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Editor's choice paper

A comprehensive study on electrochemical and photocatalytic activity of SnO_2-ZnO/clinoptilolite nanoparticles

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ABSTRACT

Mechanically prepared clinoptilolite nanoparticles (NC) and coupling were used for increasing photocatalytic activity of ZnO and SnO_2. The raw and modified catalysts were characterized by XRD, FTIR, SEM-EDX, X-ray mapping, DRS, electrochemical impedance spectroscopy (EIS) and BET techniques. The calcined catalysts at 600 °C for 2 h showed the best photocatalytic activity in metronidazole (MZ) aqueous solution. Based on the EIS results, this catalyst has the best charge transfer efficiency with respect to other catalysts calcined at lower and higher temperatures. This caused to lower e/h recombination and hence higher photodegradation activity. The mole ratio of ZnO/SnO_2 affects the degradation activity of the catalysts so the best activities were obtained for the $ZnO_{2.4}$-$SnO_{2(2.0)}$/NC (ZS-NC) and $ZnO_{3.3}$-$SnO_{2(2.0)}$/NC (Z_2S-NC) catalysts at pH 3. Cyclic voltammograms of the modified carbon paste electrodes with ZS-NC and Z_2S-NC showed increased peak current in phosphate buffer which confirm formation of the ZnO and SnO_2 semiconductors inside NC. Also, peak current dependence of the modified electrode to MZ concentration confirmed that the degradation extent of MZ can be estimated by electrochemical methods.

1. Introduction

Pollution of water by different organic/inorganic compounds, such as antibiotics, has reached at an alarming level with increased exploration in technology and industry. The large variety of antibiotics, high consumption and persistence in the environment caused to be subjected them in research area for the chemist and environmental scientists which cannot be complete removed some antibiotics during wastewater treatment [1]. Metronidazole (MZ) (2-methyl-5-nitroimidazole-1-ethanol) has been widely used to treat infections caused by anaerobic bacteria, bacteroides and protozoa [2,3]. It is known as a non-biodegradable and highly water soluble compound which can be accumulated in the aquatic environment. Because of its high toxicity, potential mutagenicity and carcinogenetic effects, its elimination from water/wastewater samples is an important research issue [4,5]. Among various methods for removing organic/inorganic pollutants (adsorption, precipitation etc), advanced oxidation methods have known as the most effective and common strategy in recent decades because catalytic oxidation reactions can mineralize organic substances to environmental friendly compounds [6–10].

Semiconductor based (heterogeneous) photocatalysis has known as one of the most successful AOP method, environmental friendly and cost effective process for effective degradation of various harmful organic compounds. In this method, the photogenerated electron–hole (e^-/h^+) pairs can react with dissolved oxygen and water/hydroxyl and produce superoxide and hydroxyl radicals, respectively. These attack to organic pollutants present in media and destroy them to smaller fragments and finally to water and carbon dioxide [11–14].

Nevertheless, one major drawback in semiconductor based photocatalysis is e/h recombination which cause to releasing the absorbed energy as heat and hence decrease the photocatalytic degradation efficiency. Two most famous strategies, supporting of semiconductors on a suitable support and coupling of two or more semiconductors, have been used for lowering e/h recombination [15–17]. It is well known that, coupling of two or more semiconductors with different band gap energies (*p-n*, *n-n* or *p-p* junction) creates new heterostructure semiconductor system that separate charge carries and significantly minimize e/h recombination. In comparison of mono components semiconductors, in photoexcited heterostructure photocatalysts, photogenerated electrons in more negative conduction band (C_B) of a semiconductor can injected

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Table 1
Amount of loaded semiconductors onto the catalysts.

Abbreviations	Catalysts	C in solution (M)		Loaded cations (meq/g)		Loaded semiconductors (W%)		(mol%)	
		Zn	Sn	Zn	Sn	ZnO	SnO_2	ZnO	SnO_2
ZS-NC	$ZnO_{2.4}$-$SnO_{2\,(2.0)}$/NC	0.1	0.1	0.24 ± 0.01	0.13 ± 0.02	2.40 ± 0.10	2.03 ± 0.08	0.29	0.13
Z_2S-NC	$ZnO_{3.3}$-$SnO_{2\,(2.0)}$/NC	0.2	0.1	0.42 ± 0.02	0.13 ± 0.01	3.27 ± 0.16	1.96 ± 0.16	0.40	0.13
Z_3S-NC	$ZnO_{4.2}$-$SnO_{2\,(1.9)}$/NC	0.3	0.1	0.52 ± 0.05	0.11 ± 0.01	4.23 ± 0.30	1.87 ± 0.30	0.52	0.12
Z_4S-NC	$ZnO_{5.4}$-$SnO_{2\,(1.8)}$/NC	0.4	0.1	0.65 ± 0.05	0.11 ± 0.02	5.35 ± 0.30	1.83 ± 0.31	0.66	0.12
Z_5S-NC	$ZnO_{6.0}$-$SnO_{2\,(1.3)}$/NC	0.5	0.1	0.72 ± 0.05	0.11 ± 0.02	6.01 ± 0.36	1.25 ± 0.18	0.74	0.08
ZS_2-NC	$ZnO_{1.6}$-$SnO_{2\,(2.7)}$/NC	0.1	02	0.19 ± 0.02	0.18 ± 0.03	1.57 ± 0.11	2.72 ± 0.07	0.19	0.18
ZS_3-NC	$ZnO_{1.3}$-$SnO_{2\,(3.7)}$/NC	0.1	0.3	0.16 ± 0.01	0.22 ± 0.02	1.34 ± 0.10	3.65 ± 0.30	0.16	0.24
ZS_4-NC	$ZnO_{1.2}SnO_{2\,(4.3)}$/NC	0.1	0.4	0.16 ± 0.01	0.28 ± 0.01	1.24 ± 0.12	4.27 ± 0.23	0.15	0.28
ZS_5-NC	$ZnO_{1.3}$-$SnO_{2\,(5.1)}$/NC	0.1	0.5	0.16 ± 0.01	0.35 ± 0.01	1.30 ± 0.15	5.06 ± 0.12	0.16	0.34

