Journal of Environmental Chemical Engineering 3 (2015) 622–629

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Preparation, characterization and visible-light photocatalytic performances of composite films prepared from polyvinyl chloride and SnO_2 nanoparticles

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ARTICLE INFO

Article history:
Received 29 October 2014
Accepted 4 February 2015
Available online 11 February 2015

Keywords:
Composite film
Visible-light photocatalytic activity
SnO_2 nanoparticles
Conjugated polymer
Polyvinyl chloride

ABSTRACT

The composite films containing polyvinyl chloride (PVC) and SnO_2 nanoparticles with the size of circa 3 nm were prepared by a facile casting method. The PVC/SnO_2 composite films were heated at higher temperatures of 150 °C to form CPVC/SnO_2 composite films with conjugated structure on their surface via dehydrochlorination reaction of PVC molecules. The CPVC/SnO_2 composite films were characterized by X-ray diffraction, transmission electron microscopy, Fourier-transform infrared spectroscopy, UV–vis diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The visible-light photocatalytic activity and stability of the as-prepared composite films were evaluated by photodegradation of Rhodamine B (RhB) solution. The results reveal that the CPVC/SnO_2 composite films possess excellent visible-light photocatalytic activity and stability, and the visible-light photocatalytic activity is about 25 times of that of graphite-like carbon nitride (g-C_3N_4) if their specific surface area is considered. As the PVC content, heat-treatment temperature or time increases, the visible-light photocatalytic activity of the composite films increases first and then decreases, and the optimum conditions are 1:3 of the mass ratio of PVC and SnO_2, 150 °C and 2 h, respectively. The visible-light photocatalytic mechanism of the CPVC/SnO_2 composite film has been discussed.

Introduction

Since Fujishima and Honda reported the photoelectrochemical water splitting by a TiO_2 electrode in 1972 [1], numerous efforts have been made to develop highly efficient semiconductor photocatalysts such as TiO_2, ZnO, SnO_2, CdS, BiOBr, and Ag_3PO_4 [2–7] for degradation of organic pollutants [8] in water and air under light irradiation. Among them, tin oxide (SnO_2) is a better electron acceptor than TiO_2 because the conduction band (CB) potential of SnO_2 (0 V versus NHE at pH 7) is more positive than that of TiO_2 (−0.5 V versus NHE at pH 7) [9]. Furthermore, SnO_2 has shown many excellent properties including high photoactivity, high photostability and thermodynamic stability, good chemical and biological inertness, nontoxicity, low cost, and easy production [10,11]. So SnO_2 has the potential to be an ideal photocatalyst. However, the wide band-gap of 3.6 eV makes SnO_2 be excited only by the ultraviolet light and leads to its inefficient utilization of solar energy or in-door light irradiation. Additionally, the fast recombination of the photogenerated electron–hole pairs in SnO_2 remarkably hinders its photocatalytic efficiency [12]. Therefore, more efforts have been dedicated on SnO_2 to overcome the above-mentioned drawbacks and improve the visible light photocatalytic activity. For instance, Sn^{2+} self-doped SnO_{2-x} [13], Sn–SnO_2/C [14], ZnO/SnO_2 [15,16], TiO_2/SnO_2 [17,18], SnO_2/Fe_2O_3 [19], Ag_3PO_4/SnO_2 [20], SnS_2/SnO_2 [21], and dye–graphene–SnO_2 [22] have been reported and exhibited enhanced photocatalytic abilities.

As a matter of fact, most of the above-mentioned photocatalysts work in a particle or particle-like state and are dispersed into waste water to degrade the organic pollutants, which is favorable to absorb visible light to decompose efficiently organic contaminants in water. However, the main drawback of them is the difficult separation of photocatalysts from the water system for their reusability, which limits their practical application in a large scale. Immobilization of photocatalysts as thin films on inorganic or polymeric substrates is one solution to the problems of recycled utilization and separation of nanostructured photocatalysts [23]. Enesca et al. [24] investigated the photocatalytic properties of hybrid structure comprised of SnO_2, ZnO and Cu_2S thin film semiconductors. Paul et al. [25] reported a novel reusable layer-by-layer coated nano metal oxides–polymer composite film for Cr(VI) removal.

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http://dx.doi.org/10.1016/j.jece.2015.02.002
2213-3437/

Polyvinyl chloride (PVC), one of the most common polymers used in many application fields, can be processed into many products with different shapes, e.g., films, fibers, rods, sheets, etc. It is well known that a partly conjugated polymer can be obtained from ordinary PVC when PVC is heated at high temperatures such as 150 °C via dehydrochlorination reaction [26–29]. The as-prepared conjugated polymer (labeled as CPVC) is a typically organic semiconductor with the band gap, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) potentials of 1.48 eV, −1.02 V and +0.46 V, respectively [30]. Since the LUMO potential of CPVC with conjugated structure is more negative than the conduction band potentials of TiO_2, ZnO, SnO_2, etc., the photogenerated electrons in the CPVC film can be easily injected into conduction band of the above metal oxides, leading to the efficient separation of photogenerated electron/hole pairs. This is advantageous to the visible-light photocatalytic activity of the as-prepared films. Therefore, it is reasonable to infer that the hybridization of polymer film with conjugated structure using these metal oxides may be an interesting approach to prepare an efficient visible-light photocatalyst for efficient separation and reusability.

