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Multi-modal TiO_2–$LaFeO_3$ composite films with high photocatalytic activity and hydrophilicity

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ABSTRACT

In this paper, a series of multi-modal TiO_2–$LaFeO_3$ composite films have been successfully synthesized through a two-step method. The resultant films were characterized in detail by several testing techniques, such as X-ray diffraction (XRD), ultraviolet–visible diffuse reflection spectrum (UV–vis DRS), photoluminescence spectrum (PL), surface photovoltage spectroscopy (SPS) and water contact angle measurements. The photocatalytic activity of different films was evaluated for degrading Methylene Blue (MB) aqueous solution. Hydrophilicity of the obtained TiO_2–$LaFeO_3$ composite films was also investigated. The results show that TL film and LT film exhibited superior photocatalytic activity and hydrophilicity.

1. Introduction

TiO_2 has many promising applications in areas ranging from photocatalysis and photovoltaics to coatings and sensors, due to the excellent photochemical, optical, electronic properties, low cost and nontoxic nature [1–6]. However, for pure TiO_2 nanomaterials, they usually exhibit poor thermal stability and relatively low quantum efficiency, which strongly limited the extended applications of TiO_2. Recent research work has proved that coupling TiO_2 with other metals or oxides can provide a beneficial solution for these problems [7–13]. Among the various TiO_2-based binary metal oxides developed so far, TiO_2–$LaFeO_3$ mixed oxide is one of the most promising materials. The introduction of $LaFeO_3$ not only maintains their original structural characteristics but also endows the resultant materials with additional properties.

In our previous work, we have successfully synthesized a series of titania materials [14–16]. In order to combine the unique characteristics of titania film and the physical and chemical properties of $LaFeO_3$, in this paper, an idea was proposed by us to design and synthesize TiO_2–$LaFeO_3$ composite films through introducing a $LaFeO_3$ source during the synthesis. To the best of our knowledge, this is the first report on the synthesis of multi-modal TiO_2–$LaFeO_3$ composite films. In comparison with pure TiO_2 and $LaFeO_3$ materials, these materials obtained with multi-modal nanostructures not only present better hydrophilicity in the absence of light irradiation but also exhibit higher photocatalytic activity.

2. Experimental details

2.1. Synthesis

Tetrabutyl titanate(IV) (Beijing Golden Dragon Company of China, analytical grade) and $La(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ (Tianjin Guangfu Company of China, analytical grade) were used without further purification. Indium-doped tin oxide (ITO) glass substrates (Shenzhen Baolai Company of China, 1.1 mm thick, sheet resistance $\leq$15 Ω/□) are ultrasonically cleaned in ethanol prior to use. Deionized water is used in all experiments. First, the nano-sized anatase TiO_2 films and the nano-sized $LaFeO_3$ films were fabricated on the ITO glass substrates by spin coating a certain amount of the mixture, which consists of 1 g of freshly prepared TiO_2 or $LaFeO_3$ hydrothermal nanoparticles via a sol-hydrothermal method [17,18], 1 mL of PEG 400 and 5 μL of acetylacetone, with the rotation speed of 1000 rpm for 15 s and 3000 rpm for 30 s in succession, followed by drying at 80 °C for 10 h and thermal treatment at 400 °C for 2 h. Then, TiO_2–$LaFeO_3$ films were fabricated on the as-prepared $LaFeO_3$ films by spin coating a certain TiO_2 hydrothermal nanoparticles via a sol-hydrothermal method [17]; $LaFeO_3$–TiO_2 films were fabricated on the as-prepared TiO_2 films by spin coating a certain $LaFeO_3$ hydrothermal nanoparticles via a sol-hydrothermal method [18], followed by drying at 80 °C for 10 h and thermal treatment at 400 °C for 2 h.

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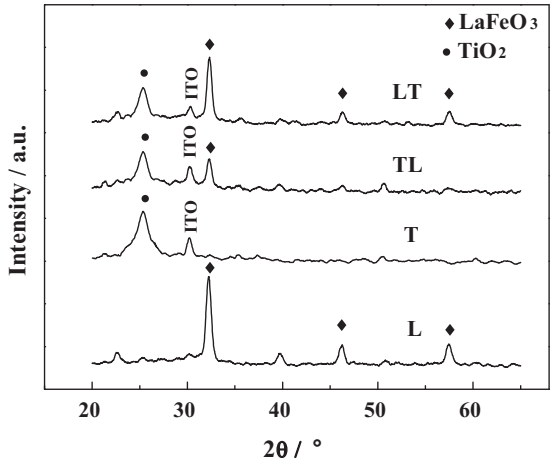

Fig. 1. XRD patterns of different films.

The as-prepared TiO_2 film, $LaFeO_3$ film, TiO_2–$LaFeO_3$ film and $LaFeO_3$–TiO_2 film were referred as T, L, TL and LT, respectively.

