Formation and performances of porous InVO₄ films

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Received 14 July 2005; received in revised form 10 November 2005; accepted 9 December 2005
Available online 20 January 2006

Abstract

Porous complex oxide films consisting of preferentially orientated orthorhombic phase of InVO₄ have been prepared using a novel simple method by pyrolysis of amorphous complex precursor. The formation and controlling of porous InVO₄ films can be easily obtained by modifying the calcination temperature. The pure orthorhombic InVO₄ phase can be obtained at a relatively lower temperature (500°C), and the films are preferential orientation of the (200) face parallel to the substrate. The phase separation mechanism was suggested for the formation of porous films. Under visible light irradiation (λ > 400 nm), porous InVO₄ films have shown the photocatalytic activity for photodegradation of gaseous formaldehyde, and can generate photocurrent. The electrochemical properties of the films with different crystal structure and pore structure were also investigated.

Keywords: InVO₄; Dip-coating; Porous films; Photocatalytic activity; Visible light; Electrochemical properties

1. Introduction

Mesoporous and macroporous films have attracted great interest for their potential uses in catalysis [1], high selective adsorbents, photodelectrodes [2–4], photocatalysts [5, 6], gas sensors [7, 8], electrochromic materials [9, 10], lithium ion batteries [11, 12], and so on. Different methods for the synthesis of mesoporous and macroporous films have been developed during the past several decades [13, 14]. The most popular methods are the template methods, using the surfactants [15, 16], block copolymer [17–19], or colloidal sphere [20–22] as the templates. By using the colloidal sphere arrays as the template and filling the void spaces with nanoparticles, the ordered macroporous materials can be obtained. This method offers the great advantage of incorporating specific nanoparticles of desirable crystalline phases into the wall structure of the macroporous framework. By using the surfactants and the block copolymer as the templates, many mesoporous films have been obtained from the hydrolysis of the metal alkoxides, such as SiO₂, TiO₂, ZrO₂, ZrP, and so on. For the limitation of the metal alkoxides, finding a simple method for the preparation of porous films from low cost raw materials is still a challenge.

InVO₄ has attracted interest for its special electrochemical and photocatalytic properties. InVO₄ belongs to the family of orthovanadates, oxides with attractive properties as Li insertion electrodes, and is proposed as an anode material for lithium rechargeable batteries [23], and electrochromic windows due to their transparency [24]. Very recently, calculated by first principles calculations, and supported by experiments, InVO₄ is a promising photocatalyst that is able to induce hydrolysis of water molecules under visible light irradiation [25–27]. The electronic structures of the thin films of InVO₄ have also been calculated by first principles calculations [28], and it is found that the band gap of InVO₄ films seems to be very sensitive to the V environment around O atom. So, it is very interesting and essential to prepare the InVO₄ films on the transparent conducting substrates. InVO₄ films have been prepared by using the sol–gel route from V-oxoisopropoxide and In-nitrate precursors by the dip-coating technique [29, 30]. Thin films of mixed In/V oxides have also been obtained by reactive RF sputtering [31]. But the preparation of porous films of InVO₄ has not been reported.
Here, we report a new simple method for the preparation of porous InVO₄ films by direct pyrolysis of an amorphous complex precursor. This kind of method has been used in the preparation of complex oxide powders or dense films [32–35]. But there are still no reports on the preparation of porous films. The homogenous amorphous complex precursor is produced by the complexation between diethylenetriaminepentaacetic acid (DTPA) and low cost metal oxides or salts. The high viscosity of the precursor makes it suitable for the preparation of complex oxide films by the dip-coating or spin-coating technique. The formation mechanism was investigated by using the TEM, FE-SEM, XRD, Raman, FTIR, and XPS. The pore size was modified easily by changing the calcination temperature. The optical, electrochemical, photocatalytic, and photo-electrochemical properties of porous InVO₄ films were also discussed.

2. Experimental section

2.1. Preparation of porous InVO₄ films

The porous InVO₄ films were prepared by using the dip-coating technique from amorphous complex precursor. The complex precursor of InV(DTPA)₁.₆ solution was synthesized by using DTPA as a ligand. All chemicals used were of analytical grade and were purchased from Beijing Chemical Factory (China). The substrates were ITO glasses, which were purchased from China Southern Glass Co. Ltd., with a thickness of ITO of 135 nm and a sheet resistance of 15 Ω/□.

