

# Synthesis of LaPO<sub>4</sub>: Ce, Tb and their application for developing enhanced latent fingerprint

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Efficient water-soluble rare earth ions (Ce<sup>3+</sup>, Tb<sup>3+</sup>) doped LaPO<sub>4</sub> modified with polyethylene glycol-400 (PEG-400) were synthesized via a novel hydrothermal process. The as-prepared nanowires were characterized by TEM, SAED, EDS and luminescence spectra. The results indicated that the synthesized nanowires were easy preparation, low cost, and had unique photoluminescence, good monodispersity, enhanced adhesive property, low-toxicity, and uniform size distribution. The nanowires emitted green fluorescence, and could be used for enhancing the latent fingerprint; resulting the delicate, clear ridges and detail features without background staining. LaPO<sub>4</sub>: Ce, Tb are utilized as alternative fluorescent labeling reagents, which have very high practical and identification value in the forensic science.

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## 1. Introduction

As an important inorganic functional materials, rare earth ions doped lanthanide orthophosphates have caused widespread concern with their remarkable features due to their high melting temperature, chemical stability, and high light yields [1]. So far, they have been widely used as light-emitting devices, laser hosts, catalysts and biomolecular markers [2-4]. In recent years, with the continuous development of nano-synthesis technology, researchers synthesized variety of rare earth ions doped LaPO<sub>4</sub> nano-structured materials, such as nano-crystalline [5-7], nanorods [8, 9], nanotubes [10], and nanowires [11], etc. In addition to the already mentioned applications areas, they have also been applied in biological fluorescence labeling area based on low toxicity, photochemical stability, and high luminous efficiency [12-14].

Semiconductor quantum dots have attracted considerable attention as fluorescence labeling reagent for developing enhanced latent fingerprint [15-19]. Menzel [15] demonstrated the first example for developing latent fingerprint by utilizing CdS QDs capped by Dioctyl Sodium Sulfosuccinate ligands in aqueous media. Thereafter, the use of fluorescent semiconductor as labeling agents in latent fingermarks development has seen a significant interest in the scientific community [16-19]. Compared with the rare earth materials, semiconductor nano-materials need to be improved to reduce the detecting toxicity. However, information was still limited

about nano-materials developing fingerprint, especially in the field of rare-earth-doped nano-materials.

In the criminal cases scene, fingerprints are referred to as "first evidence" because of its unique and lifelong unchanged characteristics. After more than a century development, fingerprint technology has become an integrated multi-discipline expertise. However, current fingerprint developing methods are still some problems to be solved, such as low sensitivity, low selectivity, high background interference, high toxicity, and the high cost. To solve the above problems, rare-earth-doped nano-materials provided a powerful means.

Herein, we first reported on the use of rare earth ions (Ce<sup>3+</sup>, Tb<sup>3+</sup>) doped water-soluble lanthanide orthophosphates as a novel fluorescent probes for labeling latent fingerprint. First, a certain proportion mixture of rare earth ions (La<sup>3+</sup>, Ce<sup>3+</sup>, and Tb<sup>3+</sup>) doped water-soluble orthophosphates were synthesized via a hydrothermal synthesis method. Then, the nanowires are utilized as alternative fluorescent labeling marks for enhancing latent fingerprint developing on different surfaces in forensic science for individual identification. The results showed that the LaPO<sub>4</sub>: Ce, Tb nanowires had significantly less background and better contrast in the developing process. They were found to be satisfactory fluorescence developing reagents that could well serve as developing enhanced latent fingerprint.

## 2. Experimental

La<sub>2</sub>O<sub>3</sub> (99.99%), Tb<sub>4</sub>O<sub>7</sub> (99.99%) were purchased from the Company of Sinopharm Chemical Reagent in Shanghai, China. Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, HNO<sub>3</sub>, and PEG-400 were purchased from the Company of Chemical Reagent in Shanghai, China. In the experiments, the water was double distilled and all chemicals reagents used were of analytical grade.

At a lower reaction temperature, the rare earth ions doped LaPO<sub>4</sub> nano-structured material synthesized by hydrothermal method. La(NO<sub>3</sub>)<sub>3</sub> was produced by the dissolve of 27 mmol La<sub>2</sub>O<sub>3</sub> in 1: 1 nitric acid along with heating and stirred it continuously, the excess nitric acid is evaporated to dryness. Then, dissolved with water in a 250 mL volumetric flask, the colorless and transparent solution is La(NO<sub>3</sub>)<sub>3</sub>. Using the same procedure, 3.75 mmol Tb<sub>4</sub>O<sub>7</sub> were converted to Tb(NO<sub>3</sub>)<sub>3</sub>.

