H. Morkoc, J. Appl. Phys. 98 (2005) 041301.
- ⁴ I.L. Medintz, H.T. Uyeda, E.R. Goldman, H. Mattoussi, Nature Mater. 4 (2005) 435-446.
- ⁵ A.H. Lu, E.L. Salabas, F. Schuth, Angew. Chem. Int. Ed. 46 (2007) 1222.
- ⁶ S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L.V. Elst, R.N. Muller, Chem. Rev. 108 (2008) 2064.
- ⁷ B. O'Regan, M. Gratzel, Nature 353 (1991) 737.
- ⁸ K.E. Sapsford, W.R. Algar, L. Berti, K.B. Gemmill, B.J. Casey, E. Oh, M.H. Stewart, I.L. Medintz, Chem. Rev. 113 (2013) 1904.
- ⁹ E. Katz, I. Willner, Angew. Chem. Int. Ed. 43 (2004) 6042.
- ¹⁰ R. Costi, A.E. Saunders, U. Banin, Angew. Chem. Int. Ed. 49 (2010) 4878.
- ¹¹ P.D. Cozzoli, T. Pellegrino, L. Manna, Chem. Soc. Rev. 35 (2006) 1195.
- ¹² C. Wang, C. Xu, H. Zeng, S. Sun, Adv. Mater. 21 (2009) 3045.
- ¹³ C.D. Donega, Chem. Soc. Rev. 40 (2011) 1512.
- ¹⁴ L. Carbone, P.D. Cozzoli, Nano Today 5 (2010) 449.
- ¹⁵ M.R. Buck, J.F. Bondi, R.E. Schaak, Nat. Chem. 4 (2012) 37.
- ¹⁶ S. Wei, Q. Wang, J. Zhu, L. Sun, H. Lin, Z. Guo, Nanoscale 3 (2011) 4474.
- ¹⁷ R.G. Chaudhuri, S. Paria, Chem. Rev. 112 (2012) 2373.
- ¹⁸ D. Dorfs, A. Eychmuller 'Multishell semiconductor nanocrystals' in Semiconductor Nanocrystal Quantum Dots, A.L. Rogach, ed., Springer, 2008, pp 101-117.
- ¹⁹ D. Dorfs, A. Eychmuller, Z. Phys. Chem. 220 (2006) 1539.
- ²⁰ P. Reiss, M. Protiere, L. Li, Small 5 (2009) 154.
- ²¹ L. Wang, Y. Yamauchi, J. Am. Chem. Soc. 132 (2010) 13636.
- ²² L. Wang, Y. Yamauchi, Chem. Mater. 23 (2011) 2457.
- ²³ M. Tsuji, M. Matsunaga, H. Kumagai, M. Ogino, S. Hikino, Y. Yoshida, T. Ishizaki, CrystEngComm 15 (2013) 1345.
- ²⁴ F. Qiu, G. Liu, L. Li, Y. Wang, C. Xu, C. An, C. Chen, Y. Xu, Y. Huang, Y. Wang, L. Jiao, H. Yuan, Chem. Eur. J. 20 (2014) 505.
- ²⁵ R. Tan, D.A. Blom, S.G. Ma, A.B. Greytak, Chem. Mater. 25 (2013) 3724.
- ²⁶ J.J. Hao, J. Zhou, C.Y. Zhang, Chem. Commun. 49 (2013) 6346.

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- ²⁷ J.J. Li, Y.A. Wang, W.Z. Guo, J.C. Keay, T.D. Mishima, M.B. Johnson, X.G. Peng, J. Am. Chem. Soc. 125 (2003) 12567.
- ²⁸ R.G. Xie, U. Kolb, J.X. Li, T. Basche, A. Mews, J. Am. Chem. Soc. 127 (2005) 7480.
- ²⁹ S. Ithurria, D.V. Talapin, J. Am. Chem. Soc. 134 (2012) 18585.
- ³⁰ S.J. Oh, N.E. Berry, J.H. Choi, E.A. Gaulding, H. Lin, T. Paik, B.T. Diroll, S. Muramoto, C.B. Murray, C.R. Kagan, Nano Lett. 14 (2014) 1559.
- ³¹ W. Kang, C.S. Spanjers, R.M. Rioux, J.D. Hoefelmeyer, J. Mater. Chem. A 1 (2013) 7717.
- ³² C. Balasanthiran, J.D. Hoefelmeyer, Chem. Commun. 50 (2014) 5721.
- ³³ A. Sathe, M.A. Peck, C. Balasanthiran, M.A. Langell, R.M. Rioux, J.D. Hoefelmeyer, Inorg. Chim. Acta 422 (2014) 8.
- ³⁴ J. Chen, Q. Meng, P.S. May, M.T. Berry, C. Lin, J. Phys. Chem. C 117 (2013) 5953.
- ³⁵ C. Lin, M.T. Berry, P.S. May, J. Lumin. 130 (2010) 1907.