Scheme 1 described the preparation process. A typical synthesis procedure was shown below. A 0.009 mol In₂O₃ powder was dissolved in 5 mL hot concentrated HCl solution. Then, 10 mL stronger ammonia water was added to the solution to get the In(OH)₃ deposit. Subsequently, the deposit was centrifuged and washed several times till the pH value of the supernatant fluid approached 7. The deposit was then immersed sequentially in ultrasonic baths of hydrochloric acid and distilled water. Then, the ITO plates were blow dried in a clean hood. Finally, each ITO plate was exposed to an 11 W mercury lamp in an enclosed housing for UV irradiation. The mercury lamp has a continuous emission spectrum starting at about 254 nm and with increasing intensities up to 190 nm.

The ITO glass substrates were dipped into the complex precursor for 2 min and the films were then deposited with a pulling velocity of 3 cm/min. After drying at 80 °C, the sample was heated to a certain temperature (400, 450, 500, and 550 °C) at 3 °C/min, and then calcined for 4 h in an air flow oven. The thickness of individual InVO₄ layers was ca. 100 nm; thicker films were obtained by consecutive dip-coating, each followed by annealing.

2.2. Samples characterization

The morphology of the samples was detected by using TEM and FE-SEM. TEM was performed by using a JEOL JEM-1200EX instrument with the accelerating voltage of the electron beam of 120 kV. FE-SEM was taken using a Hitachi S-450 electron microscope.

The crystal structure of the films was investigated by using XRD (Rigaku D/MAX-RB diffractometer) with CuKα radiation and a scan rate of 4°/min.

Raman spectra were recorded on an RM 2000 microscopic confocal Raman spectrometer (Renishaw Company) with an excitation of 514 nm laser light at 0.5 mW, and were accumulated 12 times for 30 s each. The spectra were recorded with a charge coupled device (CCD) camera.

Thermogravimetric analysis (TGA) was carried out by using the Du Pont thermal analysis system (Dupont 1090B TGA 951 thermogravimetric Analyzer) with a heating rate 10°/min in air.

FTIR patterns were acquired from a Perkin–Elmer System 2000 infrared spectrometer.

The XPS analysis was measured on a PHI 5300 ESCA instrument using an Al Ka X-ray source at a power of 250 W. The pass energy of the analyzer was set at 35.75 eV and the base pressure of the analysis chamber was <3 × 10⁻⁹ Torr. The analyses were based on the following peaks: C1s, O1s, In3d, V2p, N1s. The binding energy scale was calibrated with respect to the C1s photopeak of hydrocarbon contamination fixed at 285.0 eV.

AES spectra were obtained using a PHI 610 scanning auger microscopy system. The beam voltage was 3.0 kV and the beam current was 0.5 μA. The electron beam was incident at an angle of 60° with respect to the specimen surface in order to make the sample surface perpendicular to the ion beam. During the depth profile analysis, the energy and beam current of the Ar ion beam were 3.0 keV and 6 μA, respectively. The beam diameter was 1 mm and the sputtering rate was approximately 30.0 nm/min for a thermally oxidized SiO₂ thin film.
Electrochemical and photoelectrochemical measurements were performed in a home-made three electrode quartz cells. Pt sheet was used as counter and Hg/Hg₂Cl₂/sat.KCl used as reference electrodes, while the working electrode was the thin film on ITO under investigation. The electrodes were immersed in a 1 mol L⁻¹ solution of lithium perchlorate in propylene carbonate. The CV curves were recorded after 15 cycles at a scan rate of 50 mV s⁻¹. A 500 W Xe lamp was used as the excitation light source. The irradiated light intensity was measured with a power meter from the Institute of Electric Light Source (Beijing).

