



Photoluminescence of nanosheets doped with rare earth ions

Na Zhang^a, Caixia Li^a, Danyu Jiang^b, Jing Chu^a, Hongguang Chen^c, Jing Zhang^c, Qiang Li^{a,*}

^a Department of Chemistry, East China Normal University, 3663 Zhongshan Rd., Shanghai 200062, PR China

^b Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, PR China

^c Planning and Development Department, Shanghai Nanotechnology Promotion Center, Shanghai 200237, PR China

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ABSTRACT

Lamellar aggregates of the semiconductor nanosheets accommodating rare earth ions of Tb³⁺ or Eu³⁺ have been fabricated by flocculation of colloidal TiTaO₅⁻ nanosheet. The as-obtained composites were analyzed by a range of methods including powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) with energy dispersive X-ray spectrometer (EDS). The results indicated that the re-stacking of the nanosheets could form a uniform layered structure. Meanwhile, the RE ions could be attached to the flocculated samples. The photoluminescence (PL) spectra were also employed to explore the optical property of the hybrid. The characteristic emission from the composites either by exciting the nanosheet host with UV light or by directly exciting RE at a longer wavelength has been investigated in detail. At the same time, the energy transfer between nanosheet and RE ions could be discussed systemically.

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1. Introduction

In recent years, the novel luminescent properties of nanosheets and related materials have attracted great interest [1–9]. The thickness of a nanosheet is about 1 nm, and the lateral size ranges from several hundred square nanometers to several square micrometers, which make it possible to develop new luminescent materials by building up various functional nanosheets together with the intercalated guest ions [4–8]. Nanosheets have a considerably large surface-to-volume ratio, which could provide sufficient room to effectively adsorb the photoluminescence excitation energy. To date, the majority of nanosheet-based phosphor materials reported can be categorized into two groups. In one group, the nanosheets themselves have photoluminescence property which can be directly detected under the UV–vis irradiation without any further treatment. The reported photoluminescent materials include the nanosheets prepared by exfoliation of KLa_{0.90}Eu_{0.05}Nb₂O₇ [4] Li₂Eu_{0.56}Ta₂O₇ [5], (K_{1.5}Eu_{0.5})Ta₃O₁₀ [10], Gd_(2-x)Eu_xTi₃O₁₀⁻, La_(1-x)Tb_xTa₂O₇⁻ [6] and Bi₂SrTa₂O₉ [3]. Nanosheets give intense red, green or blue emissions, respectively. In the other group, the guest ions are inserted into the transition metal oxide nanosheets to form the phosphors [7–13]. In this system, effective energy transfer from the transition metal oxide nanosheet hosts to Ln luminescence activators may take place. In this case, a bright light also could be seen by the naked eye under the UV light. Therefore, the energy transfer could be utilized to

open a new door to design the solid practical nanosheet-based phosphor.

On the basis of the above point of view, the nanosheet-based phosphor for solid-state lighting seems feasible. The choice of the guest ions is critical issue for photoluminescence properties. Rare earth (RE) or lanthanide (Ln) ions are quite intriguing because of their excellent luminescence characteristics with extremely sharp emission bands originating from their 4f electronic transition. Among the photoactive components, Tb³⁺ and Eu³⁺ are particularly interesting because of their strong and well-defined green or red photoluminescence property, while one of the candidate host nanosheets for such an ideal phosphor material is TiTaO₅⁻ nanosheet, which could be easily fabricated by the soft chemical exfoliation described below. It must point out that the stabilities of photoluminescence properties and the efficiency of energy transfer tend to be susceptible to the amount of the cointercalated species [12–14].

In this work, we report the synthesis of restacked composites of TiTaO₅⁻ nanosheets with RE ions for the first time. In the early stage of our experiment, an attempt is made to prepare stoichiometric nanosheets of TiTaO₅⁻ successfully by the method as described previously. Then, by adding different solutions containing Tb³⁺ or Eu³⁺ into the colloidal TiTaO₅⁻ nanosheet solution, the wool-like precipitate appeared, and the hybrid of the TiTaO₅⁻/Tb or HTiTaO₅⁻/Eu are formed. The unique structural feature and the optical property are studied detailedly in the following section.

2. Experimental

TiTaO₅⁻ nanosheets were prepared according to the procedure described in the literature [15]. The addition of a TbCl₃ (0.1 M 50 ml, pH = 1) or Eu(NO₃)₃ (0.1 M 6 ml,

* Corresponding author. Tel.: +86 135 62845769; fax: +86 021 62232414.
E-mail address: qli@chem.ecnu.edu.cn (Q. Li).

pH = 1) solution to 50 ml of the supernatant nanosheet solution resulted in the immediate co-aggregation as a precipitate. Then it was kept still for a while, and the clear liquid above the cotton-like sample was removed. The collected mixture at the bottom were subjected to rotary evaporator, by vacuum evaporation at 70 °C, the dried white powder was obtained for further investigation.

