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Ultraviolet upconversion luminescence in Y_2O_3:Yb^{3+},Tm^{3+} nanocrystals and its application in photocatalysis

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Abstract Infrared-to-ultraviolet upconversion luminescence agent Y_2O_3:Yb^{3+},Tm^{3+} was prepared by a combustion method using citrate as a fuel/reductant. The prepared sample was characterized by X-ray diffraction, SEM, and fluorescence spectrophotometer. Two unusual $^1I_6 \rightarrow {}^3H_6$ ($\sim$297 nm) and $^1D_2 \rightarrow {}^3H_6$ ($\sim$363 nm) emissions from Tm^{3+} ions were observed at room temperature under 980-nm laser excitation. The change of upconversion emission intensity depending on the Yb^{3+} concentrations was discussed. The results showed that modest Yb^{3+} doping could make the upconversion emission of Tm^{3+} intense, and high Yb^{3+} concentrations might lead to fluorescence quenching. Moreover, the influence of ultraviolet upconversion luminescence on the photodegradation of methyl orange aqueous solution under solar light irradiation in the presence of TiO_2 catalyst doped with Y_2O_3:Yb^{3+},Tm^{3+} was also investigated. It was concluded from the experiment of this study that TiO_2/Y_2O_3:Yb^{3+},Tm^{3+} composite had higher photocatalytic activity than pure TiO_2 under solar light. This study would make TiO_2 utilize sunlight more efficiently and accelerate the practical application of photocatalytic technology in water treatment region.

Introduction

An upconversion luminescence is the one which takes multiple photons of lower energy and converts them to one photon of higher energy (this is an anti-Stokes process) [1]. Upconversion is an important process in RE-doped materials, owing to intrinsic energy levels matching of certain rare earth (RE) ions and the ample availability of laser diodes in the visible and IR range. Among RE ions, Tm^{3+} has attracted considerable attention owing to its stable excited levels suitable for emitting blue and UV luminescence simultaneously [2]. Meanwhile, Yb^{3+} ion is often codoped as a typical sensitizer in upconversion materials. The single electronic excited-state of Yb^{3+} ion is located at approximately 10,000 cm^{-1}, which is resonant with many inexpensive laser diodes, and has a higher extinction coefficient relative to the other RE^{3+} ions [3]. Thus, when codoped with ions that have a resonant electronic energy state (e.g., Er^{3+}, Tm^{3+}, Ho^{3+}, Pr^{3+}, etc.), Yb^{3+} ion can enhance the efficiency of the upconversion process as it actively transfers the absorbed energy to the other codopants. Moreover, Yb^{3+} ion can also cause upconversion to occur in cases where it is not normally observed in the single ion [4]. The principle of Yb^{3+}–Tm^{3+} energy transfer upconversion has been employed in various systems [5–8]. However, most upconversion studies in RE-doped materials are focused on infrared and visible regions, and the ultraviolet upconversion phenomena in many RE-doped materials remains to be explored [9].

Environmental problems have increasingly become a matter of serious concern now. As a common photocatalyst used in environmental treatment technology, TiO_2 is a promising photocatalyst for wastewater purification. However, the band-gap energy of pure anatase TiO_2 is about 3.2 eV, and only ultraviolet light can be absorbed

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($\lambda < 387$ nm, about 4% part of solar light). In recent years, in order to utilize solar energy more efficiently (mainly visible or infrared light), great efforts have been made to develop TiO_2-based photocatalysts. Many researches have shown that it is useful to extend TiO_2 photoresponse range using some modified methods. However, according to formula $E_g = hv$ (h is Planck constant, v is light frequency), the photopotential energy excited by visible light is lower than that excited by ultraviolet light. The photo-induced carriers excited by visible light only decompose azo bonds of some organic dyestuffs (such as methyl yellow, methyl red, and crystal violet) or make organic dyestuffs decolorized, while the photo-induced carriers excited by ultraviolet light can degrade organic dyestuffs completely [10, 11]. Thus, upconversion luminescence materials with their ability to transform infrared or visible light into ultraviolet light are becoming the focus of investigatation to satisfy the genuine requirement of TiO_2 [12].

