Hydrothermal assisted sol-gel synthesis and multisite luminescent properties of anatase TiO$_2$:Eu$^{3+}$ nanorods

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Uniform TiO$_2$:Eu$^{3+}$ spindlelike nanorods have been successfully prepared by a hydrothermal assisted sol-gel process with ethanediamine (ED) as the shape controller. A possible formation mechanism and luminescent properties were investigated by X-Ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL) and kinetic decays. And site-selective spectroscopy was used to research into sites of Eu$^{3+}$ in TiO$_2$ lattice at 10 K, which identifies two kinds of sites of Eu$^{3+}$ in TiO$_2$ nanocrystals. One is located in the distorted lattice sites near the surface, and the other is situated in lattice sites with ordered crystalline environment. Moreover, the luminescence decay curve of products further proved the existence of multiple sites of Eu$^{3+}$ ions in TiO$_2$ nanocrystals.

1. Introduction

Over the past decade, titanium dioxide (TiO$_2$) has attracted considerable attention due to its widespread applications in fields such as photocatalysis, dye-sensitized solar cells, sensors, especially used as luminescence materials. Because of unique optical, electrical, and photochemical properties of titania come from its own energy band gap characteristics, TiO$_2$ is suggested to be a promising host lattice for the luminescence of various optically active lanthanide ions. As we know, the properties of titania are strongly dependent on the morphology and crystallite size. Hence, much more efforts should be made to precisely control crystallinity and morphological features of titania.

Compared with other 1D nanostructures, nanorods with high aspect ratios have become the focus of scientists because of their potential applications in photoelectrochemical hydrogen production, hybrid ultraviolet photodetectors, optical materials, magnetic properties, planar device applications. Titanium oxide nanorods, up to now, have been produced using chemistry methods including hydrothermal routes, self-assembly methods, sol-gel processes, solvothermal methods, and so on. For example, Jiu et al. described that highly crystalline TiO$_2$ nanorods have been synthesized by a hydrothermal process in a cetyltrimethylammonium bromide surfactant solution. Koo et al have reported the simultaneous phase- and size-controlled synthesis of TiO$_2$ nanorods were performed via the non-hydrolytic sol-gel method. However, few studies have been reported on the synthesis and the luminescence properties of rare-earth doped TiO$_2$ nanorods, particularly the luminescence characteristics of multiple sites of Eu$^{3+}$ ions in TiO$_2$ nanocrystals.

In this article, TiO$_2$:Eu$^{3+}$ spindlelike nanorods with uniform crystallinity and narrow size distribution have been formed through hydrothermal assisted sol-gel process, which combines the advantages of sol-gel route and hydrothermal method, such as lower reaction temperature, controllable morphology, narrow particle size distribution. The influences of preparation conditions on the crystal phase, crystal shape, as well as the luminescent properties were investigated. Ethanediamine was added to act as a shape controller because it’s specifically adsorbed onto the planes parallel to the c-axis of nanoparticles. The formation mechanism of the products was proposed. Furthermore, through site-selective spectroscopy at 10 K, we have found two kinds of sites of Eu$^{3+}$ ions with different luminescent characteristics doped in TiO$_2$ nanocrystals.

2. Experimental

2.1 Materials

Tetrabutyl titanate, triethanolamine, ethylenediamine, absolute ethanol and Eu$_2$O$_3$ (99.99%) were purchased from Beijing Chemical Co. All chemicals were analytical-grade reagents and used directly without further purification. The Eu(NO$_3$)$_3$ aqueous solution was obtained by dissolving Eu$_2$O$_3$ (99.99%) in dilute HNO$_3$ solution under heating with vigorously agitation. Deionized water was used for all treatment processes.
2.2 Synthesis of the TiO$_2$:Eu$^{3+}$ nanorods

In this article, tetrabutyl titanate (TBOT) was chosen as titanium source. Firstly, TBOT and triethanolamine (TEOA) were mixed with a molar ratio of [TBOT]:[TEOA] = 1:2 to form a stable compound of Ti$^{4+}$ in order to avoid rapid hydrolysis of Ti$^{4+}$, and then the molar concentration of Ti$^{4+}$ reached to 0.5 mol/L by the addition of deionized water. The stock solution was mixed with the same volume of aqueous solution of ethylenediamine (0.6 mol/L) with magnetic stirring. Then 0.2 mL Eu(NO$_3$)$_3$ (0.5 mol/L) was added to above solution. The final solution was transferred into a Teflon stainless steel autoclave aged at 100 °C for 24 h for gelation (the first aging), and further aged at 140 °C for 72 h to achieve the nucleation and growth of titania (the second aging). The autoclave was then cooled to room temperature naturally. Finally, the white precipitate was washed with deionized water and absolute ethanol several times. The products were dried at 60 °C for 12 h in air.