X-ray diffraction (XRD) patterns were collected by using a Rigaku Rint 2000S powder diffractometer. PL spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. Transmission electron microscopy (TEM) observations were performed using a high-resolution TEM microscope (JEM-2100F) with energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

Fig. 1 showed that a set of sharp diffraction lines appeared in a lower angular range, which was indicative of a lamellar structure with a gallery height of 1.04 nm and 1.06 nm. These values roughly agreed with one layer of the nanosheet with the hydrated Tb^{3+} and Eu^{3+} [16–21]. It lead to the conclusion that when the $TiTaO_5^-$ sheets were restacked, RE ions were intercalated into the interlayers together.

The TEM image in Fig. 2 clearly showed the lamellar feature of the intercalated material, and the part marked by circle could be obviously detected as the representation of the layered form. From structure of the layered hybrids, it was assumed that when the Tb^{3+} or Eu^{3+} was added into the nanosheet solution, immediately they resulted in a precipitate. It consisted of a single phase of the RE ions intercalated the layered oxides, which was formed by electrostatic interaction between the negatively charged nanosheets and

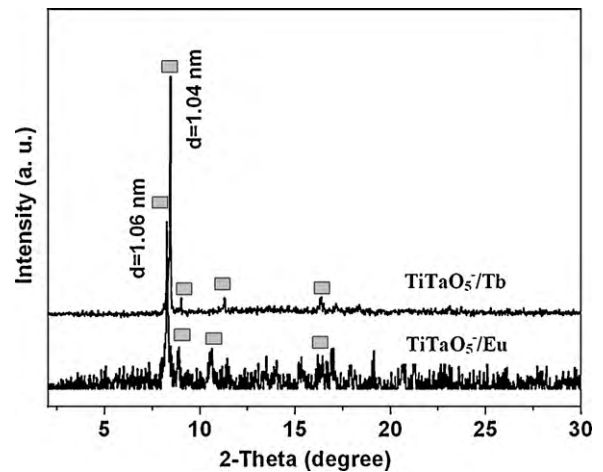


Fig. 1. XRD pattern of the composites $TiTaO_5^-/Tb$ and $TiTaO_5^-/Eu$.

positively charged RE ions as shown in Fig. 3. Meanwhile, the incorporation of RE ions in the flocculated specimen was confirmed by EDS analysis (in Fig. 4), which depicted that Tb or Eu element was co-existed in the corresponding material.

As shown in Fig. 5, the hybrids of $TiTaO_5^-/Tb$ or $TiTaO_5^-/Eu$ both exhibited intense characteristic light originated from RE ions,

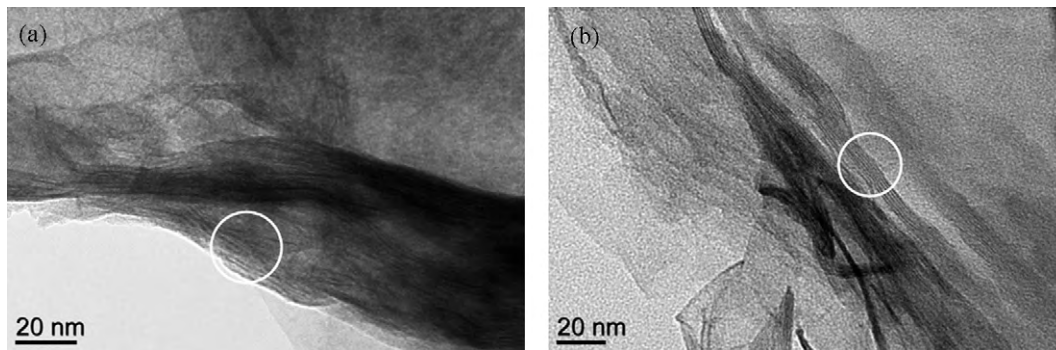


Fig. 2. TEM image of the hybrid $TiTaO_5^-/Tb$ (a) and $TiTaO_5^-/Eu$ (b).