The visible light photocatalytic activities of InVO₄ films were valued by the decomposition of gaseous formaldehyde. The photoreactor used was a 250 ml cylindrical quartz vessel, which consisted of an inlet, an outlet, and a sample port. The InVO₄ film was tested in the vessel perpendicular to the light beam. The optical system for the photocatalytic reaction was composed of a 500 W Xe arc lamp and a cutoff filter (λ > 400 nm). The distance between the film and the light source was 20 cm, where the average light intensity was 31 mW cm⁻². The area of InVO₄ film was about 4 cm². The gaseous formaldehyde in the contaminated atmosphere was obtained by the vaporization of formaldehyde liquid using predetermined values of flow rate controlled by mass flow controllers. The mixture was then forced to flow through the photoreactor for 1 h. Then, the photoreactor was sealed and the photocatalytic reaction was started by turning on the lamp. Subsequently, the concentration of formaldehyde in the photoreactor, obtained by a gastight syringe from the sample port, was measured with an SP-502 gas chromatograph (GC) equipped with a flame ionization detector and a 2 m stainless steel column (GDX-403) at 373 K.

3. Results and discussions

3.1. Morphology and phase structure of the films

The morphologies of the precursor film and as-prepared films are shown in Fig. 1. The porous films were obtained by simply calcining the precursor films and the pore size was easily adjusted by modifying the calcination temperature. The precursor film was very uniform. Under the calcination temperature of 400 °C, some white hillocks occurred, which was caused by the decomposition of hydrocarbon, amino-group organic compounds, and the...
carboxyl indium group. From the surface, it is difficult to find the obvious pores. So the products (predominately CO₂) of the decomposition are trapped in the interior of the film, leading to the internal pores, which can be confirmed by the FTIR results in next section (Fig. 6b). At 450 °C, the pressure of the gas in the internal pores becomes high enough to break the pores and lead to the formation of the open pores on the surface of the film, with the average pore size of 40 nm, which was counted from the SEM images for about 100 pores. With the increase of the calcination temperature, the pore size increased linearly (Fig. 1f). From the SEM images, we can find that the film is free of cracks and the pore do not appear “ordered” in a long range. The TEM morphology and the selected electron diffraction (Fig. 2) of the InVO₄ films obtained under 550 °C show that the pores are in the interior of the single crystal.

The XRD patterns of the precursor film and as-prepared films are shown in Fig. 3. Only the In₂O₃ phase of ITO layer can be found in the patterns of the films obtained below 400 °C, and the broad peak between 20° and 30° two theta is amorphous silica in the glass substrate. Upon further increasing the annealing temperature, several Bragg peaks of orthorhombic InVO₄-III (JCPDF 48-0898) [36] appears in the XRD pattern, so that by 500 °C we obtain the X-ray signature of the orthorhombic InVO₄ phase, which is also supported by the Raman spectra (Fig. 4). The Raman spectra of the films obtained at 500 and 550 °C show the typical bands of InVO₄-III phase [37] at 915, 391, and 342 cm⁻¹, which match well with the Raman spectra of InVO₄-III powders.

From the literature, the InVO₄ with the pure orthorhombic phase was obtained above 600 °C, and only the low temperature phase monoclinic InVO₄ and no orthorhombic phase was obtained at 500 °C [23]. For the InVO₄ films prepared by using sol–gel method [29,30], the mixture of monoclinic and orthorhombic phases were obtained at a relatively low temperature (400 °C), but the pure high temperature phase had not been obtained. In the present work, the low temperature phase of InVO₄ (monoclinic phase) have not been obtained, but it gave a new method to prepare the pure, high temperature phase of InVO₄ (orthorhombic phase) at a relatively low temperature (500 °C).

From the XRD patterns of the films obtained under 500 and 550 °C (Figs. 3f and g), we can also find that the peak of (200) was enhanced, and the peak of (112) was weakened, which suggests preferential orientation of the (200) face of InVO₄ parallel to the substrate. One possible reason for the orientated growth of the InVO₄ films on the ITO substrate may be the heteroepitaxial growth.

Anyway, we have succeeded in the preparation of the crystallographically oriented porous films of InVO₄ by simply calcinating the precursor films, and the pore size was easily adjusted by modifying the calcination temperature.

Fig. 2. TEM morphology of InVO₄ porous films obtained at 550 °C. Insert shows the ED pattern.

