Synthesis and Upconversion Luminescence of YF₃:Yb³⁺, Tm³⁺ and TiO₂-Coated YF₃:Yb³⁺,Tm³⁺ Microcrystals

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YF₃:Yb³⁺,Tm³⁺ microcrystals were prepared by a microemulsion method. The microcrystals were coated with TiO₂ by hydrolysis of titanium n-butoxide (TBOT). Transform electron microscopy and X-ray diffraction were used to characterize the core/shell materials. The results indicated that the low TBOT/YF₃ molar ratio was favorable to preparing the uniform TiO₂ coatings. The upconversion luminescence properties of YF₃:Yb³⁺,Tm³⁺ and TiO₂-coated YF₃:Yb³⁺,Tm³⁺ microcrystals were studied under 980-nm excitation. The ¹I₆ → ³H₆, ¹I₆ → ³F₄, ¹D₂ → ³H₆, ¹D₂ → ³F₄, ¹G₄ → ³H₆, and ¹G₄ → ³F₄ emissions were observed. The upconversion mechanisms were discussed in detail.

Keywords: Rare Earth, TiO₂, Core–Shell, Upconversion Luminescence.

1. INTRODUCTION

TiO₂ has been studied extensively because it has the advantages of high catalytic reactivity, physical and chemical stability, innocuity, and low cost.¹ TiO₂ coatings have also attracted much attention due to their potential applications in photocatalysis and biomedical treatments.²⁻³ A variety of materials coated with TiO₂ have been reported. TiO₂-coated SiO₂ has been studied commonly.⁴⁻⁶ The reported materials coated with SiO₂ also include (1) metals such as Ni⁷ and Ag⁸ and (2) metal oxides such as RuO₉, ZnO,⁹ Fe₃O₄,¹⁰ ZrO₂,¹¹ whereas there are a few reports on TiO₂ coating upconversion (UC) materials. Wang et al. reported TiO₂ coating oxide UC particles Y₃Al₅O₁₂: Er³⁺,¹² which can convert visible light to ultraviolet (UV) light.¹³ However, to the best of our knowledge TiO₂-coated rare-earth fluorides have not been reported to date.

Fluorides doped with rare-earth ions have been demonstrated in many applications such as lasers,¹⁴ optical communications,¹⁵ and display devices.¹⁶ They are also promising alternates to biological imaging and labeling materials.¹⁷ According to our previous work YF₃:Yb³⁺, Tm³⁺ can emit intense UV light under 980 nm diode laser excitation.¹⁸ The UV irradiation has the cytotoxicity suppression capacity to target cancer cells. Thus, YF₃: Yb³⁺, Tm³⁺ UC phosphor can be used in biomedical treatment.

However, applications of YF₃:Yb³⁺,Tm³⁺ in biological treatment have the limitation of lacking groups on the surface serving as reactive sites for combining biomolecules. On the other hand, fluoride is toxic to biological systems. Hence, modification of the fluoride phosphors surface has attracted much attention. We have prepared LaF₃:Yb³⁺, Er³⁺/SiO₂ core/shell nanocrystals.¹⁹ Herein, we prepared YF₃:Yb³⁺,Tm³⁺ particles by an inverse microemulsion method. Subsequently we synthesized a TiO₂-coated YF₃:Yb³⁺,Tm³⁺ hybrid by a simple hydrolysis method with polyvinylpyrrolidone K-30 (PVP) as a stabilizer. The effect of the amount of titanium alkoxide precursor on the morphology and the optical properties were investigated.

2. EXPERIMENTAL DETAILS

YF₃:20% Yb³⁺, 0.5% Tm³⁺ microcrystals were prepared by a microemulsion method. The starting reagents were Y₂O₃, Yb₂O₃,Tm₂O₃, cetyltrimethylammonium bromide (CTAB), n-pentanol, TBOT, PVP, and cyclohexane. The oxides were separately dissolved in dilute HCl to form 0.5 M stock solutions of YCl₃, YbCl₃, and TmCl₃.

