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Photocatalytic performance of highly transparent and mesoporous molybdenum-doped titania films fabricated by templating cellulose nanocrystals

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ABSTRACT

In this paper, the synthesis of mesoporous Mo-doped titania films templated by cellulose nanocrystals (CNCs) and their photocatalytic performance are reported for the first time. The prepared titania composite precursors containing the CNCs and molybdenum chloride were spin-coated on indium tin oxide (ITO) glass substrate, followed by calcining at 400 °C for 1 h. X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), scanning electron microscope (SEM), and UV–vis spectrometer were employed to characterize the phase composition, pore structure, morphology, and optical property of the titania films in relation to CNCs templating and Mo doping. Photocatalytic performances of the titania films were also evaluated on the photodegradation of trichloroethylene under a fluorescent light source. The Mo-doped titania films with CNCs templating were highly transparent and mesoporous, exhibiting only anatase phase, high specific surface areas ranging in 135.4 – 149.0 m^2/g, and small crystallite sizes of 9.5 – 11.1 nm. The results indicate that Mo ions were successfully doped by substituting for Ti ions in the titania lattice. The Mo doping stabilized the anatase phase and also increased the surface area of the CNCs-templated titania film while decreasing the mean pore width. Notably, the visible light absorption capacity and photocatalytic activity of the CNCs-templated titania films doped with Mo were dramatically greater than those of the pure and the CNCs-templated titania films, which is ascribed to the decreased recombination rate of photoexcited charges and the increased surface area with aids of the CNCs templating and the Mo doping.

1. Introduction

Titanium dioxide (titania) has been widely applied as a photocatalyst in diverse areas, including air and water purification [1–4], antibacterial coatings, dye-sensitized solar cells [5,6], and self-cleaning surfaces [7,8]. Since the band-gab energy of the titania is relatively wide, 3.2 eV for anatase phase, its applications are somewhat restricted because it needs only UV irradiation for photoexcitation [9]. It is therefore necessary to make the titania photosensitive even under the visible light. To increase the photocatalytic activity and shift the light absorption toward the visible region, doping of titania with either nonmetal or metal atoms has been known as one of the most effective and promising modification methods. It is well known that nonmetallic dopant in titania, such as nitrogen, carbon, and phosphorous, can decrease the band-gab energy [10]. Transition metal-doped titanias have been also reported to improve the photocatalytic performance due to the retarded recombination of photoexcited electrons and holes [11]. Of the best metallic dopants in terms of similarity of ionic radius with titanium, tungsten [12], chromium [13], molybdenum [14], niobium [15], and vanadium [16] are known to extend the photoexcitation to the visible light region.

Even though numerous studies have been carried out on the synthesis and characterization of the metal-doped titania, a majority of these reports deal with titania in the form of nanoparticulate powders with a variety of shapes and sizes, which are popularly produced by hydrothermal or sol-gel procedure [17–20]. In addition, a limited amount of research on the photocatalytic activity of metal-doped titania in the form of thin film has been reported [21–23]. Metal-doped titania thin film with a high specific surface area is often required for the better performance of titania-based devices demanding an excellent durability

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and abrasion resistance. Even though many efforts have been focused on the synthesis of metal-doped titania films by the most simple and economical method, such as a sol-gel process, resulting surface areas were not satisfactory [11–13,15,16,22]. In general, sol-gel processes using various titania precursors have been also considered difficult to tune the porous morphology of the titania films [24–27]. To achieve the desired pore structure of the titania films, soft template material such as cellulose nanocrystals (CNCs) was first introduced to fabricate the metal-doped titania thin films in current work.

Molybdenum was chosen as a dopant since Mo-doped titania in the form of either powder or film has been reported to exhibit high capability for photocatalytic performance [28–33]. In the meantime, the photodegradation properties of trichloroethylene (TCE) with Mo-doped titanias have not been reported. The present work reports a rather simple and efficient synthesis method for highly transparent and mesoporous Mo-doped titania thin films deposited on the ITO glass substrate and its photocatalytic performance of the TCE degradation. The morphological, phase characteristic, pore structural, optical, and photocatalytic properties were investigated with respect to the CNCs templating and the Mo doping to elucidate the main factors influencing the photocatalytic activity of the formed titania films. To the best of the authors' knowledge, the synthesis and photocatalytic characterization of the Mo-doped titania films fabricated by cooperating with templating CNCs are reported for the first time. The CNCs-templated titania films doped with Mo were compared with the pure titania and the CNCs-templated titania films without doping.

2. Experimental

As a source of the CNCs, cellulose powder, KC Flock W-50, was used. The extraction process for the CNCs in the form of suspension from the cellulose powder was reported in our previous papers [34,35]. The mixture of titanium (IV) ethoxide (TEOT, Sigma Aldrich, 97%) of 1.071 g and 37 wt% HCl of 0.765 g were magnetically stirred for 10 min for the complete dissolution of the TEOT and the sol reaction. The prepared CNCs suspension of 6.497 g was immersed into the sol of 1.836 g with the required amount of molybdenum (V) chloride powder (0.0625 and 0.102 g) and DI water of 12.45 g. This mixture was magnetically stirred at 250 rpm for 2 h, producing an opaque colloidal composite precursor consisted of the CNCs, Mo and titania sources. Four precursors with a different composition depending on the content of the CNCs and the Mo were prepared to fabricate four different titania films (pure titania, CNCs-templated titania with a CNCs/TiO_2 mass ratio of 1.51, CNCs-templated titania doped with 3 at% Mo, and CNCs-templated titania doped with 5 at% Mo). Each prepared precursor of 60 μL was spin-coated on 1.0 × 1.0 cm^2 ITO glass substrate at 2000 rpm for 30 s, followed by calcining in an ambient atmosphere at 400 °C for 1 h. The entire process diagram for the preparation of the CNCs-Mo-titania composite precursors and the sequent deposition of titania films on the ITO glass substrate is shown in Fig. 1.

