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Photoelectrochemical performance of birnessite films and photoelectrocatalytic activity toward oxidation of phenol

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ABSTRACT

Birnessite films on fluorine-doped tin oxide (FTO) coated glass were prepared by cathodic reduction of aqueous $KMnO_4$. The deposited birnessite films were characterized with X-ray diffraction, Raman spectroscopy, scanning electron microscopy and atomic force microscopy. The photoelectrochemical activity of birnessite films was investigated and a remarkable photocurrent in response to visible light was observed in the presence of phenol, resulting from localized manganese *d*–*d* transitions. Based on this result, the photoelectrocatalytic oxidation of phenol was investigated. Compared with phenol degradation by the electrochemical oxidation process or photocatalysis separately, a synergetic photoelectrocatalytic degradation effect was observed in the presence of the birnessite film coated FTO electrode. Photoelectrocatalytic degradation ratios were influenced by film thickness and initial phenol concentrations. Phenol degradation with the thinnest birnessite film and initial phenol concentration of 10 mg/L showed the highest efficiency of 91.4% after 8 hr. Meanwhile, the kinetics of phenol removal was fit well by the pseudofirst-order kinetic model.

Introduction

Photoelectrocatalytic (PEC) oxidation in the presence of semiconductor photoelectrodes has been proven to be an efficient process that can be used for degradation of various organic pollutants, such as dyes (Zhang et al., 2007; Yang et al., 2005; Shinde et al., 2012), pesticides (Philippidis et al., 2009), aromatics (Chen et al., 2009; Yang et al., 2006; Neumann-Spallart et al., 2013), and so on. In most of these cases, an electrode coated with TiO_2 film was used as a photoanode. However, the wide bandgap of TiO_2 (about 3.2 eV) results in a lack of absorption in the visible portion of the solar light spectrum and limits the application of TiO_2. In order to increase the photocatalytic activity under visible irradiation, extensive studies have focused on doping metals (Fe, Cu, Cr, *etc.*) or non-metals (carbon and nitrogen) into TiO_2 to narrow the bandgap of TiO_2 (Zhang and Lei, 2008; Hua et al., 2015; Yang et al., 2014; Chen et al., 2009; Lan et al., 2013). As an alternative, some novel photocatalysts with response to visible light, such as Fe_2O_3, WO_3 and metal-free g-C_3N_4, have been developed (Zhang et al., 2010; Hepel and Hazelton, 2005; Cheng et al., 2007; Shinde et al., 2013, 2016). Fe_2O_3, WO_3 and g-C_3N_4 have narrow bandgaps of about 2.0–2.2 eV, 2.5 eV and 2.7 eV and can thus absorb part of the solar spectrum (Cesar et al., 2006; Hu et al., 2008; Spichiger-Ulmann and Augustynski, 1983; Shinde et al., 2016).

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Birnessite is a naturally occurring phyllomanganate consisting of edge-sharing sheets of MnO_6 octahedra with an interlayer distance at about 0.7 nm, and hydrated alkali metal cations (Na^+, K^+, *etc.*) in the interlayers that compensate the small overall negative charge. With a bandgap energy of 1.8–2.1 eV (Sherman, 2005; Pinaud et al., 2011; Hsu et al., 2012), birnessite is also an important photoactive material that can adsorb part of solar spectrum up to *ca.*, 600 nm (Hsu et al., 2012). Over the last decades, catalytic activity of birnessite has been observed in the oxidation of indigo carmine (Zaied et al., 2011), benzene (Ye et al., 2014; Hou et al., 2014), phenolic compounds (Nakayama et al., 2010; Chien et al., 2008; Hardie et al., 2007), *etc.* However, leaching of the reduced Mn species may impede the catalytic reaction and have a negative effect on the recycling of the manganese dioxide. A PEC degradation process could avoid these problems, and usually has higher efficiency than photocatalytic processes (Yang et al., 2006; Kesselman et al., 1997). Recently, some researchers have reported the photoelectrochemical properties of functional manganese oxide used for water splitting to generate hydrogen. Sakai et al. (2005) first reported the observation of photocurrent generation by MnO_2 nanosheets on indium tin oxide under visible light irradiation in a nonaqueous electrolyte. Hsu et al. (2012) demonstrated that birnessite nanosheets delivered remarkable photocurrent in the presence of a hole scavenger. Nevertheless, the PEC behavior of birnessite has been less extensively studied than other transition metal oxides such as Fe_2O_3 and WO_3, especially the efficiency of PEC degradation of organic pollutants on MnO_2-electrodes under visible light irradiation, and there is still much work to do.

