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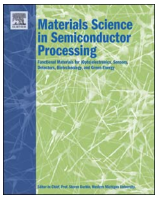

Synthesis and photocatalytic activity of ZnO-CuPc for methylene blue and potassium cyanide degradation

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ABSTRACT

In this study, samples of ZnO modified with copper (II) phthalocyanine (CuPc) (0.1% and 0.5% wt) were synthesized via the sol-gel method. The catalysts were characterized by DTA-TGA analysis, infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Ultraviolet diffuse reflectance spectroscopy (DRS-UV) was used to estimate the band gap energy (Eg) of the prepared materials, and the textural properties of the solids were determined from N_2 adsorption isotherms. The photocatalytic activity of the ZnO-CuPc catalysts was evaluated on the degradation of the methylene blue (MB) and potassium cyanide (KCN) under UV and visible light. The dye concentration was determined spectrophotometrically at 665 nm during the treatment. The CN^- content during the photocatalytic reaction was analyzed potentiometrically using a cyanide ion-selective electrode. Both pollutants were completely degraded under both light sources; however, the highest degradation rate was observed for MB decomposition achieving complete degradation in 150 min.

1. Introduction

Recalcitrant organic pollutants from industrial effluents often pose a major environmental problem. Currently, advanced oxidation processes (AOPs) are widely used for treating wastewater containing non-biodegradable compounds. The base of these methods is the formation of a highly reactive chemical species, hydroxyl radicals ($^{\bullet}OH$), which degrade non-biodegradable into biodegradable compounds, CO_2 and inorganic ions [1]. Among AOPs, heterogeneous photocatalysis has witnessed rapid progress throughout the last few decades. This process uses a semiconductor photocatalyst, of which the electrons in the valence band can be promoted to the conduction band when is excited by adequate photoenergy, producing photogenerated electron-hole (e^--h^+) pairs. The generated e^--h^+ pairs enable a series of reductive and oxidative reactions [2,3]. During this process, hydroxyl radicals are formed from water oxidation by holes (h^+) [1,4].

Zinc oxide (ZnO) is an important *n*-type semiconductor having a hexagonal wurtzite structure, and the alternating arrangement of zinc and oxygen atoms in the crystalline planes has received much attention in comparison with the other semiconductors. This oxide with a wide band gap (3.2–3.37 eV) possesses optical, electrical and piezoelectric properties, and due to its high quantum efficiency, non-toxic effects and suitable cost, it is well known as an alternative photocatalytic material in various scientific and industrial fields [5–8]. However, two important drawbacks have hampered the photocatalytic performance of ZnO. One is a high recombination rate of e^--h^+ pairs limiting its efficiency of photocatalytic reactions and the other is a large band gap, which cause to releasing the absorbed energy as heat and limits its photo-response to ultraviolet (UV) region [3,9].

Some strategies to improve the light absorption features of catalysts include photosensitization via surface adsorbed organic dyes on semiconductors as a convenient way to extend its photoresponse in the spectrum of visible light [6,9]. However, the dye must possess good thermal and photochemical stability, a high absorption coefficient in the spectral region of the excitation light, and high singlet-oxygen quantum yield [10,11]. Particular examples of visible-light absorbing dyes include phthalocyanines, rose bengal, chlorophyllin, porphyrins and ruthenium complexes [12–16]. Usually, charge injection from the excited state (generally a singlet state) into the conduction band (CB) of the semiconductor takes place during irradiation when a dye is adsorbed or chemically linked to a semiconductor [12]. The injected electron can reduce surface chemisorbed O_2 to yield strong oxidizing radicals, such as $O_2^{\bullet -}$, $HO_2^{\bullet}$, $^{\bullet}OH$, which can degrade the organic pollutants [9].

Among these dyes, metallophthalocyanines (MPc), as typical organic semiconductors, have been extensively investigated for this purpose [9]. These compounds are a *p*-type organic semiconductors that possess strong absorption in the wavelength region of 400–450 nm

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(Soret band) and in 500–700 nm region (Q-bands), excellent resistance to chemical degradation and good photosensitivity [15]. Although many studies have evaluated MPc as a sensitizer to enhance the photocatalytic activity of the matrix semiconductor [6,9,15,17–21], few works have been published to date related to dye-sensitized ZnO showing promising results [6,22]. In this work, ZnO catalysts sensitized with copper (II) phthalocyanine (CuPc) at CuPc percentages of 0.1% (ZnCu1) and 0.5% wt (ZnCu5) were prepared by sol-gel method, and its photocatalytic activity was tested on the degradation of methylene blue (MB) and potassium cyanide (KCN) compounds as models of recalcitrant pollutants under UV and visible light radiation.

2. Experimental

2.1. Sol-gel ZnO-CuPc (0.1% and 0.5% wt) synthesis

Zinc acetate dihydrate (Sigma Aldrich) was dissolved in 50 mL of water. A concentrated NH_4OH solution was added under continuous stirring, and the pH was adjusted to 7. A dissolution of copper (II) phthalocyanine (Alfa Aesar) and 30 mL of acetone was added to the zinc acetate solution. The gel was aged for 3 days at room temperature and was later dried in a water bath at 70 ºC (fresh sample). The quantities of the precursors added according to the percentage of incorporation of the CuPc were 4.995 g of zinc acetate dihydrate and 5×10^{-3} g of CuPc for obtaining ZnO-CuPc 0.1% (CuZn1); and 4.975 and 2.5×10^{-2} g of zinc acetate dihydrate and CuPc, respectively for the synthesis of ZnO-CuPc 0.5% (CuZn5).

