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Fabrication of a 12-tungstophosphate and cadmium oxide composite film and its properties

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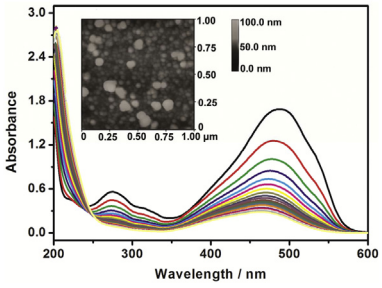
HIGHLIGHTS

- A composite film of CdO nanoparticles and 12-tungstophosphate was fabricated by LBL technique.
- The composite film exhibited enhanced photocatalytic activity toward methyl orange solution.
- The composite films displayed luminescent property assigned to the CdO nanoparticles.
- The composite film also showed reversible electrochromic property with fast response time.

GRAPHICAL ABSTRACT



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ABSTRACT

A multilayer composite film of the 12-tungstophosphate $H_3[PW_{12}O_{40}]^{3-}$ (PW_{12}) and cadmium oxide nanoparticles (CdO) was fabricated on quartz and silicon by the layer-by-layer (LBL) self-assembly method. The film was characterized by UV–vis spectroscopy, atomic force microscopy (AFM) and luminescence spectra. The proposed composite film exhibits higher photocatalytic activity toward methyl orange (MO) solution at pH 3.5, compared to single PW_{12} and CdO films. The degradation rate was affected by initial concentration of PW_{12}, pH value of MO solution, inorganic ions concentration and type in MO solution. In addition, the composite film displays luminescent property and reversible electrochromic property with fast response time.

1. Introduction

Polyoxometalates (POMs) are well-defined transition metal–oxygen clusters with remarkable structural characteristics and multiple functions, which have been significantly impacting the development of materials with catalytic, electrochemical, photochemical, electrochromic, luminescence, magnetic properties and nonlinear optical properties [1–8]. In recent years, POMs have been drawing widely attention as effective green photocatalysts. They have a number of features in common with semiconductor metal oxide clusters and can be considered as their analogs [9–18]. Both of them are constituted by d^0 transition metals and oxygen ions and exhibit similar electronic attributes including well-defined HOMO–LUMO gaps (semiconductor “band gaps”). Many POMs have been used as effective photocatalysts for the oxidation and decomposition of a variety of organic substrates, such as alcohols, alkanes, amines, chlorophenols, methyl orange, and organochlorine compounds due to their ability to undergo photoinduced multielectron transfer [19–23], which make them

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promising candidates for removing organic substrates from wastewater. The photocatalytic activities of POMs are influenced by changes in the heteroatom, addenda atoms, and incorporation of other component into the POMs-based composite materials. POMs are soluble in water and some organic media, which makes their recovery difficult. So POMs have been immobilized onto films to avoid rapid decrease of photocatalytic efficiency [24–28]. The films of POMs are typically prepared by the LBL method, which allows for the fabrication of robust, homogeneous films with fine controlled film thickness and amount of components. The general utility and vitality of these systems are further broadened when quantum dots and nanoparticles are incorporated into these multilayer films [29–31].

Nanoparticles (NPs) have attracted great interest in recent years, resulting in novel optical, electronic, magnetic, mechanical and catalytic properties [32], and their properties are different from those of either the corresponding bulk materials or single atoms. To take advantage of these remarkable properties of nanoparticles in various applications, the NPs need to be properly integrated and immobilized. Nanoparticles as components of multilayer films are of interest [33], because NPs self-assembled materials usually exhibit novel properties and special functions different from those of individual NPs. All the properties described above make NPs suitable for application in different fields, such as nanosensors, nanoelectronics and nanobiology [32].

Cadmium oxide is an N-type degenerate semiconductor with high electrical conductivity. Due to its large linear refractive index ($n_0 = 2.49$), cadmium oxide is a promising candidate for optoelectronic applications including solar cells, phototransistors, photodiodes, transparent electrodes and gas sensors [34,35]. In particularly, cadmium oxide shows a narrow direct gap of 2.3 eV between the O 2p-based valence band and the Cd 5s-based conduction band minimum [36], which makes it be photoactive. Many of the properties of CdO originated from its nonstoichiometric composition, which, in turn, strongly depends on the synthetic procedure adopted [36,37]. Because of possibilities of these interesting applications, there have been some efforts to prepare and utilize the nanoparticles of CdO.