The purpose of this article is to study ultraviolet upconversion luminescence in Yb^{3+}, Tm^{3+}-codoped Y_2O_3 nanocrystals. Moreover, the influence of ultraviolet upconversion luminescence on the photocatalytic degradation of methyl orange under solar light irradiation is also investigated in the presence of TiO_2 catalyst doped with Y_2O_3:Yb^{3+},Tm^{3+}.

Experimental section

Preparation of upconversion luminescence agent Y_2O_3:Yb^{3+},Tm^{3+} by Combustion method

The Y_2O_3:Yb^{3+}(0, 2, 4, 6, 8, and 10 mol%), Tm^{3+} (0.5 mol%) nanocrystals were prepared by a combustion method with the following starting materials Y_2O_3, Yb_2O_3, Tm_2O_3, HNO_3, and $C_6H_8O_7{\cdot}H_2O$. All of the starting materials were in the reagent grade and used without further purification. First, an appropriate amount of Y_2O_3 was dissolved in dilute nitric acid to form the $Y(NO_3)_3$ solution, and then a certain amount of 0.1 mol/L $Tm(NO_3)_3$ and 1 mol/L $Yb(NO_3)_3$ were added to $Y(NO_3)_3$ solution stoichiometrically. Second, the above mixed solution was added to citric acid solution under continuous stirring and heated to about 80 °C. As water evaporated, the solution became viscous and formed light yellow wet gel. Third, the wet gel was dried at 120 °C for 12 h to get fluffy and porous dry gel. Finally, the dry gel was calcined at 800 °C for 2 h.

Preparation of TiO_2 photocatalyst doped with upconversion luminescence agent

0.2 g upconversion luminescence agent Y_2O_3:Yb^{3+},Tm^{3+} was added into beaker filled with an amount of ethanol, and dispersed adequately by ultrasound for 30 min. Then, an appropriate amount of cetyltrimethylammonium bromide used as a dispersing agent and 1.1 mL $TiCl_4$ were dissolved in above ethanol. Ammonia was used to adjust to pH 9. After the reaction, the precipitates were filtered and washed with distilled water and ethanol, and then dried at 100 °C for 8 h. Finally, the precipitates were calcined at 500 °C. Pure TiO_2 was prepared by the same method for comparison.

Characterization and performance measurements

The crystalline phases of sintered powders were identified by powder X-ray diffraction (XRD, D/Max-λ, Rigaku, Japan) using Cu Kα radiation (1.5406 Å). The crystallite size of the nanocrystalline powders was calculated following the Scherrer's equation: $d = K\lambda/\beta\cos\theta$, where $K = 0.89$, d represents the crystallite size, λ represents the wavelength of Cu Kα radiation, β represents the corrected half width of the diffraction peak, and θ represents the Bragg angle. The morphologies of the samples were observed by SEM (Hitachi S4800). The upconversion emission spectra under 980-nm excitation were measured by a fluorescence spectrophotometer (Hitachi F-4500) with the spectral resolution of 2 nm. The pump power of the 980-nm LD was enumerated on the controller which was used to modulate the electric current of the LD.

The photocatalytic experiment was carried out for degradating of the methyl orange aqueous solution under solar light irradiation. 0.12 g photocatalyst was added into 100-mL beaker which contains 30 mL methyl orange solution with a concentration of 20 mg/L. Then, the beaker was put on a magnetic stirrer, and the solution was stirred for 30 min under dark to establish adsorption/desorption equilibrium before irradiation. After the irradiation started, 0.5 mL of the solution was taken out every 30 min during 150 min and analyzed. The extent of photocatalytic degradation was evaluated by measuring the absorbance A of the solution samples with a UV–vis spectrophotometer (UV757CRT) at $\lambda_{max} = 463$ nm. According to Lambert/Beer formula ($A = kCb$), where k and b are constants, the solution concentration C was a linear function to the absorbance A. The degradation ratio η (%) of methyl orange was estimated using the expression of

$$\begin{aligned}\text{Degradation ratio } \eta\,(\%) &= [(C_0 - C)]\,/\,C_0 \times 100\\ &= [(A_0 - A)]\,/\,A_0 \times 100\end{aligned}$$

where C_0 and C are the initial and residual methyl orange concentration in solution, respectively, A_0 and A are the pre- and post-irradiation absorbances of the methyl orange solution, respectively. All the photocatalytic experiments were conducted at a room temperature.