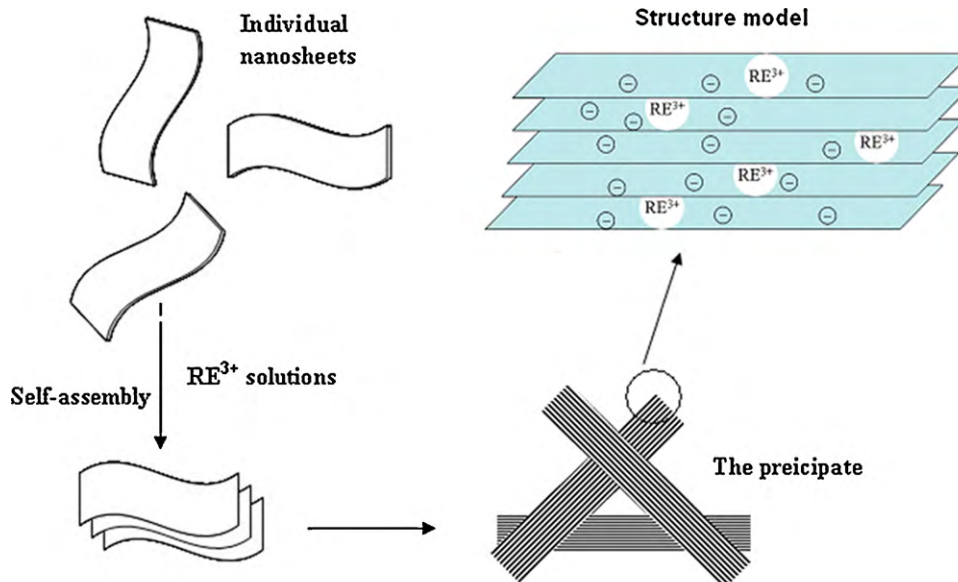


Fig. 3. Schematic illustration of electrostatic self-assembly process of the hybrids.

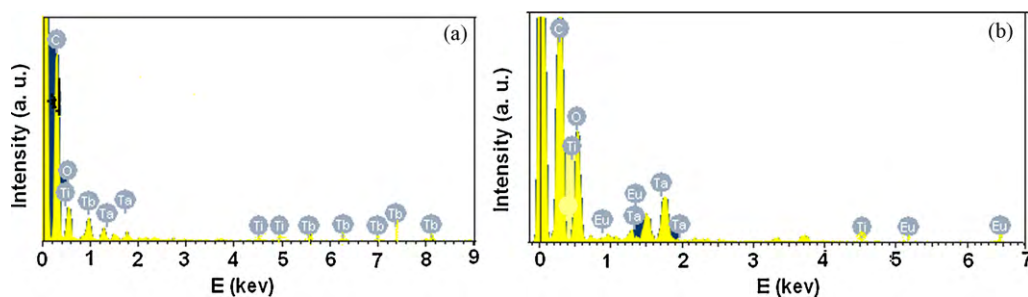


Fig. 4. EDS of TiTaO₅⁻/Tb (a) and TiTaO₅⁻/Eu (b).

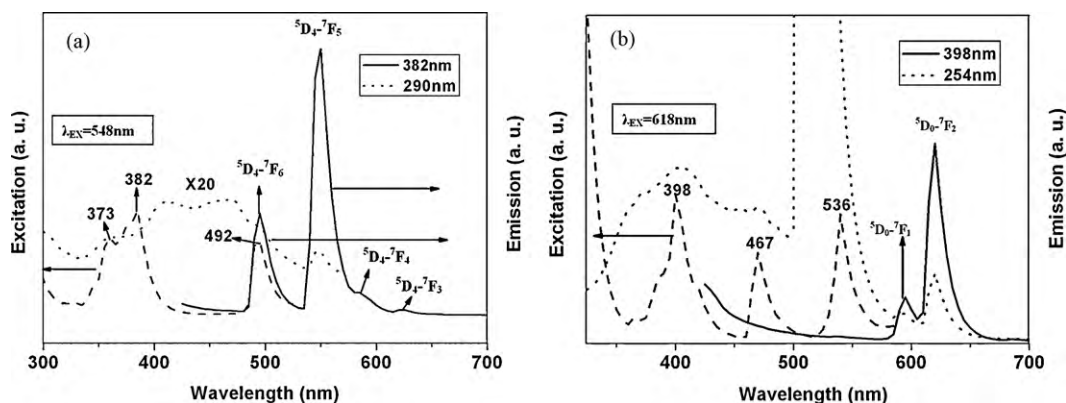


Fig. 5. PL excitation and emission spectra of the TiTaO₅⁻/Tb (a) and TiTaO₅⁻/Eu (b).