- ³⁶ A.M. Cross, P.S. May, F.C.J.M. van Veggel, M.T. Berry, J. Phys. Chem. C 114 (2010) 14740.
- ³⁷ S.V. Eliseeva, J.C.G. Bünzli, Chem. Soc. Rev. 39 (2010) 189.
- ³⁸ M. Latva, H. Takalo, V.M. Mukkala, C. Matachescu, J.C. Rodríguez-Ubis, J. Kankare, J. Lumin. 75 (1997) 149.
- ³⁹ N. Arnaud, J. Georges, Spectrochim. Acta A 59 (2003) 1829.
- ⁴⁰ E.D. Lester, A. Ponce, IEEE Eng. Med. Biol. 21 (2002) 38.
- ⁴¹ K. Ai, B. Zhang, L. Lu, Angew. Chem. Int. Ed. 48 (2009) 304.
- ⁴² C. Tan, Q. Wang, C.C. Zhang, Chem. Commun. 47 (2011) 12521.
- ⁴³ I. Lee, W.K. Oh, J. Jang, J. Hazard. Mater. 252-253 (2013) 186.
- ⁴⁴ J. Zhang, C.M. Shade, D.A. Chengelis, S. Petoud, J. Am. Chem. Soc. 129 (2007) 14834.
- ⁴⁵ J.G. Li, X. Wang, K. Watanabe, T. Ishigaki, J. Phys. Chem. B 110 (2006) 1121.
- ⁴⁶ J. Yin, L. Xiang, X. Zhao, Appl. Phys. Lett. 90 (2007) 113112.
- ⁴⁷ P. Ghosh, A. Patra, J. Phys. Chem. C 111 (2007) 7004.
- ⁴⁸ B.K. Moon, I.M. Kwon, H.K. Yang, H.J. Seo, J.H. Jeong, S.S. Yi, J.H. Kim, Coll. Surf. A 313-314 (2008) 82.
- ⁴⁹ Q.G. Zeng, Z.J. Ding, Z.M. Zhang, J. Lumin. 118 (2006) 301.
- ⁵⁰ W. Luo, R. Li, G. Liu, M.R. Antonio, X. Chen, J. Phys. Chem. C 112 (2008) 10370.
- ⁵¹ S. Sandoval, J. Yang, J.G. Alfaro, A. Liberman, M. Makale, C.E. Chiang, I.K. Schuller, A.C. Kummel, W.C. Trogler, Chem. Mater. 24 (2012) 4222.
- ⁵² H. Wang, Y. Wang, Y. Yang, X. Li, C. Wang, Mater. Res. Bull. 44 (2009) 408.
- ⁵³ M. Luo, K. Cheng, W. Weng, C. Song, P. Du, G. Shen, G. Xu, G. Han, Nanoscale Res. Lett. 4 (2009) 809.
- ⁵⁴ R.S. Ningthoujam, V. Sudarsan, R.K. Vatsa, R.M. Kadam, Jagannath, A. Gupta, J. Alloy. Compd. 486 (2009) 864.
- ⁵⁵ M. Pal, U. Pal, J.M.G.Y. Jimenez, F. Perez-Rodriguez, Nanoscale Res. Lett. 7 (2012) 1.
- ⁵⁶ D. Chen, Q. Zhu, Z. Lv, X. Deng, F. Zhou, Y. Deng, Mater. Res. Bull. 47 (2012) 3129.
- ⁵⁷ H. Zhang, Y. Sheng, K. Zheng, X. Zhou, Z. Shi, X. Xu, H. Zou, Eur. J. Inorg. Chem. 21 (2014) 3305.

-
- ⁵⁸ L. Sun, Z. Wang, J.Z. Zhang, J. Feng, J. Liu, Y. Zhao, L. Shi, RSC Adv. 4 (2014) 28481.
- ⁵⁹ J. Joo, S. G. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon, T. Hyeon, J. Phys. Chem. B 109 (2005) 15297.
- ⁶⁰ J.A. Capobianco, P.P. Proulx, M. Bettinelli, F. Negrisolo, Phys. Rev. B 42 (1990) 5936.
- ⁶¹ K.L. Frindell, M.H. Bartl, A. Popitsch, G.D. Stucky, Angew. Chem. Int. Ed. 41 (2002) 959.
- ⁶² C.A. Kodaira, H.F. Brito, O.L. Malta, O.A. Serra, J. Lumin. 101 (2003) 11.
- ⁶³ S.X. Lu, Y.C. Liu, J. Non-Crystalline Solids 353 (2007) 1037.
- ⁶⁴ P.A. Hansen, H. Fjellvag, T.G. Finstad, O. Nilsen, Chem. Vap. Deposition 20 (2014) 274.
- ⁶⁵ G. Wu, L. Zhang, B. Cheng, T. Xie, X. Yuan, J. Am. Chem. Soc. 126 (2004) 5976.
- ⁶⁶ Y. Jing-he, Z. Gui-yun, W. Bo, Anal. Chim. Acta 198 (1987) 287.