Results and discussion

XRD analysis

Figure 1 shows the X-ray powder diffraction patterns of Y_2O_3:Yb^{3+},Tm^{3+} nanocrystals calcined at 800 °C for 2 h. All the peaks correspond to the reflection of cubic Y_2O_3 (space group:Ia3) and are in line with the standard data (JCPDS No. 65-3178). No diffraction peaks of Yb_2O_3 or Tm_2O_3 appeared on the recorded XRD spectra, which implies that RE ions are doped into Y_2O_3 host efficiently. Comparing the XRD patterns of Y_2O_3:Tm^{3+} with Y_2O_3:Yb^{3+}(10 mol%), Tm^{3+}, it is known that the lattice distortion still does not occur when the doping concentration of Yb^{3+} is as high as 10 mol%, which is beneficial to the upconversion luminescence.

SEM analysis

Figure 2 displays a SEM micrograph of the Y_2O_3 nanocrystals doped with 0.5 mol% Tm^{3+} and 10 mol% Yb^{3+} calcinated at 800 °C. It's evident that the samples are congeries composed of nearly spherical particles with diameter of about 30 nm.

Fluorescence spectrum of upconversion luminescence agent

Ultraviolet upconversion emission spectra of the Y_2O_3:Yb^{3+},Tm^{3+} excited at 980 nm are shown in Fig. 3. The two ultraviolet emission peaks, which are located at about 297 and 363 nm, are assigned to the $^1I_6 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3H_6$ transitions of the Tm^{3+} ion, respectively.

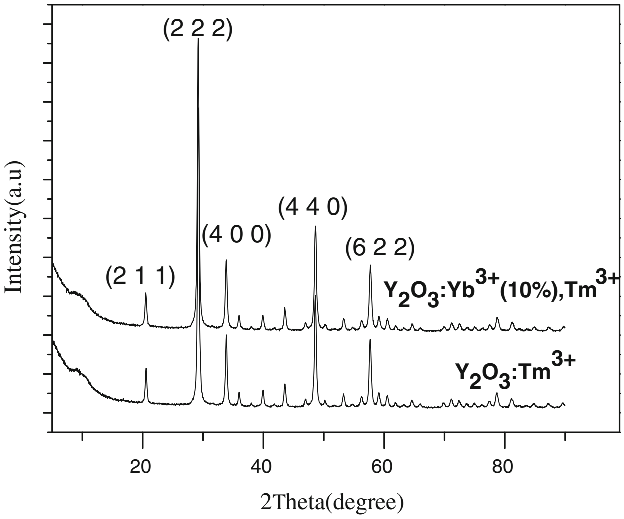

Fig. 1 XRD patterns of Y_2O_3: Yb^{3+},Tm^{3+} nanocrystals calcined at 800 °C for 2 h

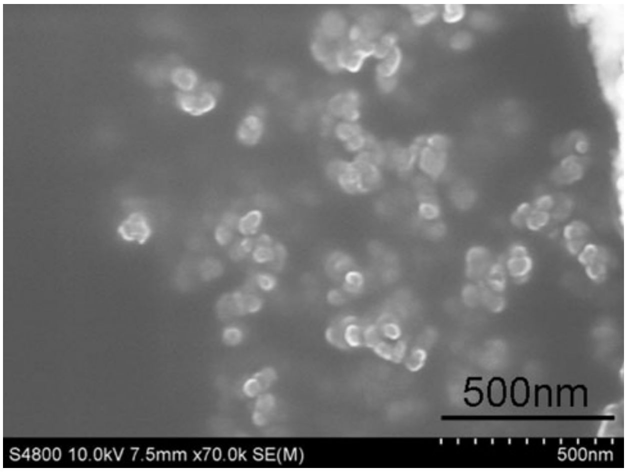

Fig. 2 SEM image of the Y_2O_3 :Yb^{3+},Tm^{3+} nanocrystals calcined at 800 °C for 2 h