Fig. 3. XRD patterns of the precursor film (c) and the as-prepared films obtained under different calcination temperature: (d) 400 °C, (e) 450 °C, (f) 500 °C, (g) 550 °C. Also shows the standard patterns of orthorhombic InVO₄ (JCPDF 48-0898, (a) and the XRD pattern of InVO₄ powders (b).
3.2. Formation process of porous InVO₄ films

In order to investigate the formation mechanism of the porous films, it is necessary to study the calcination process of the precursor films. Firstly, the decomposition process of the precursor powders was investigated by using TG and DTA spectra (Fig. 5). The TG curve indicated that the increase of temperature resulted in four different regions of weight loss. Based on the quantitative calculation of the weight loss in every region, the thermal decomposition processes can be distinguished as follows, which is similar to that of LaNi(DTPA)·6H₂O for preparation of LaNiO₃ [35]. The weight loss region from 20 to 130 °C was caused by the loss of coordinated water. The region from 130 to 240 °C resulted from the decomposition of the organic group, including the decomposition of hydrocarbon, amino-group organic compounds. The region from 240 to 410 °C resulted from the decomposition of the carboxyl indium group, and the region from 410 to 580 °C resulted from the decomposition of the carboxyl vanadium group. All organic components could have been eliminated at 600 °C because there was no further weight loss.

On the DTA curve, one endothermic and three exothermic peaks were observed. The little endothermic peak at 75.4 °C was attributed to the loss of the coordinated water. The peak at 236 °C was produced by the burning of hydrocarbon and amino-group. The peak at 340 °C was produced by the decomposition of the carboxyl indium group. The peak at 499.8 °C corresponded to both exothermic contribution from the decomposition of the carboxyl vanadium group, and the formation of InVO₄ complicated oxide for the right tail of the peak, which can be confirmed by the XRD results that the crystalline InVO₄ was formed at 500 °C. The broad peak at 671 °C corresponded to allotropic transformations of InVO₄, which had been investigated in the literature [38]. The above results suggest that the decomposition of the organic components can be divided into two main stages: the stage below 400 °C and that above 400 °C, and the InVO₄ can be formed below 600 °C.

For investigation of the decomposition process of the precursor on ITO glass substrate, the precursor film and the films obtained at the transient temperature of two stages (400 °C) and the limiting temperature of ITO (550 °C) have been investigated by using FTIR (Fig. 6) and XPS (Fig. 7).

The bands of the FTIR spectra of the precursor film (Fig. 6a) at 3426, 3224, 3034, 2973, 2538, 1724, 1604, 1463, 1365, and 1094 cm⁻¹ originated from the NH₂, C=N, C=O, C–O, and C–H bands. Above 400 °C, these bands almost completely disappeared. From the XPS results (Fig. 7 and Table 1), we can find that most of the organic components (C and N) were decomposed at 400 °C and completely decomposed at 550 °C. A part of the amounts of C and O in the films were caused by the contamination of CO₂ in the atmosphere. Compared with the decomposition of the precursor powders (from the TG-DTA results), the decomposition of the precursor film undergoes at a relatively lower temperature. The reason is that the precursor on the ITO glass is too little (the thickness of the film is only about 100 nm from the AES results) and has a big contact area with the air.

A carbon dioxide mode at 2333 cm⁻¹ was observed in the FTIR spectra of InVO₄ (400 °C) films (Fig. 6b). Their
higher intensity in the spectra of the film suggests that CO₂ is trapped inside the porous structure of the film, which has also been found in the InVO₄ film prepared by the sol–gel technique [30]. Once the calcination temperature is increased, the pores were broken, leading to the liberation of CO₂ and the disappearance of the band of 2333 cm⁻¹/C0₁.

The detailed formation mechanism of the pores in the films will be discussed in the next section.

The 926 cm⁻¹ band in the FTIR spectra of the precursor film was ascribed to the V⁴⁺–O (vanadyl) stretching mode [30]. After calcination above 400 °C, this band disappeared. The same results can also be found from the XPS investigation. The V₂p band of the precursor film is 514.8 eV, which belongs to a lower oxidation state of V (V⁴⁺) [39]. After calcination above 400 °C, the V⁴⁺ was oxidized to V⁵⁺, with the V₂p band of 517.1 eV.

In the IR spectra of the precursor film and the films obtained at 400 °C, the band of 473 cm⁻¹ is obvious, and it disappears in that of the film obtained at 550 °C (Fig. 6). From the literature, the 473 cm⁻¹ band of the FTIR spectra was ascribed to the V–O–V scissoring vibration [40]. The crystal structure of the film obtained at 550 °C belongs to the orthorhombic phase (Figs. 3g and 4f), which is composed of two kinds of polyhedra: one is InO₆ octahedron and the other is VO₄ tetrahedron. The InO₆ octahedron connects to each other by sharing edge to form chains along the [001] direction, which were linked together by the VO₄ tetrahedra [27]. The VO₄ groups separated after crystallization [30]. So the disappearance of the band of 473 cm⁻¹ was caused by the formation of the InVO₄ crystallized phase.