The morphology of pristine CNCs and prepared titania films were examined using a transmission electron microscope (TEM) and a field emission scanning electron microscope (FESEM), respectively. The X-ray diffraction (XRD) patterns of the prepared titania films were obtained using a x-ray diffractometer with a Cu K_α radiation. The specific surface area, mean pore width, and pore volume of the free-standing titania films were determined by the Brunauer – Emmett – Teller (BET) method. The optical property was also measured by UV–vis–NIR spectrophotometer (CARY 5000) in the range between 300 nm and 800 nm. The photocatalytic degradation behavior of the titania films was investigated by monitoring the decomposition of the aqueous solution of trichloroethylene (TCE) with an initial concentration of 200 ppmv. Each free-standing film of 5 mg was immersed into the TCE aqueous solution of 100 mL and then ultrasonically homogenized for 10 min, followed by irradiation under UV-A light source (black light fluorescent, 15 W, GE) for different times. After irradiation at 5 min intervals, the tested TCE solution was analyzed in terms of the irradiation time using a high performance liquid chromatography by estimating the extent of photodegradation.

3. Results and discussion

The transparent bottle which contained the prepared CNCs suspension with 8.7 wt% of CNCs and the TEM micrograph of the CNCs are shown in Fig. 2(a) and (b), respectively. The average length and the width of the CNCs were approximately 80–250 nm and 3.8–9.5 nm, respectively. Fig. 3 show the photographs of the CNCs-templated titania films doped with 0, 3, and 5 at% Mo coated on the ITO glass substrate and calcined at 400 °C for 1 h. It is clearly seen that all three CNCs-templated titania films are highly transparent as much as an ITO glass. Fig. 4 show the SEM images of all the prepared titania films: (a) non-templated titania film, pure titania film, (b) CNCs-templated titania film, (c) CNCs-templated titania film doped with 3 at% Mo, and (d) CNCs-templated titania film doped with 5 at% Mo, all coated on the ITO glass substrate, followed by calcination at 400 °C for 1 h. The film thicknesses were in the range of 1.2 and 1.7 μm. The pure titania film was consisted of titania particles with an average size of 25 nm, exhibiting no distinct pore channels. On the other hand, all the CNCs-templated titania films with and without doping Mo present the porous morphology as shown in Fig. 4(b) – (d). It is clearly seen that the CNCs-templated titania films all exhibit slit-like pore channels surrounded with titania particles. It is obvious that the formation of the pore channels resulted from the templated CNCs, which provided the vacant sites during the calcination. The effect of Mo doping of titania film on the shape of pore channels could not be identified microscopically. It appeared that the Mo doping of titania film had little effect on the gross pore structure of the titania film unless the titania films are further analyzed by BET.

X-ray diffraction patterns of the pure titania film and the CNCs-templated titania films doped with 0, 3, and 5 at% Mo coated on the ITO glass substrate are shown in Fig. 5. The diffraction patterns of the pure titania film in Fig. 5(a) show main peaks pertaining to the anatase phase along with two different diffraction peaks corresponding to the rutile and brookite phases. The peak intensity of the rutile phase significantly decreased with templating the CNCs. In the meantime, the CNCs-templated titania films doped with Mo revealed the presence of only anatase peaks. It is thus known that the templated CNCs and the doped Mo played a role of activating the phase transformation of both the rutile and the brookite into the anatase during calcining at 400 °C for 1 h. It is noteworthy that the presence of peaks corresponding to molybdenum oxides was not identified in the CNCs-templated titania films doped with 3 at% and 5 at% Mo. This can be attributed to the substitutional solid solution of Mo ions for Ti ions in the titania lattice. In other studies [36–39], peaks of molybdenum oxide such MoO_3 were also undetected for the TiO_2 materials doped with Mo. Meanwhile, all the CNCs-templated titania films showed the anatase (101) peak broadness compared with the pure titania film. This result indicates that the templated CNCs might decrease the crystallite size of the titania film during calcination. The peak intensity of the anatase (101) increased with an increase in doping level up to 5 at%, suggesting that the Mo might also induce the decreased crystallite size of the titania film.

The Scherre equation was therefore used to estimate the crystallite size from the average full width at half maximum of anatase (101), (004), and (200) peak intensities. Table 1 lists the average crystallite sizes of the prepared titania films. It was confirmed that the crystallite sizes for all three CNCs-templated titania films were in the range between 9.5 and 10.5 nm, which are quite smaller than the value of pure titania film of 16.9 nm. It is worth noting that the templated CNCs provided heterogeneous nucleation sites for the crystallization of titania during calcination, resulting in a creation of more and smaller titania crystallites. Up to a point, the templated CNCs are believed to play an important role in creating the interconnected pore channels as well as