The possible upconversion mechanism is shown in Fig. 4. Yb^{3+} ions can be excited by the pump light, and three successive energy transfers from Yb^{3+} to Tm^{3+} populate $^3H_5$, $^3F_3$($^3F_2$), and $^1G_4$. Though the Tm^{3+}–Tm^{3+} interaction is weak in the sample with low Tm^{3+} concentration owing to the large energy mismatch (about 3516 cm^{-1}) in the transfer $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}):$^1G_4 \rightarrow {}^1D_2$ (Tm^{3+}), the cross relaxation process $^3F_2 \rightarrow {}^3H_6$ (Tm^{3+}):$^3H_4 \rightarrow {}^1D_2$ (Tm^{3+}) may alternatively play the most important role in populating $^1D_2$. Then, the state $^1I_6$ can be populated by $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}):$^1D_2 \rightarrow {}^1I_6$ (Tm^{3+}) [13].

It can also be found from Fig. 3 that Yb^{3+} doping can make the upconversion emission to increase the intensity owing to the sensitizing effect of Yb^{3+}. However, the upconversion emission intensity decreases with the increase of Yb^{3+} concentration when the concentration of Yb^{3+} exceeds 2 mol%. The possible reason is analyzed as

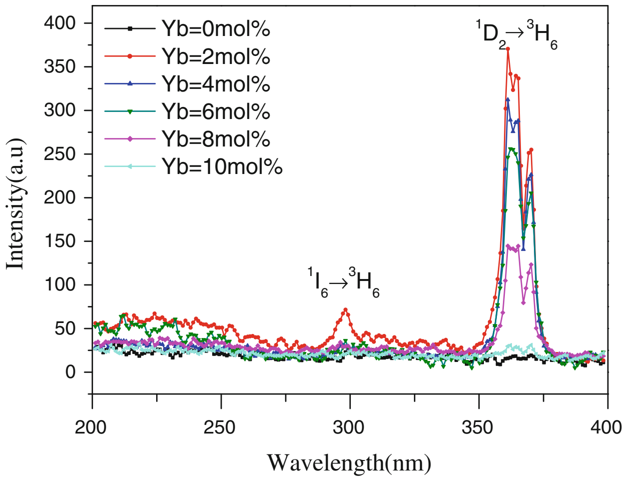

Fig. 3 Ultraviolet upconversion emission in the Y_2O_3:Yb^{3+},Tm^{3+} calcined at 800 °C for 2 h ($\lambda_{ex} = 980$ nm)

follows. It is well known that Yb^{3+} ion has lager absorption cross section to 980-nm pumping photons than Tm^{3+} and can sensitize Tm^{3+} efficiently. Therefore, it is believable that the population of the excited states of Tm^{3+} takes place mainly by energy transfer from Yb^{3+} to Tm^{3+} ion [14]. However, an excessively high concentration of Yb^{3+} may lead to the formation of "ion pairs" or "ion clusters" and reduce the number of Yb^{3+} ions playing a sensitization role. Moreover, the number of Yb^{3+} ions around each Tm^{3+} increased with the further increase of Yb^{3+} concentration, leading to the reverse energy transfer from Tm^{3+} to Yb^{3+}. Noginov et al. have predicted that the reverse energy transfer of $^1G_4 \rightarrow {}^3H_4$ (Tm^{3+}):$^2F_{7/2} \rightarrow {}^2F_{5/2}$ (Yb^{3+}) could lead to the quench of $^1G_4$ level [15]. This is consistent with the fact that the luminescence peak almost disappeared when the concentration of Yb^{3+} ion reached 10 mol% in our experiment.

Photocatalytic degradation of doped TiO_2 catalyst under solar light irradiation

Photocatalytic activity of the samples is estimated by measuring the photodegradation rate of methyl orange aqueous solution under solar light irradiation. The photodegradation curves of methyl orange solution over pure TiO_2 and TiO_2 doped with upconversion luminescence agent Y_2O_3:Yb^{3+},Tm^{3+} are shown in Fig. 5. It is obvious that the photocatalytic activity of doped TiO_2 is higher than that of pure TiO_2. After irradiation for 2.5 h, the methyl orange is degraded by 99.2% for doped TiO_2, while the photodegradation rate is only 43.9% for pure TiO_2 after the same irradiation time.