2.3 Characterization

The crystalline phase of the TiO$_2$:Eu$^{3+}$ nanorods were distinguished by standard X-ray diffraction (XRD) (Rigaku D/max-B II) with Cu-Kα radiation (λ = 0.15405 nm) over a 2θ range from 10° to 70°. The morphology of the products was inspected using a scanning electron microscope (S-4800, Hitachi) and transmission electron microscopy (FEI Tecnai G$^2$S-Twin) with a field-emission gun operating at 200 kV. Photoluminescence excitation and emission spectra were recorded with a Jobin Yvon FluoroMax-4 equipped with a 150 W xenon lamp as the excitation source. For low temperature measurement, the samples were mounted in the helium-exchange gas chamber of a closed-cycle refrigeration system, and their temperature was maintained at 10 K. A Rhodamine 6G dye laser pumped by the second harmonic of an Nd:yttrium–aluminum–garnet pulsed laser was used as the excitation source. The site-selective spectra were obtained with a Spex 1403 spectrometer. The photoluminescence signals were detected with a photomultiplier, averaged with a boxcar integrator, and processed by a computer.

3. Results and discussion

3.1 Crystal Structure and phase composition

As is known to all, TiO$_2$ exists in three mineral forms: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Generally, TiO$_2$ is preferred in anatase form with wide band gap (3.2 eV) and higher electron mobility. In this article, X-ray diffraction (XRD) analyses were performed to investigate the phase and purity of the products. As illustrated in Figure 1, all diffraction peaks match well with the crystal structure of the anatase TiO$_2$ (JCPDS card 21-1272), and no additional peaks for others phases have been found, which indicates that Eu$^{3+}$ ions have been built into the TiO$_2$ host lattice effectively. The main diffraction peaks may shift slightly because of the different radius between Eu$^{3+}$ ions and Ti$^{4+}$ ions. However, the shift of diffraction peaks has not been detected in our experiments due to the low doping concentrating of Eu$^{3+}$ ions. The energy dispersive X-ray (EDX) spectrum was further used to analyse the compositions of the as-obtained TiO$_2$:Eu$^{3+}$ nanorods, as shown in Figure 2. The result confirms the presence of Ti, O, and Eu elements in the products, which is in agreement with the XRD result above.

Figure 1. XRD patterns of the as-synthesized TiO$_2$:Eu$^{3+}$ nanorods, along with the standard data for the anatase TiO$_2$ (JCPDS card 21-1272) as references.

3.2. Morphology

The morphology and microstructure details of the as-prepared nanorods were surveyed by means of SEM and TEM. Figure 3a shows the SEM image of Eu$^{3+}$ doped titania nanorods. It can be seen that the sample is composed of the uniform spindle-shape nanorods. To further study the texture of the products, a TEM micrograph (Figure 3b) for the as-prepared sample clearly shows the obvious spindlelike nanorods with an average size of 45 nm in width and 500 nm in length, which is in consistent with the SEM result.

Figure 3. (a) SEM, and (b) TEM images of TiO$_2$:Eu$^{3+}$ spindlelike nanorods.

3.3. Effect of the dosage of the shape controller
Many 1D compound nanostructures were obtained with the assistant of additives. As a shape controller, ethanediamine played an important role in the synthesis of TiO$_2$:Eu$^{3+}$ spindlelike nanorods for its complete growth. And the reaction time is 96 h.

As shown in Figure 4, different dosages of ED were added to understand its effect on the growth of TiO$_2$:Eu$^{3+}$ nanocrystals. When ED was absent in the raw materials while other conditions remained the same, the products were composed of uniform ellipsoidal nanoparticles with lower aspect ratio (Figure 4a).

When the dosage of ED rose to 0.2 mol/L and 0.4 mol/L (Figure 4b, and 4c), some imperfect spindlelike nanorods formed by aggregation of the smaller nanoparticles which have already formed. And the monodisperse and uniform nanoparticles with higher aspect ratio have been achieved when the amount of ED is 0.6 mol/L (Figure 4d). As the amount of ED further increased to 0.8 mol/L and 1.0 mol/L (Figure 4e, and 4f), a large number of nanoparticles aggregated together with no definite shape. In this work, ED plays a decisive role to produce the uniform spindlelike nanostructure (i) as a shape controller by adsorbing onto the planes parallel to the c-axis of nanoparticles and (ii) as a capping agent to balance the growth rates of different facets.