In view of the reasons for above all, we fabricated the multilayer film comprising the Keggin-type polyoxometalate PW_{12} and CdO nanoparticles based on the LBL self-assembly method for the first time. The photocatalytic degradation of methyl orange solution by the composite film was systematically investigated and luminescent and electrochromism properties also were performed.

2. Experimental

2.1. Materials

Poly(ethylenimine) (PEI, MW = 750,000) and poly(sodium-*p*-styrenesulfonate) (PSS, MW = 70,000) were obtained from Aldrich Chemical Co. and used without further purification. $H_3PW_{12}O_{40}$ (PW_{12}) was prepared according to the literature method [38]. CdO nanoparticles were synthesized according to the method in the literature [39] and examined by fluorescence spectra, X-ray diffraction (XRD) and scanning electron microscope (SEM). The solution of PSS-coated CdO nanoparticles (PSS–CdO) was formed by ultrasound of CdO nanoparticles (0.0026 g) in 2 mM PSS solution. The solvents used in all experiments were deionized water with a resistivity of 16–18 MΩ cm^{-1}. All other reagents were of reagent grade.

2.2. Instrumentation

UV–vis spectra of quartz-supported films were recorded on a U-3010 UV–vis spectrophotometer (Hitachi, Japan). XRD patterns were obtained with a Rigaku D/max 2000 X-ray diffractometer with Cu–Kα radiation. SEM images were obtained on a Hitachi S-570 scanning electron microscope operating at 20 kV. AFM image was obtained by using a Digital Nanoscope IIIa instrument (DI, Santa Barbara, CA) operating in the tapping mode with silicon nitride tips. Fluorescence spectra were performed with a LS55 luminescence spectrometer (Perkin Elmer, USA) using a 150 W xenon lamp as excitation source. All the electrochemical experiments were performed on a CHI760D electrochemical workstation with the ITO electrode coated by the self-assembled film as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode and platinum coil as the counter electrode.

2.3. Preparation of the film

The substrate (quartz slide or silicon wafer) was thoroughly cleaned with Piranha solution (H_2O_2:H_2SO_4 = 3:7 v/v) at 80 °C for 20 min, followed by rinsing with deionized water. Further purification was carried out by immersing in $NH_3 \cdot H_2O$:H_2O_2:H_2O (1:1:5 v/v) solution at 70 °C for 20 min and then extensively washing with water and drying under a nitrogen stream. Then, the cleaned substrate was immersed in 2 mM PEI solution for 20 min and a precursor layer of PEI was modified on the surface of the substrate. Next, the precursor film was dipped into the 2 mM POM solution, 2 mM PEI and 2 mM PSS–CdO solution for 20 min in rotation, rinsed with deionized water and dried in a nitrogen stream after each dipping. The procedure results in the build-up of the multilayer films containing both PW_{12} and CdO, which can be expressed as $\{PEI/[PW_{12}/PEI/PSS–CdO/PEI]_n/PW_{12}\}$, where n is the number of bilayers.

2.4. Photocatalytic procedure and light source

Photocatalytic reactions were carried out as follows. Methyl orange (MO) was selected as the target to study the photocatalytic activity of multilayer composite film. A proposed multilayer composite film was immersed into a fresh aqueous dye MO solution (20 mg L^{-1}). The reactor was maintained at room temperature by cooling water and fume cupboard during the irradiation. The UV light source was a 250 W high-pressure mercury lamp (HPML, $\lambda = 365$ nm), located away from the solution about 10 cm. After the signal intensity of the HPML became stable, the solution was irradiated. The degradation of the MO was monitored by measuring the maximum absorption of MO solution at 465 nm. The degradation efficiency of the film was evaluated by the following equation [40]:

$$\text{Degradation}(\%) = (A_0 - A)/A_0 \times 100\%$$

where A_0 is the initial absorbance of MO solution at λ_{max} (the wavelength with a maximum absorption) and A is the absorbance of MO solution at λ_{max} after UV light irradiation.

3. Results and discussion

3.1. Characterization of nano-CdO

Fig. 1 shows the XRD pattern of the CdO nanoparticles. All of the peaks in this pattern can be indexed as a pure cubic phase (space group *Fm3m* (No. 225)) of CdO with a measured lattice constant of a = 4.692 Å (JCPDS 65-2908). Only the (200) reflection was observed, whereas the (400) remained hardly evident, which suggests highly oriented CdO [41,42].

XPS experiments of the multilayer composite film $\{PEI/[PW_{12}/PEI/PSS–CdO/PEI]_3/PW_{12}\}$ were carried out to identify the components of the composite film. The multilayer film exhibits peaks $P2_p$