



# Fabrication and visible-light photocatalytic behavior of perovskite praseodymium ferrite porous nanotubes



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## HIGHLIGHTS

- Perovskite PrFeO<sub>3</sub> porous nanotube was prepared by electrospinning and calcination.
- Annealing the as-spun nanofibers at a low temperature played a key role.
- The porous PrFeO<sub>3</sub> tubes showed high optical absorption in the UV–visible region.
- The porous PrFeO<sub>3</sub> tubes showed good visible-light photo-catalytic ability.

## ARTICLE INFO

### Article history:

Received 28 November 2014

Received in revised form

13 March 2015

Accepted 14 March 2015

Available online 17 March 2015

### Keywords:

Perovskite

Orthoferrites

Nanotube

Visible-light photocatalyst

## ABSTRACT

Perovskite praseodymium ferrite (PrFeO<sub>3</sub>) porous nanotubes are prepared by electrospinning of the precursor solution into nanofibers, subsequently by annealing the precursor fibers at a low temperature (e.g. 40 °C) and finally by calcination at a high temperature. The low temperature annealing treatment is found to play a key role in the formation of porous nanotube. The porous tubes show a perovskite-type PrFeO<sub>3</sub> crystal characteristic with high optical absorption in the UV–visible region and an energy band gap of 1.97 eV. When compared with PrFeO<sub>3</sub> porous nanofibers and PrFeO<sub>3</sub> particles, the PrFeO<sub>3</sub> porous nanotubes show better visible-light photo-catalytic ability to degrade Rhodamine B in aqueous phase because of the increased surface area and more active catalytic sites on the inner walls and outer surfaces.

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## 1. Introduction

Considerable interest has been devoted to developing efficient photocatalysts to deal with environment pollution over recent decades. Photocatalysts working in visible light are especially desired for the reasons that (1) visible light takes 40% of sunlight, (2) it is safer than UV light which is often used for photocatalysis degradation of pollutant, and (3) sufficient visible light is available widely from not only sunlight but also indoor lighting devices. Traditional metal oxide semiconductors (e.g. TiO<sub>2</sub> [1], ZnO [2], SnO<sub>2</sub> [3]) after modification show photocatalytic activity in visible light.

However, stronger visible light photocatalytic ability was reported on some novel semiconductors including Ag<sub>3</sub>PO<sub>4</sub> [4], Bi<sub>2</sub>WO<sub>6</sub> [5], BiVO<sub>4</sub> [6] and LaFeO<sub>3</sub> [7]. Among them, the rare-earth orthoferrites (formulated as ReFeO<sub>3</sub>) with a perovskite-type crystal structure are highly promising because they are stable and environmental friendly [7–16]. LaFeO<sub>3</sub> typically has an energy band gap in the range of 2.06–2.36 eV, regardless of the crystal structure and morphologies, facilitating visible-light photocatalysis [7–10].

In theory, photocatalysts on nano-scale have higher photocatalytic activity than the bulk counterparts because of the larger surface area and more reactive sites on the surface. Reducing catalyst size is expected to increase photocatalytic activity. However, the size decrease does not always lead to a positive result, which is in particular the case for particulate catalysts. Fibrous nanomaterials show advantages in maintaining a highly porous structure no matter whether they disperse in a liquid phase or stay in a solid state. Dong et al. [17] reported that Perovskite-type LaCoO<sub>3</sub> nanofibers prepared by an electrospinning process and

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subsequent thermal treatment have better photocatalytic activity than LaCoO<sub>3</sub> particles. It is expected that photocatalytic fibers having a porous or hollow structure would have an increased surface, providing more active sites [18–24], hence high photocatalytic activities. However, to the best of our knowledge, the preparation on porous orthoferrites (ReFeO<sub>3</sub>) nanotubes and their visible-light photocatalytic performance have not been reported in research literature.

Herein, we for the first time report on the preparation of a perovskite PrFeO<sub>3</sub> porous nanotube and its visible photocatalysis property. The nanotubes were synthesized by electrospinning of a polymer solution containing inorganic oxide precursor, subsequently annealing at a low temperature and finally calcination at a high temperature. Normally, without low temperature annealing, porous fibers were prepared from this process. However, our study indicated that annealing the as-spun nanofibers at a low temperature (e.g. 40 °C) played a key role in the formation porous tubes. The nanotube formation mechanism was proposed. Rhodamine B (RhB) was employed to test the photodegradation ability of PrFeO<sub>3</sub> nanotubes in aqueous phase, which showed higher photocatalytic activity than their porous fiber and nanoparticle counterparts.