3.4. Effect of reaction time

In order to investigate the growth mechanism of the TiO$_2$:Eu$^{3+}$ spindlelike nanorods, the SEM images of the products obtained at different time intervals are shown in Figure 5. And you can notice that when the dosage of ED rose to 0.6 mol/L, uniform spindlelike nanoparticles were formed from Figure 4. So this dosage has been selected for optimizing the time. When the reaction time was 36 h and 48 h (Figure 5a and 5b), no definite shape was obtained. With the extension of the reaction time (Figure 5c-5e), more and more spindle-shaped nanorods appeared. Until the reaction time was increased to 96 h, the final products were uniform and monodispersed spindlelike nanorods (Figure 5f).

3.5. Formation mechanism

According to the above experimental results, a possible formation mechanism of the spindlelike TiO$_2$:Eu$^{3+}$ nanorods is illustrated in Figure 6. The formation process includes chelation, gelation, nucleation and growth stage. Firstly, the stable complex formed through reaction of tetrabutyl titanate (TBOT) and triethanolamine (TEOA), TEOA plays the role of a stabilizer of Ti (IV) ions against its rapid hydrolysis to Ti(OH)$_4$ in the alkaline range. The first aging at 100 °C for 24 h in autoclave provides a high temperature and high pressure environment, so the chelating ability of the stable complex would become weaker. Almost all TEOA molecules were found to be liberated after the hydrolysis of Ti$^{4+}$ ions, then the Ti(OH)$_4$ gel formed. The gel network acts as a reservoir of the Ti$^{4+}$ ions to reduce the excessive supersaturation leading to extensive nucleation during their growth and as an anticoagulant fixing the growing nanoparticles in the matrix, which plays a decisive role to produce the monodisperse titania nanoparticles. After the dissolution of the Ti(OH)$_4$ gel, the nucleation and growth of TiO$_2$ happened at 140 °C for 72 h in the second aging process. As the shape controller, ED adsorbed selectively onto the different crystal facets of the growing nanoparticles and changed the relative surface energy of different crystal facets, and brought about an effect on the growth rates along certain orientations. In our research, ED specifically adsorbed onto the planes parallel to the c-axis, so these crystal nuclei aggregated to grow along this direction simultaneously and formed spindle-shaped nanorods. Therefore, in the presence of ED, the nanoparticles finally form uniform TiO$_2$:Eu$^{3+}$ spindlelike nanorods.
3.5. Luminescence Properties

Figure 7 shows the excitation and emission spectra of the as-prepared TiO$_2$:Eu$^{3+}$ spindlelike nanorods at room temperature. The excitation spectrum was obtained by monitoring the emission of the Eu$^{3+}$ ions $^5$D$_{0}$-$^7$F$_J$ transition at 612 nm (Figure 7a). The excitation spectrum consists of Eu$^{3+}$ ions characteristic excitation peaks (382, 393, 414, 464, and 525 (533) nm), which are due to the f-f transition of Eu$^{3+}$ ions from the $^5$D$_{0}$ to $^5$D$_{J}$ ($J = 0, 1, 2, 3, 4$) transitions of the Eu$^{3+}$ ions, respectively. The major emissions are 590 nm ($^5$D$_{0}$-$^7$F$_J$) and 612 nm ($^7$D$_{0}$-$^7$F$_J$) corresponding to the magnetic dipole transition and electric dipole transition. The Eu$^{3+}$ ions can be used as a probe for the crystal field environments through comparison of the intensity of the $^5$D$_{0}$-$^7$F$_J$ (590 nm) transition with that of the $^7$D$_{0}$-$^7$F$_J$ (612 nm) transition.

As shown in Figure 7b, the electric dipole transition is much stronger than the magnetic dipole transition, so the emission spectrum is dominated by the $^7$D$_{0}$-$^7$F$_J$ (612 nm) transition of the Eu$^{3+}$ ions which is hypersensitive to the environment. It suggests that Eu$^{3+}$ ions occupy low-symmetry sites without an inversion center. The site symmetries for the Ti$^{4+}$ ions are D$_{2d}$ in anatase lattice. According to the branching rules of the 32 point groups, because of a large mismatch in ionic radius and the charge imbalance between Ti$^{4+}$ and Eu$^{3+}$, the substitution of the Ti$^{4+}$ with Eu$^{3+}$ ions created oxygen vacancies and caused the lattice distortion, which makes a descent of the D$_{2d}$ to lower site symmetry.