Subsequently, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Na<sub>3</sub>PO<sub>4</sub>, La(NO<sub>3</sub>)<sub>3</sub>, Tb(NO<sub>3</sub>)<sub>3</sub>, and polyethylene glycol-400 (PEG-400) were transferred to a conical flask and the mixture were fully mixed for 10 min. The molar ratio of La<sup>3+</sup>:Ce<sup>3+</sup>: Tb<sup>3+</sup> was fixed at 0.9:0.5:0.25. Finally, the rare earth ions doped LaPO<sub>4</sub> precursors were transferred into a pot of polytetrafluorethylene. The stable LaPO<sub>4</sub>: Ce, Tb were synthesized at a temperature controllable cabinet drier via heating different 4h at 150°C. The freshly prepared LaPO<sub>4</sub>: Ce, Tb were precipitated by methanol, taking the volume ratio of LaPO<sub>4</sub>: Ce, Tb to methanol to be 1:4. The precipitate was isolated by centrifugation at 8000 rpm for 10min. The obtained LaPO<sub>4</sub>: Ce, Tb were dried in vacuum at the room temperature until the samples were dry enough. The QY of LaPO<sub>4</sub>: Ce, Tb at room temperature was estimated by using Rhodamine 6G in ethanol (QY = 95%) as fluorescence reference [20].

Fluorescence spectra were obtained on a LS-55 luminescence spectrometer (Perkin-Elmer, USA). Absorption spectra were recorded on a UV-2100 spectrometer (Rui Li Analytical Instrument Co., Beijing, China). Transmission electron microscope (TEM) of Philips EM420 was used to characterize LaPO<sub>4</sub>: Ce, Tb. The powder X-ray diffraction (XRD) were carried out on a PW3040/60 X'Pert Pro MDP by using CuKα (1.5418 Å) radiation. EDX spectrum was recorded using Hitachi SEM 3400.

All fingerprint samples are taken from the same volunteer who washes hands with soap thoroughly. After the fingers were dried naturally, the volunteers gently wiped across the forehead and then pressed on the

surfaces.

LaPO<sub>4</sub>: Ce, Tb powder was gently brush the surface of the object, and the excess powder were removed with gentle and smooth motion. The fingerprint samples were shown in the darkroom and took a picture with a digital camera (Nikon D80) under ultraviolet excitation of 254 nm from an UV LED.

## 3. Results and discussion

Under UV excitation, rare earth ion doped LaPO<sub>4</sub> nano-particles, which exhibit characteristic emission of doped rare earth ions LaPO<sub>4</sub>, respectively. Fig.1a and b is the obtained excitation and emission spectra of LaPO<sub>4</sub>: Ce, Tb, respectively. The nanowires emit green fluorescence along with UV excitation, which is shown in the middle of Fig.1. As can be seen in Fig.1, Tb<sup>3+</sup> emitting wavelength at 543 nm (<sup>5</sup>D<sub>4</sub>-<sup>7</sup>F<sub>5</sub>) as the detection wavelength, a strong excitation peak was obtained at 269 nm, which was attributed to Ce<sup>3+</sup> ions from the ground state 4f (<sup>2</sup>F<sub>5/2</sub>) energy level transitions to excited state energy; the f-d transition of Ce<sup>3+</sup> at 269 nm as excitation wavelength, receiving stronger emission spectrum at 489nm (<sup>5</sup>D<sub>4</sub>-<sup>7</sup>F<sub>6</sub>), 543 nm (<sup>5</sup>D<sub>4</sub>-<sup>7</sup>F<sub>5</sub>), belonging to the characteristic emission of Tb<sup>3+</sup>. Due to the Tb<sup>3+</sup> ion electronic configuration (4f<sub>8</sub>) is a non-allowed transition in earth ions doped LaPO<sub>4</sub> luminescence system, resulting in the lower UV absorption efficiency. Ce<sup>3+</sup> can be effectively sensitized Tb<sup>3+</sup> green emission, leading to Ce<sup>3+</sup>, Tb<sup>3+</sup> co-doped LaPO<sub>4</sub> is a kind of high luminescent material. The relative quantum yield of the nano-particles were estimated to be 23 %, respectively by comparison with that of Rhodamine 6G in ethanol.

Fig. 2 shows TEM images of LaPO<sub>4</sub>: Ce, Tb powder for heating 4h, the nanowires were nearly well-proportioned and slightly aggregated, indicating that LaPO<sub>4</sub>: Ce, Tb are of good monodisperse and uniform. TEM image indicates diameter of green nanowires with an average diameter of 30 nm and the length up to about 150nm. The corresponding SAED pattern (the right of Fig. 2) are taken from the nanocrystals in Fig. 2, shows spotty polycrystalline diffraction rings, indicating the Hexagonal phase structure of the LaPO<sub>4</sub>: Ce, Tb, which is consistent with the XRD results.