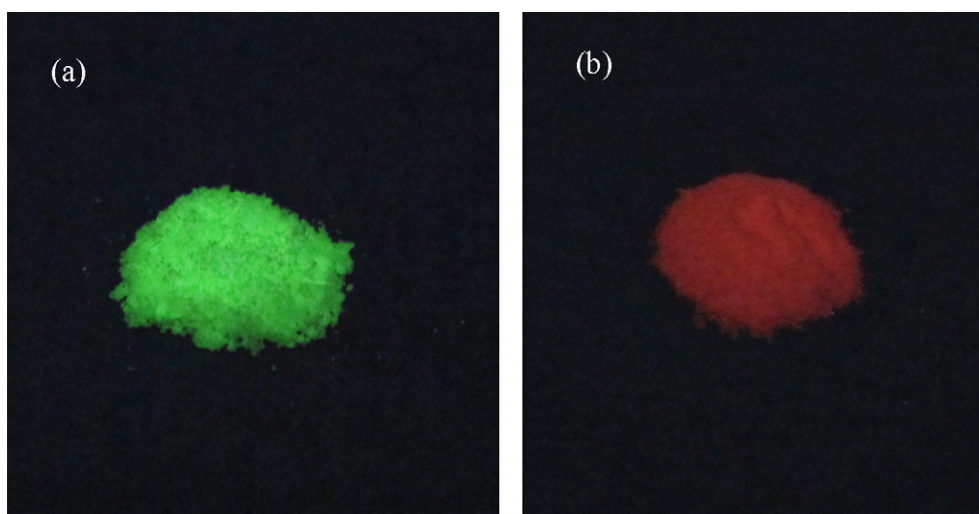


Fig. 6. The real color image for the TiTaO₅⁻/Tb (a) and TiTaO₅⁻/Eu (b) under UV-irradiation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

by being excited at a wavelength longer than the absorption edge (300 nm) of the TiTaO₅⁻ nanosheet host. It was worth to be noted that the emission spectra were due to the absorption of RE ions as confirmed by the excitation spectra. In the case of TiTaO₅⁻/Tb excitation spectra, the three peaks centered at 373 nm, 382 nm and 492 nm were attributed to the f^l-f^l electron transition, which coincided well with the UV–vis absorption lines not shown here. The sample exhibited intense green emission with the excitation of 382 nm, and the emission peaks at 492 nm, 548 nm, 588 nm, and 625 nm were assigned to $^5D_4-^7F_j$ ($j=3-6$) transitions of Tb³⁺, respectively. When excited at a wavelength of 290 nm, TiTaO₅⁻/Tb emitted light both from the TiTaO₅⁻ nanosheet host and Tb³⁺ ions.

The UV region of 350–490 nm was due to the emission from the TiTaO₅⁻ nanosheet host, while the left lower peaks were characteristic lines from Tb³⁺. Although the emission intensity from Tb³⁺ was lower than that from the host, it was suggested that Tb³⁺ ions could be excited via the TiTaO₅⁻ nanosheet host. Under the irradiation of UV light, the green luminescence of TiTaO₅⁻/Tb sample was shown in Fig. 6(a).

In the same manner, for the TiTaO₅⁻/Eu excitation spectra, the three peaks located at 398 nm, 467 nm and 536 nm, which were ascribed to the intraconfigurational $^7F_0-^5L_6$, $^7F_0-^5D_2$, $^7F_1-^5D_1$ transition as that was usually observed [22–25]. These peaks could also be detected from the corresponding UV–vis spectra.

Meanwhile, specific red emissions of Eu^{3+} (${}^5\text{D}_0/{}^7\text{F}_n$ ($n = 1,2$)) were observed. The emission at 593 nm was due to the magnetic dipole transition of ${}^5\text{D}_0-{}^7\text{F}_1$, while the emission at 618 nm was due to the electric dipole transition of ${}^5\text{D}_0-{}^7\text{F}_2$, induced by the lack of inversion symmetry at the Eu^{3+} site, which was much stronger than that of the transition at the ${}^7\text{F}_1$ site [20–23], suggesting that the site symmetry of the Eu^{3+} site decreased because of the local adsorption of the chemical species to the nanosheets [6]. At the same time, $\text{TiTaO}_5^-/\text{Eu}$ emitted red light both from the TiTaO_5^- nanosheet host and Eu^{3+} ions, while excited at a wavelength of 254 nm, the red emission could be seen by the naked eyes. Fig. 6(b) is the photograph taken when the $\text{TiTaO}_5^-/\text{Eu}$ sample was illuminated by the UV lamp. It was assumed that Eu^{3+} ions could be excited via the TiTaO_5^- nanosheet host, confirming the efficient nonradiative energy transfer from TiTaO_5^- nanosheet to Eu^{3+} ions.

4. Conclusion

In summary, photoluminescence materials based on the oversized nanosheets inserted with RE ions were synthesized by the simple electrostatic self-assembly deposition method. The nanosheets with Tb and Eu specimen exhibited intense photoluminescence with bright green and red emissions at room temperature. This series of solid lighting material could be controllable with the alternative of different categories of nanosheets. Such a fascinating intralayer RE ion-doped nanosheet phosphor materials could be widely applied in optoelectronic devices.

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