## 2. Experimental

### 2.1. Materials

Pr<sub>6</sub>O<sub>11</sub> (99.9%) was purchased from Shanghai Yuelong Rare Earth New Materials, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98.0%), citric acid (99.5%) and poly(vinyl pyrrolidone) (PVP, Mw 1,300,000) were purchased from Sigma Aldrich. All the chemicals were used as received. The precursor solution for electrospinning was prepared as follow: 0.25 mmol Pr<sub>6</sub>O<sub>11</sub> was dissolved in 10 mL concentrated nitric acid. After drying, greenish Pr(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O resulted. Pr(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (1.5 mmol) was dissolved in a solution containing 8 mL DMF, 12 mL ethanol, 1.5 mmol Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 3 mmol citric acid. 3.0 g PVP powder was then added to that metal nitrate/citric acid solution and mixed to form a homogeneous solution. The citric acid here was used as a complex agent for metal cations in the solution and helped to prevent the growth of the perovskite oxide into bulky crystals [25].

### 2.2. Preparation of PrFeO<sub>3</sub> nanotube

Electrospinning was performed on a purpose-built electrospinning setup [26]. The applied voltage, spinning distance and solution flow rate were controlled at 18 kV, 22 cm and 1.6 mL/h, respectively. The as-electrospun fiber mat was placed in a blast oven at 40 °C for 15 h to completely remove solvent from the fibers (the process was also referred as annealing). The sample was then calcined at different temperatures in air to produce PrFeO<sub>3</sub>.

### 2.3. Characterization

Nanotube morphology was observed under a scanning electron microscope (SEM) using a Zeiss Supra 55 VP instrument and transmission electron microscope (TEM) on a JEOL JEM-2100. XRD patterns were recorded on a Panalytical X'PertPro X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at 40 kV and 30 mA. Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) were measured on a Netzsch STA 409 PC/PG thermal analyzer at a heating rate of 10 °C/min from room temperature to 800 °C in compressed air gas flow. The X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Axis Ultra HAS (Kratos) monochromatic Al K $\alpha$  radiation at a reduced power of 100 W, where the step size for the high-resolution scan was 0.1 eV and the

pass energy was 40 eV. UV–vis diffuse absorption spectra were recorded with a Hitachi UV-3010 spectrophotometer using BaSO<sub>4</sub> as a reference, while absorption spectra of the dye solution were obtained using a Varian Cary 3E UV–vis spectrophotometer at room temperature. FTIR spectra were recorded on a Nicolet 5200 FTIR 5DX instrument. Nitrogen adsorption desorption isotherms were obtained using a Tristar 3000 apparatus. Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated by the Barret–Joyner–Halenda (BJH) method.

### 2.4. Photocatalytic activity test

Photocatalytic activity was evaluated by the degradation of RhB aqueous solution under the irradiation of a 60 W desk lamp with a filter to cut off light beam of wavelength below 400 nm. In a typical test, 30 mg PrFeO<sub>3</sub> sample and 60 mL RhB solution ( $5 \times 10^{-5} \text{ mol/L}$ ) were mixed and stirred for 30 min in the dark followed by light irradiation in a hood (temperature ~25 °C). The RhB concentration was measured at different irradiation time points based on the optical absorption. The photodegradation efficiency ( $\eta$ ) was calculated according to the following equation.

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$

where  $C_0$  and  $C$  are the initial RhB concentration and the residual RhB concentration after photodegradation for certain period of time.

## 3. Results and discussion

### 3.1. Preparation and morphology

Scheme 1a schematically illustrates the procedure for preparing PrFeO<sub>3</sub> nanotubes. Precursor nanofibers were produced from a homogeneous solution consisting of PVP, citric acid and metal nitrate using an electrospinning technique. PVP in the electrospinning solution functions to improve the electrospinning ability. The precursor fiber mats were subsequently subjected to an annealing treatment at 40 °C and a calcination treatment at higher temperature (550–700 °C).

Scheme 1b shows the morphology of as-spun precursor nanofibers which look uniform with a smooth surface. As-spun fibers had a diameter in the range of 200–260 nm and a length up to several tens of micrometers (see Supporting Information Fig. S1a). The fiber mat after annealing at a blast oven at 40 °C for 15 h showed no obvious change in the SEM image (see Scheme 1c). After calcination treatment at 550 °C for 6 h (also marked as 550 °C/6 h in this paper), sample became a yellow solid (see photo in Scheme 1a).

Under SEM, fibrous structure can still be seen after the calcination treatment. However the fibers broke into short sections with a rough porous surface (Scheme 1d). The fiber diameter was reduced to 70–80 nm. The cross-section of the fibers clearly indicated that the fibers had a hollow structure (tubes). TEM imaging verified the hollow tube structure. As shown in Scheme 1e, PrFeO<sub>3</sub> nanotube (diameter ~70 nm) has a porous inner structure with the wall thickness approximately 10 nm.

The calcination condition was found to affect nanotube morphology and diameter. The tube diameter decreased from 80 nm to 50 nm with increasing the calcination temperature at the last stage. However the particle size and wall thickness inclined to increase (see Supporting Information Fig. S2). When the temperature was 700 °C, beaded fiber resulted. This was attributed to the formation of larger PrFeO<sub>3</sub> crystal particles (size ~40 nm) at such a

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