ARTICLE IN PRESS

Arabian Journal of Chemistry (2012) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Study of photocatalytic asset of the $ZnSnO_3$ synthesized by green chemistry

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Received 6 April 2012; accepted 2 October 2012

KEYWORDS

Photocatalyst;
Mechanochemical synthesis;
Green chemistry;
XRD;
TEM;
BET

Abstract In this paper, we report a simple one-step mechanochemical synthesis method with a green chemistry approach for a light-induced heterogeneous oxide photocatalyst, $ZnSnO_3$. The catalyst was characterized by various investigative techniques, like Infrared Fourier Transform Spectroscopy, Diffused Reflectance UV–visible Spectroscopy, X-ray Diffraction, Scanning Electron Microscopy, Tunnelling Electron Microscopy, and Thermogravimetric analysis to carry out structural and spectroscopic properties of the photocatalyst. The synthesized $ZnSnO_3$ particles had an average size of 105 nm with a band gap of 3.34 eV. The photocatalyst was thermally stable over a wide range of temperatures. The sunlight mediated degradation of Methyl blue, Indigo carmine and Acid violet dyes were achieved by using $ZnSnO_3$.

1. Introduction

With growing industrialization and population, environmental contamination caused by organic pollutants is being one of the overwhelming problems all over the world. However, its horrible adverse effects have appeared in the shape of environmental collapse. The domestic use and industrial activity both produce a large amount of wastewater, which then disposed into natural channels leading to a high pollution risk. A small quantity of polluted water is sufficient to contaminate much greater capacity of clean water. Synthetic dyes are toxic refractory chemicals, which generate murky colour to the water and are hazardous to the environment. The dyes were detected in a dissolved state in wastewater (Esther et al., 2004). Most of these dyes are toxic and carcinogenic in nature (Blake et al., 1999). One must note down that, a wide spectrum of compound can transform themselves into potentially dangerous substances during the water treatment process. A non-biodegradable pollutant present in wastewater is a point of major serious pain to the researchers in the world.

Various methods have been suggested for the purification of polluted water, these includes; surface adsorption (Meshko et al., 2001 and Iqbal et al., 2011), and bio-degradation (Elias et al., 2000; Saratale et al., 2009, and Shah et al., 2012), use of membrane (Joong et al., 2008). The light induced photocatalytic process has received considerable attention in the last few decades. The photocatalytic reactions on semiconductors have been utilized for many applications, such as air cleaners (Hoffmann et al., 1995), self-cleaning materials (Libby, 1971), and antibacterial materials (Wang et al., 2010). In photocatalysis, light used to activate a substance that alters the rate of a chemical reaction without involvement of itself. The

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2012.10.001

great significance of photocatalysis process is that, it can degrade and/or detoxify various complex organic chemicals, which has not tackled by other methods of purification. Furthermore, it increases the chance of reuse of water. Generally, the reaction recognized as phenomena originating from electrons and holes excited by absorption of photons with energy greater than the band gap energy of the semiconductors. The holes have a strong potential to draw electrons out of organic and inorganic contaminants, resulting in the decomposition of hazardous materials, such as dyes, (Borhade and Baste, 2011 and Lodha et al., 2011), pesticides (Lafi and Al-Qodah, 2006), fungicides (Fenoll et al., 2011) and insecticides (Kitsiou and Filippidis, 2009), and many organic pollutants. When aqueous suspension of the photocatalyst was irradiated with light energy greater than the band gap energy of the semiconductor oxide, conduction band electrons (e^-) and valance band holes (h^+) are formed. The photogenerated electrons react with absorbed molecular O_2 reducing it to superoxide radical anion $O_2^{\cdot}$, and photogenerated holes can oxidize organic molecules directly or the OH and the H_2O molecule adsorbed at catalyst surface to OH radical. These electron hole pairs act as a strong oxidizing agent and can easily attack on organic molecules or those located close to the surface of the catalyst, thus leading to complete degradation of organic molecules.

Literature survey shows that, very little attention is given to the mixed oxide photocatalyst. The TiO_2 is widely studied and demonstrated its photocatalytic activity (Chen and Weiwei, 2009; Konstantinou and Albanis, 2004; Gupta et al., 2011). The ZnO is another broadly studied photocatalyst for the dye degradation (Chakrabarti and Dutta, 2004; Daneshvar and Salari, 2008). Few reports are available on the studies related to the photocatalytic activity of coupled semiconductor photocatalyst, such as TiO_2–CeO_2 (Baoshun and Xiujian, 2005), TiO_2–WO_3 (Bojinova et al., 2008), TiO_2–SnO_2 (Tada et al., 2000) and ZnO–SnO_2 (Wang et al., 2004; Azam and Ali, 2011).