The binding energy of In3d₅/₂ has been used to justify the crystallinity of the ITO film, i.e. the peaks at 444.08 and 445.24 eV are assigned to crystalline indium oxide (In₂O₃) and amorphous indium oxide, respectively [41]. Similar phenomenon has been found for the InVO₄ films. At 400 °C, the binding energy of In3d₅/₂ at 444.8 eV was assigned to amorphous InVO₄, and at 550 °C, the binding energy of 444.2 was assigned to crystalline InVO₄ [39]. The structure of the InVO₄ films was also confirmed by the XRD and Raman results.

In summary, the calcination process of the precursor films can be divided into three stages: the decomposition of the organic components, the formation of the amorphous InVO₄ phase, and the formation of the crystalline InVO₄ phase.

3.3. Formation mechanism of porous InVO₄ films

Formation mechanism of the pores in InVO₄ films is similar to the phase separation mechanism put forward by Nakanishi [42] for the pore structure control of silica gel. The pores were formed by the CO₂ gas phase separation from the solid phase, which can be confirmed by the FTIR results. During the calcination process of the precursor film, the organic components decomposed into CO₂ firstly. Subsequently, the CO₂ gas separated from the solid phase, which led to the interior pores in the film.

If we suppose that the gas in the pores submits the perfect gas equation ($PV = nRT$, where $P$ is pressure, $V$ volume, $n$ mole number, $R$ perfect gas constant, and $T$ temperature), with the increase of the calcination temperature, the pressure in the pores increases, which is the driving force for the enlarging of the pore and the merging of the solid phase. The increase of the volume of the pore will lead to the merger of adjacent pores to form a bigger one, and the decrease of the amount of the pores. Once the pore was big enough, the pore broke to form an open one. At the same time, the solid phase of InVO₄ also merged together into the big sheet with the pores imbedded.

The amorphous phase of InVO₄ at lower calcination temperature is propitious to the merging of the solid phase. The schematic formation mechanism of the pore is shown in Fig. 8.
For our experiments, all the films displayed in Fig. 1 were formed by a single application of the precursor solution followed by an annealing for 4 h at a given temperature, with the same heating-up rate of 3 °C/min. If we want to get the small pore and well-crystallized InVO₄ films, we can calcine the precursor film at a relatively low temperature for a longer time to decompose the organic components, and then crystallize the film at a relatively high temperature. From the SEM results (Fig. 1), we can find that there are some open pores on the films obtained at a low temperature (450 °C), and then it is possible to decompose the organic components at a low temperature for a long time. From the TG and DTA curves (Fig. 5), the last stage of the weight loss of the precursor begins at 410 °C, so it is necessary to decompose the organic components at a temperature above 410 °C.

3.4. Optical and photocatalytic properties

Fig. 9 shows the UV–visible light transmittance spectra of the as-prepared films. The fringes are the result of interference between radiation from the air-film and film-substrate interfaces. The presence of these fringes indicates that the films are quite uniform in thickness, as nonuniform thickness would destroy all interference effects resulting in a smooth transmittance curve. At lower calcination temperature, the transmittance is lower, owing to the residue of the free carbon without liberation from the film. With the increase of the calcination temperature, the transmittance increased.

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Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>In₃d₅/₂ (eV)</th>
<th>V₂p₃/₂ (eV)</th>
<th>In/V</th>
<th>O/V</th>
<th>C/V</th>
<th>N/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>444.2</td>
<td>514.8</td>
<td>1</td>
<td>12.5</td>
<td>30.5</td>
<td>5</td>
</tr>
<tr>
<td>Calcined at 400 °C</td>
<td>444.8</td>
<td>517.2</td>
<td>1.3</td>
<td>3.6</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Calcined at 550 °C</td>
<td>444.2</td>
<td>517.1</td>
<td>1.2</td>
<td>2.5</td>
<td>1.9</td>
<td>0</td>
</tr>
</tbody>
</table>

O and C are the oxide- and carbonate-related components in the O₁s and C₁s complex peak, respectively, containing that of the contamination CO₂ in the atmosphere.
The photocatalytic activity of InVO$_4$ films under visible light irradiation was evaluated by the photocurrent and the photodegradation of gaseous formaldehyde.