In this work, CPVC/SnO_2 composite film possessing good visible-light photocatalytic activity and stability was prepared by hybridization of SnO_2 nanoparticles and CPVC derived from ordinary PVC using a facile casting method, which can be a cost-effective approach to synthesize cheap and recycled visible-light photocatalyst for the practical application in a large scale. The as-prepared CPVC/SnO_2 composite films were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), and photoluminescence (PL) spectroscopy. The visible-light photocatalytic activity and stability of the composite films were investigated by evaluating the Rhodamine B (RhB) photodegradation in the presence of these films, and their visible light photocatalytic mechanism has been discussed in detail.

Experimental

Materials

Methanol, absolute ethanol and tetrahydrofuran (THF) were purchased from Tianjin Yongda Chemical Reagent Co., China. Stannic chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were of analytical grade and used without further purification. PVC powders (R-1069) were supplied by Tianjin Botian Chemical Co., Ltd., China and refined by reprecipitation method, i.e., the tetrahydrofuran solution of PVC was put into methanol. The refined PVC was obtained via vacuum drying at room temperature. The deionized water was used throughout the experiments.

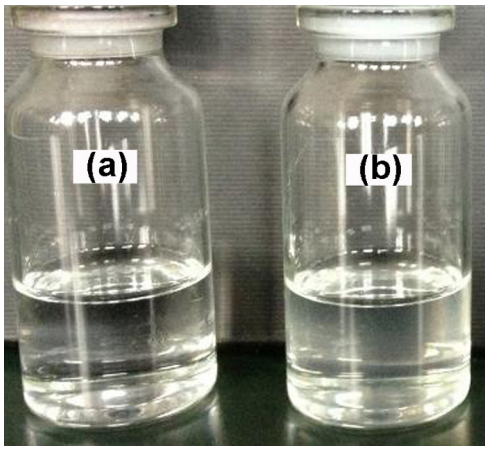


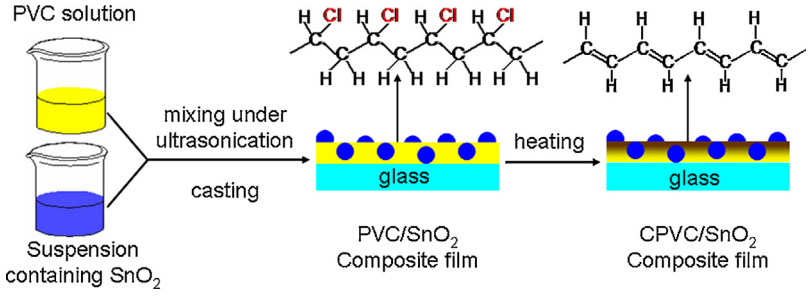
Fig. 1. Photograph of PVC solution (a) and suspension containing SnO_2 nanoparticles (b).

Synthesis of SnO_2 nanoparticles

SnO_2 nanoparticles were synthesized using a microwave-assisted hydrothermal method described in literature [31–33]. Firstly, 0.018 mol of $SnCl_4{\cdot}5H_2O$ was completely dissolved into 30 mL of methanol in a 250 mL glass conical flask. After that, 0.015 mL of 19.16 mol L^{-1} ammonia and 100 mL of deionized water were added into the above solution successively. The glass conical flask containing the above solution was put into a microwave reactor and heated at 100 °C for 20 min. The final product was obtained by filtration, washing with deionized water and ethanol several times respectively, and drying at a 540 W microwave oven for 20 min.

Synthesis of CPVC/SnO_2 composite films

The synthesis procedure of CPVC/SnO_2 composite films can be described as follows. Firstly, two solutions were prepared, one was a suspension containing SnO_2 nanoparticles and THF with the mass ratio of 1:50, the other one was a PVC solution with THF as solvent (2 wt%) (shown in Fig. 1). Then, 5 g of the above-mentioned suspension (0.1 g of SnO_2) and 5 g of PVC solution (0.1 g of PVC) were put into a 500 mL beaker to be volatilized under ultrasonication until a composite film with PVC to SnO_2 mass ratio of 1:1 was formed. The obtained composite film was heated at higher temperature to form CPVC/SnO_2 composite film. Using the same method, a series of CPVC/SnO_2 composite films with different mass ratios of PVC to SnO_2 (1:1, 1:2, 1:3, 1:4 and 1:5) were prepared and labeled as CPVC/SnO_2 (1:x), where 1:x is the mass ratio of PVC to SnO_2 in the composite films. CPVC film and SnO_2 film were prepared by volatizing a PVC solution without SnO_2 nanoparticles



Scheme 1. The idealized preparation procedure for CPVC/SnO_2 composite films.