to the more positive C_B of other semiconductor, while the holes are injected in opposite direction between valence bands. These transitions significantly reduce e/h recombination [18,19]. Coupled semiconductor systems have a high ability to shift the required energy for excitation of coupled system towards longer wavelengths. For example, ZnO semiconductor has a wide band gap of about 3.37 eV (in UV-light region) and hence it has low efficiency under visible light illumination. Doping of ZnO with metals or nonmetal ions or combining it with another semiconductor are the strategies used to overcome this drawback [20–22].

Regarding to above discussion, to enhance photodegradation activity of ZnO and SnO_2 their coupled system as supported onto clinoptilolite nanoparticles was used in photocatalytic degradation of Metronidazole pharmaceutical capsule (MZ) aqueous solution. High adsorption capacity of zeolites brings pollutant molecules near the catalyst surface and hence they immediately react with generated radicals because hydroxyl and superoxide radicals have very short life time about a few nanoseconds and they should immediately react after production. Zeolitic bed can also prevent from aggregation of supported semiconductors, because semiconductor molecules formed on ion exchange sites of zeolite. Zeolites with strong electric field strength, can also inhibit recombination of e/h pairs via distribution of photogenerated electrons inside zeolitic network [23,24].

2. Experimental

2.1. Materials and preparations

All the chemicals used were prepared from Merck Company. Metronidazole pharmaceutical capsule was purchased from Iran Daru (IRAN). An Iranian clinoptilolite tuff (obtained from Afrand Touska Company (Isfahan, Iran)) was converted to nanoparticles (NC) by using a planetary ball mill (PM100; Retsch Corporation). Procedures for pretreatment of the zeolite and its digestion were reported in our previous work [23]. Aliquot amount of the MZ powder was dissolved in water and diluted to 50 mL in a volumetric flask to obtain 100 mg L^{-1} MZ. Diluter solutions were prepared by serial dilution method of the stock solution.

During the ion exchanging of 2 g NC powder in solutions containing different concentrations of Zn(II) and Sn(IV), reported in Table 1, Zn(II)-Sn(IV)-NC samples were obtained (10 mL, 8 h at continuous stirring). After centrifugation of the suspensions, the ion exchanged samples were calcinated at 600 °C (as optimized calcinations temperature) to prepare ZnO-SnO_2-NC catalysts with different ZnO/SnO_2 ratios).

2.2. Characterization methods

The methods used for characterization/determination of samples are summarized below: XRD analytical diffractometer (X'PertPro, with Ni-filtered CuK_α radiation at 1.5406 Å, V: 40 kV, i: 30 mA; Netherland); FT-IR spectrophotometer (PerkinElmer Spectrum 65); UV–vis diffuse reflectance spectrophotometer (JASCOV 670, using $BaSO_4$ as reference, Japan); MIRA3LMU scanning electron microscope (TESCAN Co., Czech Republic). A BET instrument (Belsorp max, BEL Japan Ins.); a double beam spectrophotometer (Carry 100 Scan); atomic absorption spectrometer (AAnalyst 300, PerkinElmer Co., USA); A potentiostat/galvanostat (Autolab, PGSTAT-101, EcoChemie, Netherlands) for carrying out the electrochemical experiments (containing three-electrode cell as: Ag/AgCl reference electrode, platinum wire counter electrode and the zeolite-modified carbon-paste electrode as working electrode) and A pH meter (Jenway model 3505). Electrochemical impedance spectra (EIS) were recorded by a Ivium (IEC 61326, Netherland). Preparation of raw and modified carbon paste electrodes has illustrated in our previous work [24]. HPLC analysis of samples was performed by an Agilent Techonologies 1200 Series instrument with Quaternary pump, column XDB-C18. A GC-Mass Agilent Techonologies GC system 6890 Series and Mass system 5973 was used for analysis of MZ solutions before and after photodegradation process.

2.3. Photodegradation experiments

In photodegradation experiments, 10 mL MZ aqueous solution (2 mg L^{-1}) containing 0.25 g L^{-1} of the catalyst (in a cylindrical Pyrex-glass cell; 5 cm inside diameter and 10 cm height) was irradiated by moderate pressure Hg-lamp (35 W, Philips, type G-line with maximum emission at 435.8 nm, positioned 10 cm above the reactor) under continuous stirring on a magnetic stirrer. At definite time intervals, the suspension was sampled out and centrifuged. Here C/C_o ratio was considered for degradation extent of the pollutant.

3. Results and discussion

3.1. Characterization studies

3.1.1. Loaded percentage of the semiconductors

Based on the atomic absorption spectroscopic results of Zn and Sn determination, amount of loaded semiconductors onto NC particles were calculated and the results are summarized in Table 1.

3.1.2. XRD patterns

The XRD patterns of $ZnO_{3.3}$-$SnO_{2(2.0)}$/NC catalyst is shown in Fig. 1A. The characteristic lines of clinoptilolite crystallites are assigned which have good agreement with JCPDS No. 39-1383. The XRD pattern reflections of ZnO phase were observed at 31.8° (110), 34.4° (002), 36.2° (101), 47.5° (102), 56.6° (110), 62.8° (103), 67.9° (112) and 75.2° (004) which agree with JCPDS No. 89-1397. Typical XRD reflections of SnO_2 were also assigned which agree with JCPDS PDF No. 88-0287. As shown, some reflections belong to ZnO

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