2.1. Preparation of YF₃:Yb³⁺,Tm³⁺ Microcrystals

In a typical synthesis, two identical solutions, marked as I and II, were prepared by dissolving 9 g of CTAB in...
200 mL of cyclohexane and 10 mL of \( n \)-pentanol. The two solutions were stirred for 30 min until each became transparent. Appropriate amounts of LnCl\(_3\) (Ln = Y, Yb, and Tm) and NH\(_4\)HF\(_2\) aqueous solutions were added to microemulsions I and II, respectively. The microemulsion solutions were mixed and stirred for another 30 min. After aging for 12 h, the microcrystals were collected by centrifugation and washed with ethanol and distilled water several times. Then, the microcrystals were dried in vacuum and annealed at 700 °C for 2 h in an argon atmosphere.

### 2.2. TiO\(_2\) Coatings Formation

TiO\(_2\)-coated YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) microcrystals were synthesized by hydrolysis of TBOT with PVP as a steric stabilizer. YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) microcrystals (0.01 g) were dispersed in ethanol (15 ml) and mixed with PVP (5 g/L) and an appropriate concentration of TBOT. Then, 0.1 ml of distilled water and 5 ml of ethanol was added dropwise to the above suspension with continuous stirring. The product was centrifuged, washed, and dried at 60 °C for 12 h. The hydrolysis reactions over the YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) nuclei can be written as follows.

\[
\begin{align*}
\text{Ti(OC}_4\text{H}_9)_4 + 4\text{H}_2\text{O} & \rightarrow \text{Ti(OH)}_4 + 4\text{C}_4\text{H}_9\text{OH} \quad \text{(Hydrolysis)} \quad (1) \\
\text{Ti(OH)}_4 & \rightarrow \text{TiO}_2 \text{ (amorphous)} \\
& + 2\text{H}_2\text{O} \quad \text{(Condensation)} \\
\end{align*}
\]

### 2.3. Measurements

The crystal structure was analyzed by a Rigaku RU-200b X-ray powder diffractometer (XRD) using a nickel-filtered Cu K\( \alpha \) radiation (\( \lambda = 1.4518 \) Å). The size and morphology were characterized by transmission electron microscope (TEM, JEM 2010 with operating voltage of 200 KV). The UC luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer under 980-nm excitation.

### 3. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD pattern of YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) microcrystals. It was found that all of the diffraction patterns could be indexed to orthorhombic phase YF\(_3\) (ICPDS 74-0911). No other impurity peaks were detected. Figure 1(b) shows the XRD pattern of TiO\(_2\)-coated YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\). No characteristic peaks of TiO\(_2\) were found. This may be because the TiO\(_2\) coatings were amorphous. Figure 2(a) shows the TEM image of YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) microcrystals. Obviously, the microcrystals tended to aggregate. Figures 2(b–d) show the typical TEM images of TiO\(_2\)-coated YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) with different TBOT/YF\(_3\) ratios. When the TBOT/YF\(_3\) molar ratio was 1:1, the TiO\(_2\) shells were smooth and uniform, and the thickness was about 15 nm. When the TBOT/YF\(_3\) ratios were 2:1 and 3:1, the TiO\(_2\) shells became non-uniform. This may be because increasing the concentration of TBOT can lead to the fast rate of hydrolysis reaction, and therefore, the concentration of the titanium alkoxide precursor plays a key role in the synthesis of TiO\(_2\) coatings. As the concentration of TBOT increased, the shell thickness did not increase apparently, which can be attributed to the asymmetric shape and the broad size distribution of YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) microcrystals. Furthermore, the hydrolysis reaction might not occur over the YF\(_3\):Yb\(^{3+}\),Tm\(^{3+}\) microcrystals, which resulted in
the independent formation of amorphous TiO$_2$ particles besides YF$_3$:Yb$^{3+}$,Tm$^{3+}$ microcrystals.

