The role of carbon nanotube in zinc stannate photocatalytic performance improvement: Experimental and kinetic evidences

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The Zn_2SnO_4/MWCNTs (ZSC) nanocomposite was synthesized by a facile two-step process. The as-prepared nanocomposite was characterized by Powder X-ray diffraction, scanning electron microscopy, Transition electron microscopy, UV–vis diffuse reflectance spectroscopy and photoluminescence spectra analysis. The ZSC nanocomposite exhibits much higher photocatalytic activity (94% removal in 120 min) in comparison with bare Zinc stannate (ZS) (17% removal in 120 min) under UV-A irradiation, toward degradation of Basic Red 46. The role of the MWCNTs on the observed enhancement in photocatalytic activity was revealed by investigating the effect of radical scavengers on degradation efficiency. The addition of BQ had no effect on photocatalytic efficiency and t-buthanol decreased the photocatalytic activity to some extent. However, the addition of iodide ion, as a hole scavenger, inhabited completely the photocatalytic degradation of BR46, indicating that the degradation of the BR46 occurs mostly by direct oxidation on photogenerated holes. Based on the results of experiments, DRS and PL spectra, two possible mechanisms were proposed. Moreover, a new kinetic model was developed based on the intrinsic elementary reactions and the proposed mechanism. The correlation coefficient (R^2) and root-mean-square-error (RMSE) of 0.990 and 7.12×10^{-4} indicates the good agreement between the calculated apparent rate constants and experimental ones.

1. Introduction

Over the past two decades, the fascinating mechanical, chemical and electrical properties of Carbon Nanotubes–the one dimensional form of sp^2-hyridized carbon- [1], have open a new window toward solving the well-known issues in different research areas including, nanoelectronics [2], polymer science [3], electrochemical energy storage devices [4], catalysis and photocatalysis [5].

Regarding to the domain of photocatalysis, the major challenges are to increase the visible light absorption capability, decrease the recombination rate of photo-induced electron-hole pairs and preventing the aggregation of catalyst particles [6]. The unique features of CNTs namely, conductivity and electron accepting and transporting properties, ability to respond to visible light and high specific surface area, make them capable to overcome these prob-

lems [7–10]. Hence, enormous interest have been promoted in synthesize CNT-semiconductor nanocomposites and great amount of literature have been reported the enhanced photoactivity of these nanocomposites [10–19].

The enhancement of photocatalytic performance of studied nanocomposites can be explained by different mechanisms. It has been reported that CNTs can act as a macromolecule photosensitizers, which enhanced the visible light absorption capability by photoexcitation of electrons from the ground state of CNTs to its excited state. The excited electrons can then injected into the conduction band of semiconductor, allowing the formation of superoxide radicals [16,17]. Another different mechanism, is introducing a new carbon energy level into the semiconductor band gap and thereby extending the light absorption of composite to longer wavelengths [18]. The other proposed mechanism is attributed to the fact that CNTs have large electron-storage capacity, hence the photo-excited electrons can be transferred from the space-charge region of semiconductor into CNTs upon illumination, resulting in prolongation of life span of photoexcited electron-hole pairs [8,19]. CNTs can also make it possible to obtain a higher surface area and

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play a role as a dispersing template to prevent the agglomeration of catalyst particles [12,20].

Even though the photocatalytic activity of CNTs-semiconductor nanocomposite have been widely investigated, proposing a more detailed mechanism for understanding the photocatalytic processes in these systems is still a major challenge. To achieve this purpose, modeling a photocatalytic process can significantly enhance the understanding of the responsible mechanism of photoactivity [21]. The kinetic study plays an important role in discovering the reaction mechanism and estimating the influences of different operation parameters [22]. Hence, modeling of processes based on the kinetic studies is one of the best modeling methods, since it is based on correct understanding of happened reactions in the process [23].

The previous studies mostly focused on CNTs-binary oxide semiconductor nanocomposites (e.g., TiO_2, ZnO, ZnS, and CdS) [24–28]. Nevertheless, in comparison with simple binary oxides, ternary oxides have more ability to tune the chemical and physical properties by altering the compositions [29]. Zinc stannate (Zn_2SnO_4), as one of the most important ternary oxides, have been studied in wide range of applications such as anode material for dye sensitized solar cells (DSCs) [30], Li^+ batteries [31] and photocatalysts for pollution decomposition [32,33]. However the high charge separation rate induced by surface oxygen-vacancies and high chemical stability, make ZS a good candidate for photocatalysis [22,34], but, the high band gap energy of 3.0–3.9 eV, hinder its applicability in photocatalytic processes [35].