**Fig. 10** shows the result of the photodegradation of gaseous formaldehyde on the six layer porous InVO$_4$ films, where $C$ is the concentration of formaldehyde at the irradiation time $t$ and $C_0$ is the concentration in the adsorption equilibrium on InVO$_4$ before irradiation (about 430 ppm). The result indicated that the concentration of gaseous formaldehyde reduced from 430 to 310 ppm in 520 min. $C/C_0$ linearly decreases with the increase of irradiation time. Namely, the photocatalytic reaction of gaseous formaldehyde on the surface of InVO$_4$ films can be considered a zero grade reaction.

Photoelectrochemical experiments were also conducted in a propylene carbonate solution containing 1 mol L$^{-1}$ LiClO$_4$. An anodic photocurrent of significant magnitude (sub-$\mu$A cm$^{-2}$) was observed when the six layer porous InVO$_4$ film electrode was irradiated with visible light ($\lambda>400$ nm) at 0 V (**Fig. 11**).

In our experiments, the efficient area of InVO$_4$ films is about 4 cm$^2$. The thickness of six layer films is about 600 nm. The density of the orthorhombic crystalline stable InVO$_4$-III phase is 4.7 g cm$^{-3}$ [36]. The amount of InVO$_4$ in the six layer dense films is only about 1.128 mg. For the porous films, the amount is far smaller than this value. So it is possible to improve the photocatalytic activity by modifying the structure of the films, such as increasing the thickness. The further investigations are now ongoing.

### 3.5. Electrochemical properties

The porous structure and the crystal structure of the films have great effects on the film properties. Denis et al. [23] have found that the amorphous InVO$_4$ powders exhibit a better charging/discharging capacity and smaller charge capacity fade with cycling than the crystalline counterparts. Santato et al. [3] have found that the mesoporous WO$_3$ films can be penetrated by the electrolyte down to the back contact to form high-surface-area semiconductor/liquid junctions.

In order to evaluate the electrochemical properties of the porous InVO$_4$ films, they were submitted to cyclic voltammetry in a solution of 1 M LiClO$_4$ in propylene carbonate. The cyclovoltammetric curves of the as-prepared films were shown in **Fig. 12**. At 400°C, the surface of the film is uniform and has no pores, and still has some residue organic components in the film, which lead to the lower charge capacity. Owing to the amorphous phase of InVO$_4$ films and their porous structure, CV curve of the film obtained at 450°C shows the highest charge densities and one anodic peak at 0.22 V. After crystallization (at 500
and 550 °C), with increase of the calcination temperature, the pore size increases, and leads to the smaller surface-area semiconductor/liquid junctions, and then the lower charge capacity, with one cathodic peak at −1.14 V and two anodic peaks at −0.35 and 0.42 V. Our results show a similar phenomena as those in the literatures. By changing the crystal structure and the pore structure, it is easy to modify the properties of the films.

4. Conclusions

We have successfully prepared the porous InVO₄ films on ITO substrate by direct pyrolysis of the amorphous complex oxide. The amorphous complex oxide is produced by the complexation between diethylenetriaminepentaaetetic acid and the cheap inorganic metal salts or metal oxides. The films with crystallographically orientated and the pure orthorhombic InVO₄ can be obtained at high temperature (500 and 550 °C). The pore size can be easily modified by changing the calcination temperature. The porous InVO₄ films have shown the photocatalytic activity for photo-degradation of gaseous formaldehyde, and can generate photocurrent under visible light irradiation (λ > 400 nm).

We have established a clear correlation between the crystallinity and the pore structure of the InVO₄ films and their electrochemical properties. This method has a potential use in the preparation of porous films of other complex oxide. And some porous films of the complex oxide have the potential applications in catalysis, photo-electrodes, photocatalysts, gas sensors, electrochromic materials, lithium ion batteries, and so on.

Acknowledgments

This work was partly supported by the Chinese National Science Foundation (20433010), Trans-Century Training Program Foundation for the Talents by the Ministry of Education, P.R.C., the Excellent Young Teacher Program of MOE, P.R.C., and the China Postdoctoral Science Foundation.

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