Site-selective spectroscopy at 10 K were performed to research into doped positions of Eu$^{3+}$ ions in TiO$_2$ nanocrystals using the experience of Chen et al. for reference. As shown in Figure 8, under excitation at 464.6 nm, we can see that electric dipole transition (614 nm) is much stronger than magnetic dipole transition (590 nm), suggesting that Eu$^{3+}$ ions occupy low-symmetry sites without an inversion center, which has further proved that Eu$^{3+}$ ions have doped in the distorted lattice sites near the surface. However, under excitation at 470.7 nm and 472.1 nm, the magnetic dipole transition intensity is stronger than the electric dipole transition intensity, indicating that the Eu$^{3+}$ ions may occupy the C$_{2v}$, D$_2$ high symmetry sites with an inversion center in tetragonal anatase TiO$_2$, which can interpret that Eu$^{3+}$ ions have doped in lattice sites with ordered crystalline environment. G. K. Liu et al. have discussed the mechanisms for anomalous luminescence properties of Eu$^{3+}$ ions at two main sites of BaFCl microcrystals through charge transfer vibronic excitation (CTVE) model. In this article, CTVE model and oxygen vacancy can be used to interpret the multisite structure of Eu$^{3+}$ in anatase nanocrystals. The C$_{2v}$ symmetry site is formed because of lattice uniform relaxation at different directions and the formation of oxygen vacancy. However, for D$_2$ symmetry site, the oxygen vacancy is not completely formed, instead, the charge transfer vibronic exciton has been formed to compensate for the charge.
imbalance and lattice uneven expansion at different directions.

![Image](image.png)

**Figure 8.** 10 K emission spectra of TiO$_2$:Eu$^{3+}$ nanorods with $\lambda_{ex} =$ (a) 464.6, (b) 470.7, and (c) 472.1 nm. The nanorods were excited with a xenon lamp at 464–472 nm under the same experimental condition. To eliminate the influence of excitation light, a 495 nm long-pass glass filter was used.

To further confirm the multiple sites of Eu$^{3+}$ ions doped in TiO$_2$ crystalline host lattice, decay curve of the $^5$D$_{0}$→$^7$F$_2$ transition of the Eu$^{3+}$ ($\lambda_{em} =$ 612 nm) in the TiO$_2$:Eu$^{3+}$ nanorods was determined, which can provide dynamics evidence for the different multiple sites. As shown in Figure 9, the curve cannot be fitted into the single-exponential function but can be fitted well into a double-exponential function as $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, in which $A_i$ ($i = 1, 2$) is a pre-exponential factor obtained from the curve fitting, and $\tau_i$ ($i = 1, 2$) is the decay lifetime. The PL lifetimes for the $^5$D$_{0}$ state of the Eu$^{3+}$ ions in the TiO$_2$ nanorods are 0.563 ms and 0.106 ms, corresponding to Eu$^{3+}$ ions ordered lattice sites and distorted lattice sites near the surface, respectively. However, we have noticed that decay time in the distorted lattice sites becomes short due to the quenching effect of the surface defects which come from surface states of TiO$_2$:Eu$^{3+}$ nanorods. When the excited luminescent centers are near quenching centers which exist in the products, the excited energy will be transferred to these quenching centers, leading to the shorter lifetime.

![Image](image.png)

**Figure 9.** Decay curve for the $^5$D$_{0}$→$^7$F$_2$ (612 nm) emission of the Eu$^{3+}$ ions in TiO$_2$:Eu$^{3+}$ nanorods.

**Conclusions**

In summary, a hydrothermal assisted sol-gel process has been introduced to incorporate Eu$^{3+}$ ions into TiO$_2$ spindlelike nanoparticles. Ethanediamine acted as a shape controller and specifically adsorbed onto the planes parallel to the c-axis of the TiO$_2$ nanoparticles. The possible formation mechanism includes chelation, gelation, nucleation and growth stage has been discussed in detail. Most importantly, we have confirmed that the multiple sites structure of Eu$^{3+}$ ions doped in TiO$_2$ through site-selective spectroscopy at 10 K. Using Eu$^{3+}$ as an optical probe, the relationship between local structure of Eu$^{3+}$ ions and luminescence properties was discussed. We have found two kinds of sites of Eu$^{3+}$ in TiO$_2$ nanocrystals, one is in the distorted lattice sites near the surface, and the other is lattice sites with ordered crystalline environment. And the decay curve has further proved this point. Furthermore, the TiO$_2$:Eu$^{3+}$ spindlelike nanorods without any calcination treatment exhibit bright red ($^5$D$_{0}$→$^7$F$_2$) luminescence under ultraviolet excitation. Owing to the uniform sizes and favorable luminescent properties of the products, TiO$_2$:Eu$^{3+}$ nanorods possess a prosperous application in the fields of optics and electronics in the future.

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**Note and references**


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The relationship between local structure of Eu$^{3+}$ ions and luminescence properties were discussed through site-selective spectroscopy at 10 K.