In this study, direct growth of birnessite films with a series of thicknesses on FTO-coated glass was carried out by cathodic reduction of aqueous MnO_4^- ions. The photocatalytic activity of birnessite films of different thickness was evaluated in the presence of phenol. The influence of bias potential, thickness of birnessite sheet and initial phenol concentrations on phenol degradation was considered. The results showed that birnessite exhibits favorable photocatalytic properties and has application potential for organic pollutant degradation.

1. Experimental

1.1. Sample preparation

The cathodic deposition of birnessite-type manganese oxide was performed in a three-electrode electrochemical cell at room temperature (Nakayama et al., 2012). A platinum sheet (1 cm × 1 cm) and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Fluorine-doped tin oxide (FTO) substrates on glass supports served as the working electrodes. Prior to electrodeposition, the electrode surface was cleaned by ethanol and distilled water ultrasonically for 30 min each. A solution with 2 mmol/L $KMnO_4$ and 50 mmol/L KCl acted as electrolyte for the electrodeposition. The exposed area of the working electrode was 2.5×2 cm^2. A potentio/galvanostat electrochemical workstation (CHI 760E) was used to maintain a constant potential of −0.05 V (vs. SCE) during the deposition process. The film thickness was controlled by varying the delivered charge from 0.3 to 2.0 C.

1.2. Film characterization

X-ray diffraction (XRD) patterns were recorded using an X'Pert Pro MPD powder diffractometer (PANalytical B.V., Netherlands) with CuKα radiation ($\lambda = 0.15406$ nm). The instrument was operated at a tube voltage of 40 kV and a tube current of 40 mA. Intensities were measured at $2\theta = 5°–70°$ with 0.017° two-theta steps and a count time of 0.3 sec per step.

The mineral micro-morphologies were observed using an FEI NanoSEM 430 Field Emission Gun scanning electron microscope (SEM) (FEI Corp., USA). The samples were mounted on an aluminum SEM stub via conductive tape and coated with gold using a Denton Desk II Gold Sputter Coater before SEM observations. The SEM was operated at an accelerating voltage of 10 kV.

Raman spectra were measured using a Renishaw inVia Reflex system (Renishaw, UK) equipped with a 532 nm laser and a 50× objective. To obtain a high signal-to-noise ratio, each Raman spectrum was the average of 12 successive scans obtained at a spectral resolution of 1 cm^{-1}. The frequency stability and accuracy of the apparatus were checked by recording the Raman spectrum of silicon.

Thickness measurements were performed using a Bruker Dimension ICON Atomic Force Microscope (AFM) (Bruker, USA). The film was partially lifted off the substrate using a scalpel and then laid on the sample stage with the boundary between birnessite-coated and uncoated regions beneath the AFM tip. Imaging was performed in ScanAsyst® mode over a range of 50 × 10 μm. Average step heights along the X-axis were obtained using the "step" feature in NanoScope_Analysis software. The height diagrams obtained for each image gave three stages corresponding to the average heights of substrate, coating and transition region. By subtracting the substrate height from the coating height, the film thickness was obtained.

1.3. Photoelectrochemical measurements and analytical method

Photoelectrochemical measurements were carried out with a set-up consisting of a 30 mL cylindrical quartz glass reactor, external simulated solar light (white LED lamp) and a three-electrode configuration. The initial volume of the working solution was 20 mL with different initial phenol concentrations. The pH of the solution was fixed at 6.0 using a Mettler Toledo pH meter. Ultrapure water (18 MΩ·cm) was used throughout the experiments. To maintain suitable solution conductivity, 0.1 mol/L Na_2SO_4 was chosen as the supporting electrolyte. The incident light was irradiated onto birnessite film electrodes from the back face through the quartz window. The intensity of radiation at the position of the sample was approximately 60 mW/cm^2. Cooling of the reactor was assured by means of air flow using an incorporated fan. A potential of 1.0 V (vs SCE) was applied in the photocurrent measurement and the phenol degradation process.

In the PEC phenol oxidation process, samples were collected from the reaction solution at regular time intervals to determine the residual concentration of phenol. Total organic carbon

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