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Low bias photoelectrocatalytic (PEC) performance for organic vapour degradation using TiO_2/WO_3 nanocomposite

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ABSTRACT

In this study, a novel photoelectrocatalytic (PEC) flat-plate type device used in the gas-phase was fabricated by the technology of screen printing. The TiO_2/WO_3 nanocomposite (2:8 in mole ratio) was prepared by a simple milling-anneal method and printed onto the device. The obtained device was attempted to investigate the PEC performance by applying low biases for degrading the volatile organic compounds (VOCs). The apparent pseudo-first-order kinetic model was used to describe the degradation process. The results showed that the applied low bias had a distinct enhancement effect on the degradation activity compared to photocatalytic (PC) degradation. The PEC degradation rate under UV-light (365 nm) irradiation by applying only 0.2 V bias was about 12.28×10^{-3} min^{-1}, which was 2.42 times of PC degradation rate. Under the blue-light (475 nm) irradiation, the composite still had good degradation efficiency and the rate constant was about 2.6×10^{-3} min^{-1}. Furthermore, the explanation was proposed that the degradation activity of TiO_2/WO_3 composite could show obviously enhancement for gas-phase PEC process by applying bias at a very low level, compared to pure TiO_2.

1. Introduction

The technique of photoelectrocatalytic (PEC) oxidation for water and air effluent treatment has attracted increasing attention in the field of environmental protection [1–3]. The application of an external bias voltage on the catalyst can draw the photo-generated electrons away via the external circuit, leaving the holes for mineralization of organic pollutants by their oxidation [4,5]. Therefore, compared to the photocatalytic (PC) process, the probability of the rapid recombination of electron–hole pairs is largely reduced and the photo-degradation ability can be raised, which is the main characteristic of PEC process.

Until now, the PEC degradation researches are mainly carried out in aqueous solution [6–9], but rarely in gas phase. However, the volatile organic compounds (VOCs) in the environment have been very serious problems at present and directly harmful to human health [10–13]. A setup for the PEC reaction in aqueous solution is similar to a photoelectrochemical cell, comprising of a counter electrode, a working electrode coated with catalyst film, and a reference electrode in an electrolyte solution [14]. But, this mode is obviously unsuitable for the removal of volatile organic compounds (VOCs) and other gaseous pollutants [4]. Herein, we presented a new flat-plate type PEC device suitable for gas-phase application, in which catalyst is used as an active layer printing on the Au interdigital electrode. This type of PEC device was fabricated by the technology of screen printing. Such a biased device was tested to promote the photocatalytic degradation of acetone relative to unbiased.

In our previous work, on the basis of the idea of combinational material science, a material library of the $TiO_2/WO_3/MnO_2$ composite material system was designed. The photocurrent of each composite under different light sources was measured, respectively. The largest photocurrent at 0.2 V bias was observed when the mole ratio of TiO_2/WO_3 was 2/8 in the composite system. Pure TiO_2 had relatively higher photocurrent by applying a bias voltage of 10 V. However, the value was still smaller than the TiO_2/WO_3 composite at 0.2 V bias two orders of magnitude [15]. As can be seen, the TiO_2/WO_3 composite had much more excellent photoelectrical properties than pure TiO_2. However, the PEC device used for the photooxidation of organic vapours, in present researches, mainly consisted of plain TiO_2. Lately recently, Ye et al. found that the K_{PEC}/K_{PC} value of TiO_2 PEC processes obtained from the kinetic constant was 1.26 by applying a high bias of 82.5 V in the gas-phase [16]. Catalyst efficiency of traditional TiO_2 was improved with very high bias, which needed special potentiostat or voltage booster and consumed more electric energy. Therefore, it is obviously more worthwhile to deal with the improvement by applying a relative low bias.

Nowadays, the view of low carbon economy was strongly advocated. The above discoveries inspired us to consider that TiO_2/WO_3 composite was more suitable for PEC application than pure TiO_2 at

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low bias in gas phase. To the best of our knowledge, there was no report of TiO_2/WO_3 composite performance in gas-phase PEC process, especially for its low bias research. When the PEC degradation activity can easily get improvement than PC degradation with the bias less than 0.5 V, the bias is promising to be just provided by a small area of solar cell. We expect that the realization of low bias PEC degradation in gas phase will promote the rapid development of this technology in practical application.

Simply stated, the aim of this paper is (i) to fabricate and test the operation of a flat-plate type PEC device composed of Au interdigital electrode and printed catalyst film and (ii) to investigate the photooxidation of VOCs in the PEC process using TiO_2/WO_3 composite by applying very low biases under UV and visible light irradiation.

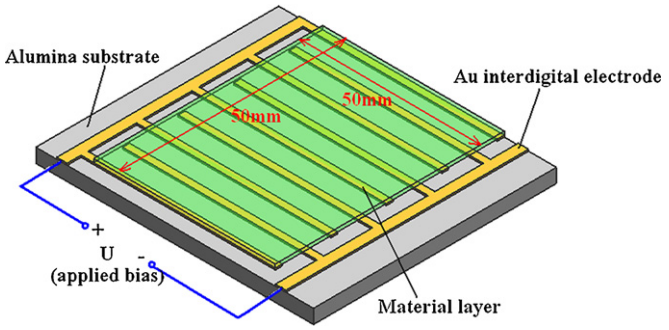

Fig. 1. Schematic of the PEC device (alumina substrate, Au electrode and TiO_2/WO_3 composite film from bottom to top).