As far as degradation of Methyl blue, Indigo carmine and Acid violet is concerned, different researchers have worked and efficiently degraded the dyes. Madhu et al. (2009) degraded Methyl blue in 120 min with TiO_2 and in presence of H_2O_2 at different concentrations. Tianyong Zhang et al. and Kuo degraded Methyl blue with TiO_2 by adjusting pH of the solution (Tianyong et al., 2001; Kuo and Ho, 2001), and N. Barka degraded Indigo carmine by TiO_2-coated non-woven fibre by adjusting pH and temperature (Barka et al., 2008). Krushnakumar and Swaminathan (2012) have degraded Acid violet-7 using direct sunlight at pH-12. The study follows pseudo first order kinetics but, all above study is not environmentally friendly. The main advantage of photocatalytic is that, the process takes place at ambient temperature without overpressure. The oxygen used for oxidation can be directly obtained from atmosphere.

We report the synthesis of $ZnSnO_3$ photocatalyst by simple one-pot mechanochemical method using a green chemistry approach. Various routine methods are available for the synthesis of mixed metal oxide such as; sol–gel (Gao et al., 2002; Wongkalasin et al., 2011), hydrothermal (Bao et al., 2005; Lee et al., 2012) and thin film vapour deposition method (Sun and Wang, 2008). These methods are complicated, cost effective and cause environmental pollution. Whereas the solid-state mechanochemical synthesis method is an environmentally friendly method, easy, and also gives less energy to the environment (Yoon and Ischay, 2010). The structural properties of the synthesized $ZnSnO_3$ photocatalyst were approved by various techniques like, FTIR, UV-DRS, XRD, SEM, TEM, BET surface area and TGA. The aim of the present work was to investigate the degradation of Methyl blue (MB; colour index-42780), Indigo carmine (IC; colour index-75781) and Acid violet (AV; colour index-60730) in aqueous $ZnSnO_3$ suspension under sunlight irradiation.

2. Experimental

2.1. Synthesis of $ZnSnO_3$ photocatalyst

Apart from reported methods we have synthesized mixed metal oxide photocatalyst using a green chemistry approach. Starting reagents were of ZnO (Merck, Batch No. MD6M561095 CAS No 1314-13-2, 99.9% pure) and SnO_2 (Loba Chem. Batch No. 27685, CAS No 18282-10-5, 99.9% pure). Equimolar mixture of ZnO and SnO_2 was grinded with mortar and pestle to acquire fine powder for 20 min and calcinated at 500 °C for 3 h. Again the obtained powder was further calcinated at 800 °C following milling after each interval of three-hour time. The calcination was continued for next twenty hours with milling. Afterwards, at the end mixture was heated up to the terminal temperature. The furnace was programmed as 10 °C per min from one temperature to subsequent higher temperatures. The product $ZnSnO_3$, thus obtained, was used for characterization.

2.2. Characterization

The vibrational frequency in the range of 400–4000 $cm^{-1}$of the synthesized catalyst was studied by FTIR, 8400S-Shimadzu. The optical property of $ZnSnO_3$ photocatalyst was evaluated by scanning over the wavelength range of 200–800 nm by using Perkin Elmer-λ-950, UV–visible spectrophotometer. The structural properties of the material were studied by using X-ray diffractometer, Rigaku-D/MAX-2500 with Cu-Kα radiation, with $\lambda = 1.5406$ Å. The surface morphology and chemical compositions of the synthesized catalyst were analysed by using a scanning electron microscope JEOL, JED-2300LA, coupled with an energy dispersive spectrometer-JED-2300LA. The TEM images were recorded on Philips, CM-200. The Surface area (S_{BET}), pore volume(V_p) and pore diameter (D_p) were evaluated by Quntachrome Autosorb automated gas sorption system, Autosorb-1 NOVA-1200 and Mercury Porositymeter Autosoeb-IC. The stability of the catalyst was evaluated by thermogravimetric analysis on Perkin Elmer-TG, Thermogravimetric analyzer.

2.3. Photocatalytic activity

The photocatalytic activity of the synthesized $ZnSnO_3$ photocatalyst was evaluated by studying degradation of Methyl blue, Indigo carmine, and Acid violet dyes. Experiments were conducted with 20 and 10 ppm dye solution: with 6 and 10 g/L photocatalyst to study the effect of amount of dye concentration and amount of catalyst concentration on degradation. During the experiment, three types of observations were recorded. In one set of the experiment, dye solution (20 and

Please cite this article in press as: Borhade, A.V., Baste, Y.R. Study of photocatalytic asset of the $ZnSnO_3$ synthesized by green chemistry. Arabian Journal of Chemistry (2012), http://dx.doi.org/10.1016/j.arabjc.2012.10.001