Figure 3 shows the UC luminescence spectrum of YF$_3$:Yb$^{3+}$,Tm$^{3+}$ microcrystals under 980-nm excitation. The $^{1}I_{6} \rightarrow ^{3}H_{6}$ ($\sim$290 nm), $^{1}I_{6} \rightarrow ^{3}F_{4}$ ($\sim$346 nm), $^{1}D_{2} \rightarrow ^{3}H_{6}$ ($\sim$362 nm), $^{1}D_{2} \rightarrow ^{3}F_{4}$ ($\sim$451 nm), $^{1}G_{4} \rightarrow ^{3}H_{6}$ ($\sim$477 nm), and $^{1}G_{4} \rightarrow ^{3}F_{4}$ ($\sim$643 nm) emissions were observed.

Figure 4 shows the UC luminescence spectra of TiO$_2$-coated YF$_3$:Yb$^{3+}$,Tm$^{3+}$ with different TiO$_2$/YF$_3$ ratios. The emission intensities decreased gradually with the increase of amorphous TiO$_2$, which was attributed to the shielding effect of TiO$_2$. Although the thickness of TiO$_2$ coatings did not apparently increase with the increase of the concentration of titanium alkoxide, the TiO$_2$ coatings became dense and heterogeneous, which enhanced the shielding effect of TiO$_2$ coatings and weakened the luminescence intensity. Thus, the UC emissions from the thin and uniform TiO$_2$-coated YF$_3$:Yb$^{3+}$,Tm$^{3+}$ were strongest. In addition, because the penetrating ability of short wavelength light is weaker than that of the long wavelength light, the intensities of short wavelength emissions decreased more quickly with increasing amorphous TiO$_2$.

Figure 5 shows the UC luminescence mechanism and population processes in TiO$_2$-coated YF$_3$:Yb$^{3+}$,Tm$^{3+}$ microcrystals. The pump light excited only the Yb$^{3+}$ ions, and three successive energy transfers from Yb$^{3+}$ were needed to Tm populate $^{3}H_{6}$, $^{3}F_{2}$, and $^{1}G_{4}$. Though the Tm$^{3+}$–Tm$^{3+}$ interaction was weak in the sample with low Tm$^{3+}$ concentration owing to the large energy mismatch in the transfer $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ (Yb$^{3+}$):$^{1}G_{4} \rightarrow ^{1}D_{2}$ (Tm$^{3+}$), the process $^{3}F_{2} \rightarrow ^{3}H_{6}$ (Tm$^{3+}$):$^{3}H_{4} \rightarrow ^{1}D_{2}$ (Tm$^{3+}$) may alternatively play the most important role in populating $^{1}D_{2}$. Thereafter, the state $^{1}I_{6}$ could be populated by $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ (Yb$^{3+}$): $^{1}D_{2} \rightarrow ^{1}I_{6}$ (Tm$^{3+}$).

4. CONCLUSION

We have successfully prepared YF$_3$:Yb$^{3+}$,Tm$^{3+}$ microcrystals by a microemulsion method. The microcrystals were coated with TiO$_2$ by hydrolysis of TBOT. The transform electron microscope and XRD were used to characterize the core/shell materials. The results indicated that the shell thickness could be well controlled by changing the TBOT concentration, and the relatively low TBOT concentration was favorable to preparing the uniform TiO$_2$ coatings. The UC luminescence properties of YF$_3$:Yb$^{3+}$,Tm$^{3+}$ and TiO$_2$-coated YF$_3$:Yb$^{3+}$,Tm$^{3+}$ microcrystals were studied under 980-nm excitation. The $^{1}I_{6} \rightarrow ^{3}H_{6}$, $^{1}I_{6} \rightarrow ^{3}F_{4}$, $^{1}D_{2} \rightarrow ^{3}H_{6}$, $^{1}D_{2} \rightarrow ^{3}F_{4}$, $^{1}G_{4} \rightarrow ^{3}H_{6}$, and $^{1}G_{4} \rightarrow ^{3}F_{4}$ emissions were observed. The UC mechanisms were discussed in detail. The core/shell microcrystals have the potential in the application of biomedical treatment.

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References and Notes

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