2. Experimental

2.1. Chemicals

Titanium dioxide (TiO_2) (Beijing F&F Chemical Co. Ltd., China) and tungsten oxide (WO_3) (Tianjin kermel Chemical Reagent Co. Ltd., China) were of analytically pure grade and nano-sized particles. Both of them were used as received without any pretreatment.

2.2. Samples preparation and planar PEC devices fabrication

There are many methods to prepare semiconductor photoelectrodes, e.g., sol–gel, sputter deposition, coprecipitation. However, few works are reported to investigate the photocatalyst spreading on electrode by screen printing technique which was suitable to be used under gas-phase condition [17]. In this experiment, the synthesis of TiO_2/WO_3 composites was carried out in a ball miller (Nanjing University Instrument Factory, China). TiO_2 and WO_3 was first taken in a mole ratio of 2/8 (20 g in total), and then, the powder and a certain amount of organic solvent (composed of terpineol, butyl carbitol, ethyl-cellulose, span 85 and di-n-butyl phthalate) were put into the agate ball milling tank in a mass ratio of 1/10 between the powder and agate ball. Organic solvent was used mainly as a thickening agent and a rheological agent for screen printing. After ball milling for 4 h at the speed of 300 rpm, the suitable pastes used for the progress of screen printing were obtained.

TiO_2/WO_3 flat-plate type devices were fabricated by a screen printing technique, and the structure of the device was showed in Fig. 1. Firstly, the paste was printed onto the Au interdigital electrode which had been preprinted on the alumina substrate. The thickness of photocatalyst film was 10 μm which could be controlled by the screen printing machine. Then, the samples were preheated at 200 °C for 15 min to eliminate the organic solvent. In the end, the samples were heated up to 550 °C and then sintered at 550 °C for 2 h.

Following the above procedures, the PEC planar devices could be successfully obtained. Then, the composite film in the device was characterized by field-emission scanning electron microscopy (SEM, Sirion 200, FEI), X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V.) and UV–vis DRS spectrophotometer (Lambda 35, Perkin–Elmer).

2.3. Photoelectrocatalytic (PEC) reactor system

As shown in Fig. 2(a), the PEC reactor system used in this study mainly consisted of propulsion chamber, detection chamber, catalysis chamber and three pipes for connection. In the propulsion chamber, there was a direct current fan in order to ensure that the air was circulatory in the system during the test process. The concentration of the acetone gas in the reactor was monitored by the in situ gas sensors installed in the detection chamber. The detailed descriptions of the signal processing process and quantitative analytical method for gas sensor could be referred to our previous work [18–21]. The internal structure of catalysis chamber was detailed in Fig. 2(b). In our experiments, two PEC devices could be placed in the catalysis chamber during a test. LED-lights, which were ultraviolet (365 nm) and blue (475 nm), were selected as the light source because of their narrow wavelength width of 10 nm (i.e., UV-LED from 360 nm to 370 nm) and extremely low calorific effect compared to Xenon light. When Led-light irradiated the devices through the quartz glass, the light intensity at the surface of the device was about 5 mW/cm^2. A DAQ card (USB-6008, National Instruments Co.) precisely supplied potential bias to the PEC device and had a voltage control range of 0–5 V. The total volume of the reactor system was 825 ml, and the area of the photocatalyst film in the PEC device was 50 mm × 50 mm.

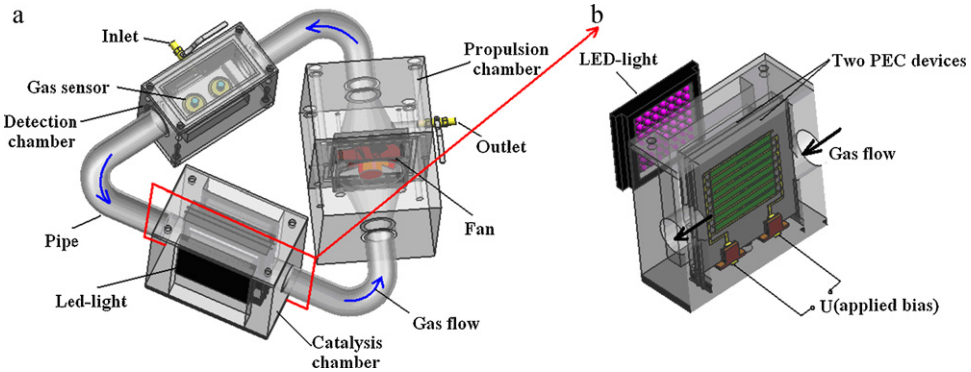

Fig. 2. (a) Schematic of the PEC reactor system; (b) schematic diagram of the catalysis chamber (sectional view).