The gel was washed with distilled water and acetone, and the solvents were measured spectrophotometrically to confirm that CuPC was anchored to ZnO. The CuPc signal did not appear in the UV–Vis spectrum, which indicates that the phthalocyanine was not released from the prepared material. Finally, the sample was calcined at 350ºC for 6 h using an electrical furnace (Barnstead Thermolyne 47900). The calcination temperature was chosen based on thermal analysis results (TGA-DTA).

2.2. Characterization

The DTA and TGA curves of the fresh samples were recorded in a TA-Instruments SDT-2960 thermal analyzer under an argon atmosphere using a heating rate of 10 °C $\min^{-1}$, with alumina as the reference substance.

The samples were characterized by X-ray diffraction (XRD) in a Siemens D-5000 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). The reflection intensities were measured by step scanning in the 2θ range between 10 and 85º, with a step size of 0.05º. From the XRD pattern, the Scherrer formula (Eq. (1)) was used to estimate the average crystallite size of the synthesized particles:

$$D = \frac{k\ \lambda}{\beta\ \cos\ \theta} \tag{1}$$

where D is the crystallite size, λ is the X-ray wavelength, β is the half-height width of the wurtzite diffraction peak (101) and *k* is the Scherrer constant, usually taken as 0.89 [23,24].

FTIR spectra of samples in KBr pellets were recorded with a Paragon 1000 PC Perkin Elmer FTIR spectrometer in the 4000–450 cm^{-1} wavenumber range.

Nitrogen adsorption isotherms of the samples were measured using an Autosorb-1 instrument (Quantachrome Corporation), and the surface area was calculated by the BET equation.

UV–Vis diffuse reflectance spectra (DRS) were obtained on a Nicolet, Evolution 300 PC spectrophotometer coupled to an integration sphere Praying Mantis, the samples were measured in the 200–800 nm wavelength range. The band gap (Eg) value was calculated from modified Kubelka Munk function with the plots of the value $(F(R)^{*}h\nu)^{1/2}$ versus the energy of excitation light, associated with a direct electronic transition [25].

The chemical composition of the material, the oxidation states and the bonds between elements contained in ZnO surface were determined by X-ray photoelectron spectroscopy (XPS). The samples were analyzed on a Thermo Scientific XPS K-alpha instrument equipped with Al Kα monochromatic radiation ($h\nu^{1/4}$, 486.6 eV). A low vacuum Nano SEM microscope with a maximum acceleration voltage of 10.0 kV was used to analyze the morphology of the materials.

2.3. Photocatalytic degradation of pollutants

Photocatalytic experiments were carried out at room temperature; 150 mg of catalyst was added to a glass reactor containing 250 mL of an aqueous solution of the dye (15 mg L^{-1}) adjusted to a pH 7 with 0.1 M NaOH.

A Spectroline XX-15N UV lamp (365 nm, 2000 μW cm^{-2} radiation intensity) was used as the UV light source. The light intensity was measured using a Mannix UV–340 UV Light Meter over the range 290–390 nm (UVA-UVB). The visible light source was provided using a metal halide Philips lamp (25 W) that emits polychromatic radiation from 400 to 700 nm, with the maximum in the wavelength range of 540–620 nm.

The suspension was stirred in the dark for 30 min to establish the adsorption/desorption equilibrium before irradiation. The reaction rate was analyzed by taking aliquots every 20 min over 6 h of reaction time. The UV–Vis spectrometry was used to determine the MB concentration during the photocatalytic degradation at the maximum absorption wavelength of 665 nm.

Regarding to KCN degradation, the experiments were carried out using the same UV and Vis light sources as described for MB tests. The reactor contained 250 mL of KCN solution (30 mg L^{-1}) at a pH 11 using 0.6 g L^{-1} catalyst loading. This pH value was selected to avoid the formation of gaseous HCN (pKa = 9.2) [26]. The suspension was stirred in the dark for 30 min to establish the adsorption/desorption equilibrium before irradiation, and the reaction rate was followed by taking aliquots every 20 min throughout 6 h of reaction time.

The CN^{-} content during the reaction was analyzed by a potentiometric method with an Orion ISE meter (Model 720A) using a cyanide ion selective electrode. A certificated KCN standard (Ricca Chemical Co.) was used to prepare the calibration curve.

3. Results and discussion

3.1. Characterization

The thermal analysis curves of the fresh samples are shown in Fig. 1. The DTA and TGA analyses were conducted to determine the thermal events (exothermic or endothermic) associated to chemical and physical changes of the analyzed materials during their thermal decomposition, such as evaporation of the solvent, decomposition of residual organic compounds or formation of crystalline phases. In TGA curve, a first weight loss (10%) from room temperature to 100ºC was observed, which is associated with loss of acetone and water physically adsorbed onto the solid. The endothermic peaks in the DTA curves of both thermograms at 90 °C were associated with this phenomenon. The posterior weight loss zone (55–60%) from 100 to 300 ºC was attributed to desorption of residual acetate groups, which is associated with the endothermic peak detected in the DTA curve at approximately 240 ºC. On the other hand, the exothermic peak, which indicated the ZnO crystallization process, was broader and observed at a lower temperature for ZnCu5 (290 ºC) than that seen for ZnCu1 (340 ºC). After this temperature, the weight loss remained constant.

Fig. 2 shows the FTIR spectra of the $Zn(CH_3CO_2)_2(H_2O)_2$, CuPc, ZnCu1 and ZnCu5 fresh samples. Spectra of sensitized ZnO (Figs. 2c and 2d) exhibited a wide absorption band at 3100 cm^{-1} assigned to the stretching vibrations of hydroxyl groups from water molecules occluded