Fig. 3 shows energy dispersed X-ray spectrum (EDS) of LaPO<sub>4</sub>: Ce, Tb powder, the nanocomposites shows peaks of lanthanum (La), phosphorous (P), oxygen (O), cerium (Ce), and terbium (Tb), which indicates the

presence of corresponding element in the nanocomposites.

Fig. 4 shows the X-ray diffraction (XRD) patterns of vacuum-dried as-prepared LaPO<sub>4</sub>: Ce, Tb powder. The major peak positions of the nanocrystals were in good agreement with the calculated values for planes of the hexagonal phase structure LaPO<sub>4</sub>: Ce, Tb crystal (JCPDS No. 04-0635).

Fig. 5 shows the photographs of fluorescence fingerprints on semi-permeable object surface, clear green fluorescence fingerprint images can be seen in the picture. The detail characteristics were obvious and the ridges were smooth. The as-prepared LaPO<sub>4</sub>: Ce, Tb nanocrystals are suitable for identification in forensic science and criminal investigation.

Fig. 6 shows the photographs of fluorescence fingerprints on impermeable objects, such as stainless steel, aluminum, plastic plates, tiles, and glass, clear green fluorescence fingerprint images can be seen in the picture. The friction ridges and detail characteristics of fingerprints on various smooth object surfaces are clearly defined without background interference. It is showed the LaPO<sub>4</sub>: Ce, Tb nanocrystals are excellent fingerprints showing reagents, which could meet the demands of the court detection.

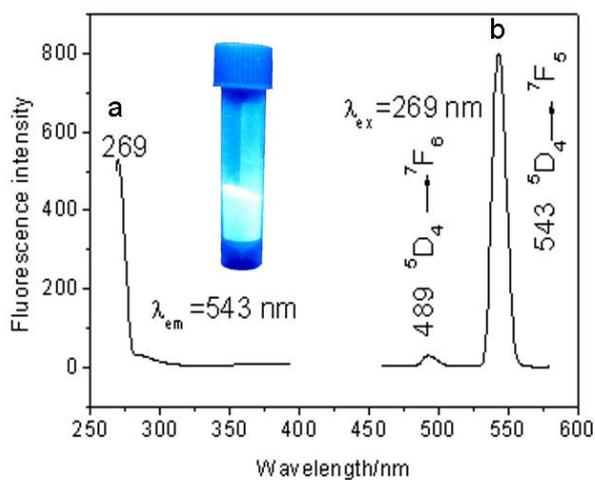


Fig.1. (a) Fluorescence excitation spectra (left curve), (b) Fluorescence emission spectra (right curve) and image of LaPO<sub>4</sub>: Ce, Tb illuminated under an ultraviolet lamp (middle).

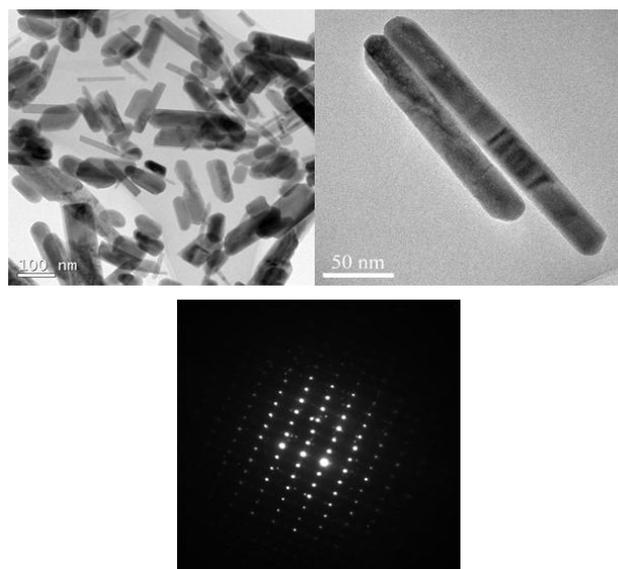


Fig. 2. TEM images of LaPO<sub>4</sub>: Ce, Tb with SAED pattern.

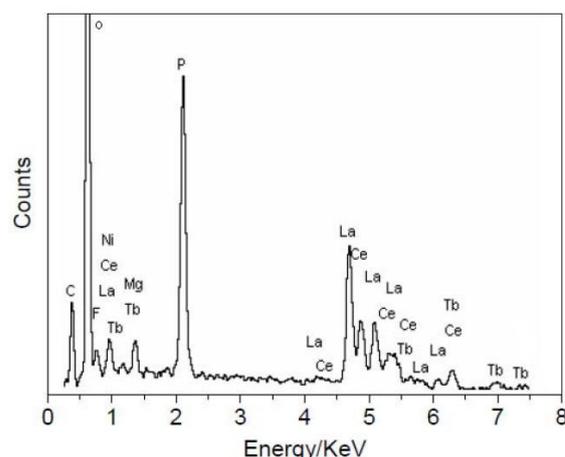


Fig. 3. The EDS spectrum of LaPO<sub>4</sub>: Ce, Tb.