2.2. Characterization

The samples were characterized by X-ray powder diffraction (XRD) with a Rigaku D/MAX-γA powder diffractometer (Japan), using Cu Kα radiation (λ = 0.1506 nm). The ultraviolet–visible diffuse reflection spectrum (UV–vis DRS) of the samples were recorded with a PE Lambda 900 spectrometery. The PL spectra of the samples were recorded with a PE LS 55 spectrofluorophotometer. The SPS measurement of the samples was carried out with a home-built apparatus that had been described elsewhere [19].

2.3. Photocatalytic activity

The photocatalytic activity evaluation of films for the photodegradation of Methylene Blue (MB) aqueous solution was carried out at ambient temperature. The experiments were carried out in a quartz photochemical reactor, open to air, having the shape of a vertical cylinder. A 125 W high-pressure fluorescent Hg lamp was used as a light source without filter, which was placed at about 20 cm from the reactor. For each run, the film of determinate surface area (2.25 cm^2) was immersed in 20 mL of MB aqueous solution with a concentration of 10 mg L^{-1}. Absorbance of irradiated samples was determined with a PerkinElmer Lambda 900 UV/vis/NIR spectrometer immediately after irradiation and removal of the films.

2.4. Measurements of water contact angles

Water contact angles were measured on a commercial contact angle meter (JY-82) at ambient temperature. The average contact angle was obtained by measuring more than five different positions of the same film.

3. Results and discussion

3.1. XRD and DRS measurements

XRD is used to determine the phase structure of the samples. XRD patterns of different films after calcined at 400 °C are shown in Fig. 1. The two XRD peaks at about 30.20° and 35.30° result from the ITO glass. The XRD pattern of T film has only one weak Bragg peak located at $2\theta = 25.28°$, which can be indexed as the typical diffraction peak of TiO_2 anatase phase (JCPDS (Joint Committee on Powder Diffraction Standards) No. 21-1272). The XRD pattern of L film has

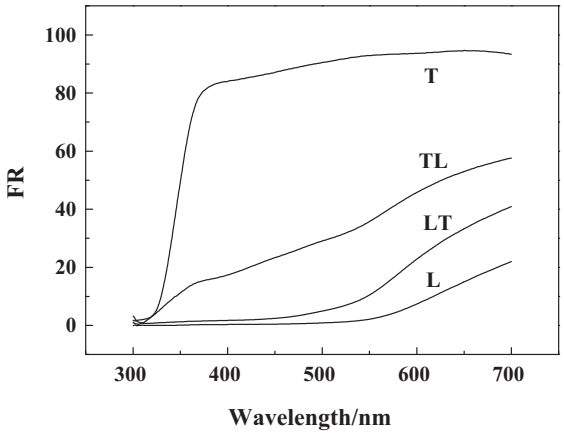

Fig. 2. DRS patterns of different films.

Bragg peaks located at $2\theta = 32.196°$, 46.158°, 57.439°, which can be indexed as the typical diffraction peaks of $LaFeO_3$ orthorhombic system with an ABO_3-type perovskite structure (JCPDS No. 15-0148). The XRD patterns of LT and TL films both have the typical diffraction peak of the anatase phase and the $LaFeO_3$.

The UV–vis diffuse reflection spectra of different films are shown in Fig. 2. It can be seen that all films have distinct DRS response threshold. But the DRS spectra of all films exist obvious increase of the absorbance and decrease of the reflection in visible light area from top to bottom, which will influence the photocatalytic activity of films.

3.2. PL and SPS measurements

The photoluminescence (PL) technique has been widely used to investigate the structure and properties of the active sites on the surface of metal oxides [20,21], because of its high sensitivity and non-destructive character. The PL technique is also useful in the field of photocatalysis over semiconductors for understanding the surface processes. The PL spectrum is an effective way to study the electronic structure, optical and photochemical properties of semiconductor materials, by which information such as surface oxygen vacancies and defects, as well as the efficiency of charge carrier trapping, immigration and transfer can be obtained [22–24]. Therefore, it is of great significance for environmental photocatalysis.

Fig. 3 showed the PL spectra of L film and LT film with the excitation wavelength of 350 nm. It can be found that the L film exhibits obvious PL signals at the wavelength range from 400 to

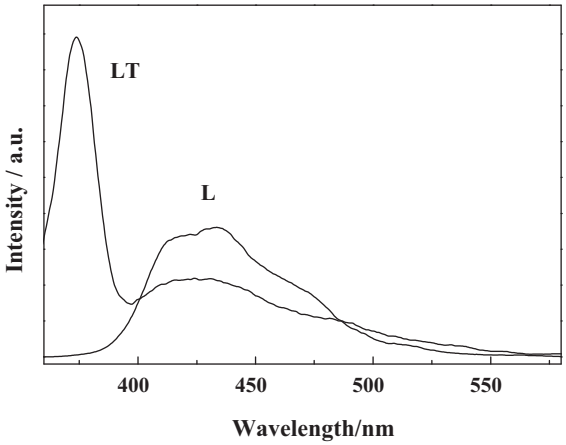

Fig. 3. PL patterns of L and LT films.