The reason is that the upconversion luminescence agent doped in TiO_2 powder can transform the unavailable infrared light into available ultraviolet light for TiO_2 efficiently. It is well known that the band-gap energy of pure anatase TiO_2 is about 3.2 eV, and that only ultraviolet light can be absorbed by pure TiO_2. Ultraviolet light is about 4% part of solar energy, and 96% part of solar energy (mainly visible or infrared light) cannot be used efficiently.

The possible photodegradation mechanism in the doped TiO_2 powder under solar light irradiation is supposed as follows: first, the upconversion luminescence agent absorbs and transforms infrared light part of solar light into ultraviolet light continuously (Fig. 3), then the ultraviolet light (including the ultraviolet light part of solar light) is absorbed immediately by TiO_2 catalyst around the upconversion luminescence agent to generate cavities. These cavities with high oxidative ability can not only directly decompose the organic pollutants in wastewaters, but also can degrade them indirectly through oxidation of H_2O molecules to ·OH with high oxidative ability[16].

Conclusion

An infrared-to-ultraviolet upconversion agent Y_2O_3:Yb^{3+}, Tm^{3+} and a novel composite photo catalyst TiO_2/Y_2O_3:Yb^{3+},Tm^{3+} have been synthesized by combustion method and precipitation method, respectively. Two ultraviolet emission peaks at 297 and 363 nm have been detected using 980-nm CW LD as excitation source. Since the upconversion luminescence agent can efficiently transform the unavailable infrared light into available ultraviolet light by TiO_2, TiO_2/Y_2O_3:Yb^{3+},Tm^{3+} composite has higher photocatalytic activity than pure TiO_2 under solar light irradiation.

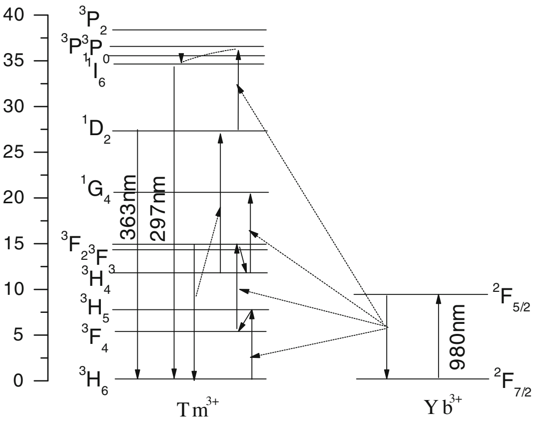

Fig. 4 The energy level diagrams of the Tm^{3+} and Yb^{3+} dopant ions and upconversion mechanism under 980-nm laser excitation

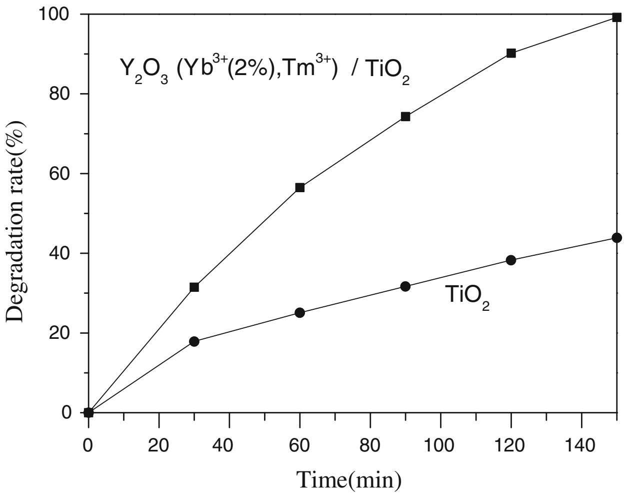

Fig. 5 photocatalytic degradation rate of the methyl orange over pure TiO_2 and doped TiO_2 under solar light irradiation

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