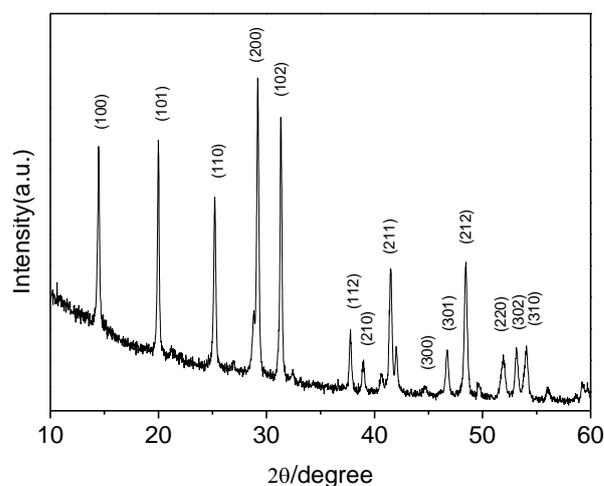


Fig. 4. XRD patterns of the as-prepared LaPO<sub>4</sub>: Ce, Tb.

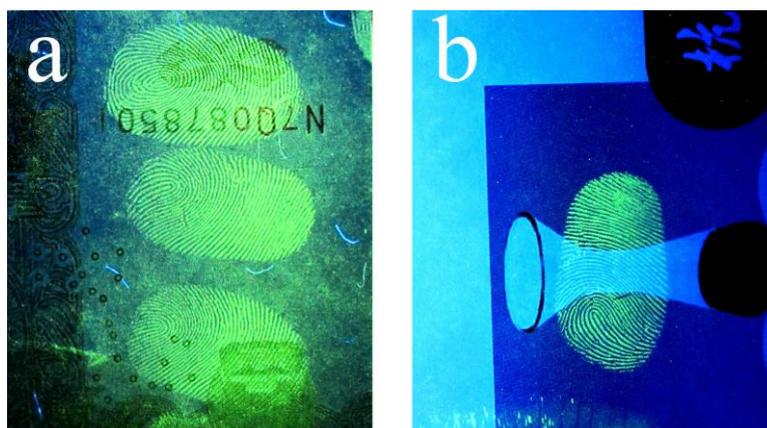


Fig.5. Photographs of latent fluorescence fingerprints on (a) one yuan RMB and (b) color paper surface.

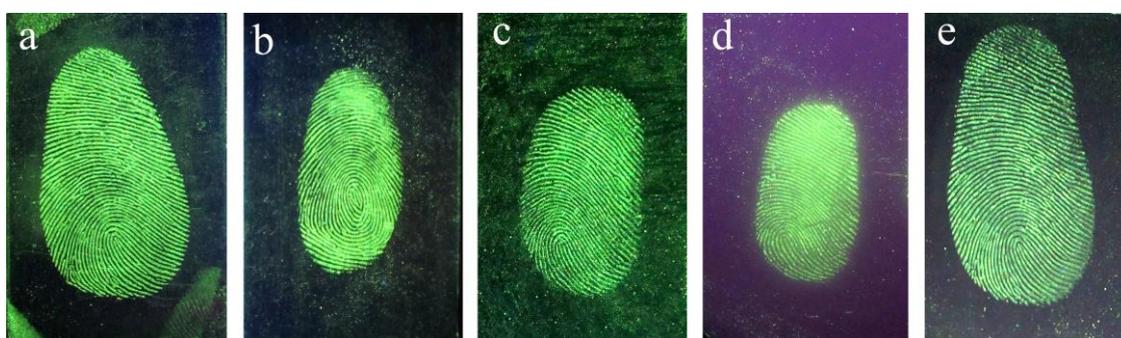


Fig.6. Photographs of latent fluorescence fingerprints on various objects: (a) stainless steel, (b) aluminum, (c) plastic plates, (d) tiles, and (e) glass.

#### 4. Conclusions

In summary, we reported synthesis of aqueous-dispersible  $\text{LaPO}_4$  using a combination of  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  as doped ions via a novel hydrothermal process. The nanowires were of well hydrophilic, strong fluorescence intensity, and high fluorescence quantum yields. They have been characterized by TEM, SAED, EDS, XRD, fluorescence excitation spectra, and fluorescence emission spectra. In addition, the as-prepared nanowires were successful used for developing latent fingerprint on various objects surfaces. The results show that the nanowires could be developed into applications to many areas of new fluorescent probes, especially in forensic science and technology system.

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