Herein, we have synthesized Zn_2SnO_4/MWCNTs nanocomposite via a simple two-step process and the photocatalytic performance of the prepared sample was investigate by photodegradation of Basic Red 46 as a model organic pollutant. As the photocatalytic activity is closely related to the type and amount of the produced active species, a series of experiments were conducted in the presence of appropriate scavengers. Moreover, in order to dig out the more detailed mechanism of photocatalytic performance of CNT-semiconductor nanocomposite, a kinetic model was developed based on the intrinsic elementary reactions and the proposed mechanism and the adequacy of the proposed model to fit the experimental results was further discussed.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs, 20 nm in diameter and 30 μm in length, purity >95 wt%) were purchased from Neutrino Co,Iran. The stannic chloride pentahydrate ($SnCl_4·5H_2O$) and zinc nitrate [$Zn(NO_3)_2$] was purchased from Sigma-Aldrich CO. NaOH and BR46 were obtained from Merck (Germany).

2.2. Synthesis

In order to synthesize ZCS nanocomposie, 0.05 g MWCNTs was dispersed into deionized (DI) water by sonication for 15 min. $SnCl_4·5H_2O$ (3 mmol) and $Zn(NO_3)_2$ (3 mmol) were dissolved in 20 mL of double distilled water separately to give two transparent solutions. Afterward, 20 mL NaOH (1 M) was added dropwise into the tin chloride dihydrate solution and then the resultant solution was added drop by drop into mentioned MWCNT solution. After the addition was completed, zinc nitrate solution was added drop by drop into above mixed solution under vigorous stirring at room temperature until the formation of grey precipitate of the hybrid complex. Finally, the grey precipitate was transferred into a 100 mL Teflon-lined stainless. The autoclave was sealed and maintained in a furnace at 220 °C for 48 h. The autoclave was cooled naturally to room temperature. The obtained precipitate was washed several times in double distilled water and absolute ethanol by repeated centrifugation and ultrasonication. Finally, the product was dried in an oven at 80 °C for 20 h.

2.3. Characterization

The structure, phase composition and real size of prepared nanocomposites were determined by Powder XRD investigations using Siemens X-ray diffraction ((D5000, Germany), with Cu $K\alpha$ radiation(1.54065 Å and $\theta = 5$–$75°$)). The surface morphology was analyzed by TEM (JEOL, JEM 2200) and FESEM (MIRA3 FEG-SEM, Tescan). DRS and PL spectra were obtained with a Perkin-Elmer, Lambda 25 and JASCO FP-6200, respectively

2.4. Procedure

The photocatalytic activity of ZSC nanocomposite was evaluated by the degradation of Basic Red 46 as a dye pollutant. In a typical process, 140 mg/L of catalyst was suspended into aqueous solution of BR43 with a known initial concentration. The suspended solution was irradiated by 390 nm emmiting UV-LED with a maximum power of 150 W. At specific time intervals, suspension was sampled and centrifuged to remove the catalyst particles. The pH of solution kept constant at 9. The light intensity and initial dye concentration were kept constant at 36 W/m² and 14 mg/L respectively, except for investigating the effect of these two factors on photocatalytic efficiency. Photocatalytic activity experiments using different radical scavengers were performed similar to the above procedure but in the presence of 1 mM different radical scavenger.

3. Results and discussion

3.1. Characterization of the ZSC nanocomposite

The crystal structure and phase composition of ZSC nanocomposite were determined by X-ray powder diffraction. Fig. 1 shows the XRD pattern of the as-prepared sample. The reflection peaks of (111), (220), (311), (220), (400), (422), (511) and (440) are attributed to the spinel structure of Zn_2SnO_4 [30,32]. The small marked residual peak at around $2\theta = 26°$ can be assigned to 002 plane of MWCNTs [36,37]. High crystallinity of the prepared Zn_2SnO_4/MWCNT is confirmed by the strong, narrow and intense reflection peaks in the XRD. Additionally, no diffraction peaks of SnO_2 were observed confirming the phase purity of the prepared nanocomposite.

The morphology of Zn_2SnO_4/MWCNT nanocomposite was investigated using scanning electron microscopy (Fig. 2). SEM images show the distribution of Zinc Stannate nanoplates across 1D CNTs. Fig. 2b also confirms that Zn_2SnO_4 have been synthesized in nanoplates form. TEM micrograph of Zn_2SnO_4/MWCNTs nanocomposite indicates the presence of Zn_2SnO_4 nanoplates on the walls of MWCNTs. The diameter of the MWCNTs is about 20 nm and the thickness is about 7 nm.

The optical absorption properties of prepared ZS and ZSC nanocomposite are investigated by diffuse reflectance spectroscopy (Fig. 3a). UV–vis absorption spectra revealed that the ZS could only absorb wavelengths shorter than 340 nm, which is attributed to its inartistic band gap. It is obvious in ZS UV–vis spectrum that the addition of the CNTs to ZS yields to shift in adsorption edge toward the longer wavelengths (400 nm). The optical band gap energies for prepared photocatalysts were determined by Tauc-Mott plot (TM) derived from following Eq. [38]:

$$(AE)^{1/m} = B \left(E - E_g \right) \tag{1}$$