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Short communication

Disperse orange 30 dye degradation by assisted plasmonic photocatalysis using Ag-CdZnSO/zeolitic matrix nanocomposites

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ABSTRACT

A highly efficient photocatalyst based on Ag-metal and CdZnSO-semiconductor nanoparticles, grown on a zeolitic matrix, was successfully synthesized by a solvent- and template-free procedure, and tested on the photodegradation of recalcitrant disperse orange 30 dye.

The Ag-CdZnSO/ZM nanocomposite showed great synergistic interaction between the surface plasmon resonance of the Ag nanoparticles, the photoactive properties of CdZnSO nanoparticles, and the catalytic properties of the zeolitic, which leads to the degradation of the dye (99.5% in 90 min, from optical absorbance). The reaction mechanisms are presented and discussed. Also, the small amount of acetone required as sensitizer was eliminated during the process.

1. Introduction

Textile and other dyestuff industries generate a large variety of toxic residual organic pigments. The most complex environmental problem associated with the textile industry is the presence of pollutants in their effluents. For example, azo dyes are widely used and of great hazard to human health [1–3]. In total, colorants represent about 60–70% of the waste generated by this industry [2,3].

The elimination of dyes from textile wastewater effluents is of vital importance for all living organisms, including humans. Specifically, disperse dyes are toxic due to their bio-accumulation and insolubility in water, making impossible the action of traditional photocatalysts. Disperse dye degradation routes include high concentrations of organic solvents to photosensitize the dyes, but these solvents must eventually be removed as well [4]. In recent years, a new family of plasmonic photocatalysts have been developed, taking advantage of the localized surface plasmon resonance (SPR) feature for photodegradation [5–9]. Metal–semiconductor/zeolite composites, are among the most promising photocatalysts [10–12] for the mineralization of disperse dyes because of their exceptional properties, such as the ability to harvest a wide range of wavelengths and their chemical stability [12,13].

In this study, a nanostructured metal–semiconductor/zeolitic matrix composite, based on nanoparticles of the biphasic Ag-CdZnSO compound, were grown on a mordenite-type zeolitic matrix. The synthesis process consisted of a solvent-free and organic template-free variant of the sol–gel procedure. The synthesized Ag-CdZnSO/ZM photocatalyst was characterized by several techniques. For evaluation of the photocatalytic activity, the recalcitrant and water-insoluble disperse dye orange 30 (DO30) was selected. Operational parameters of the DO30 degradation under UV illumination and experimental results are presented and discussed.

2. Experimental

2.1. Synthesis and characterization

Photocatalysts used in this work were synthesized following a previously reported route [13]. The powders were obtained by an aqueous solvent-free and organic template-free process using geothermal solid wastes. Nanostructured composites were studied by X-ray diffraction (XRD) using a Philips X'Pert diffractometer (CuKα radiation), scanning electron microscopy (SEM) using a JEOL JSM-5300 microscope with energy dispersive X-ray spectroscopy (SEM-EDX) attachment, and high resolution transmission electron microscopy (HRTEM) with EDX attachment (TEM-EDX) using a JEOL JEM-2010. Optical properties were studied by UV–Vis spectroscopy using an AvaSpec-ULS2048-UA-50 spectrophotometer.

2.2. Photocatalysis experiments

Photocatalytic degradation of DO30 (Sigma-Aldrich) was performed in a reactor equipped with five UV lamps ($\lambda = 254$ nm, 8 W). An aqueous dispersion of DO30 (50 ppm) was used as standard, commercial

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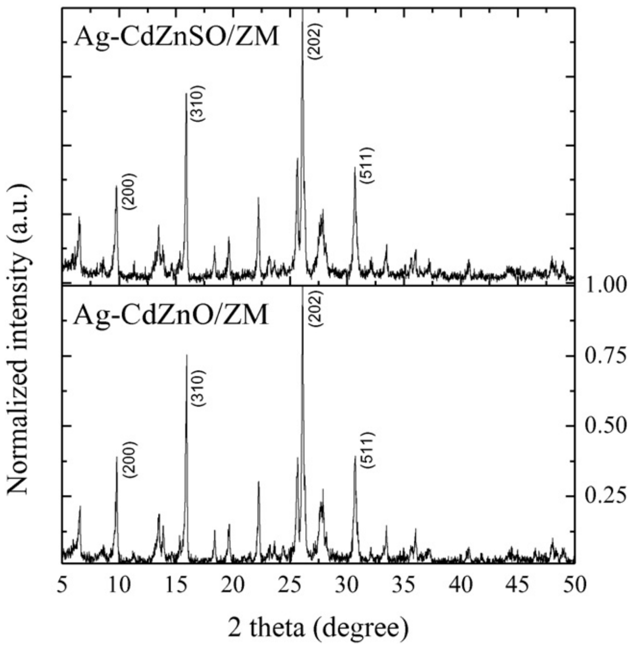

Fig. 1. XRD patterns of synthesized non-sulfided Ag-CdZnO/ZM and sulfided Ag-CdZnSO/ZM nanocomposites.

grade acetone (Sigma-Aldrich) as sensitizer, and Ag-CdZnSO/ZM nanocomposite as the photocatalyst. For photodegradation evaluation, samples of 1 mL were taken at regular 10 min intervals, and analyzed on a UV–Vis Multiskan GO spectrophotometer. Dye concentration was determined from absorbance at $\lambda = 440$ nm.

3. Results and discussion

X-ray diffraction patterns of the synthesized non-sulfided and subsequently sulfided Ag-CdZnSO/ZM nanostructured composites are illustrated in Fig. 1. The phase matches with the ICSD 68445 file reported for mordenite-type zeolite. The crystalline structure of the matrix was not affected by the presence of Ag, Zn and Cd, and the sulfided species. SEM images (Fig. 2(A)) provide information about nanocomposite morphology. Powders of both samples show crystallites with needle shape morphology (of 25 μm average length), which are packed in grains of elliptic shape. These characteristic crystallites grew along the *c-axis* crystallographic direction [13]. TEM and TEM-EDX results (Fig. 2(B) and (D), respectively) show that the nanoparticles grow on the zeolitic matrix surface with homogeneously dispersed size distributions (Fig. 2(D)). Fig. 2(D) illustrates the TEM-EDX analysis of the nanoparticles, proving the presence of metal and semiconductor nanoparticles on the matrix surface. Results confirm that the Ag-CdZnSO nanoparticles are strongly bound to the zeolitic matrix. Values of the global chemical composition obtained by SEM-EDX for non-sulfided Ag-CdZnO/ZM and sulfided Ag-CdZnSO/ZM nanocomposites are reported in Table 1.

Nanoparticle type, size and distribution are a consequence of the synthesis procedure and can be responsible of various optical effects. Therefore, the UV–Vis absorbance spectrum (Fig. 2(C)) of the nanocomposite powders was obtained before and after of the UV irradiation process. Both Ag-CdZnSO/ZM samples showed high photoactivity. However, there are noticeable differences between the spectra in the high wavelength region, where the irradiated sample shows higher absorption than the non-irradiated sample. Such behavior can be due to the plasmonic effect associated to silver nanoparticles [12], demonstrating their metallic character and the capacity of Ag ions to modify the oxidation state.

The semiconductor nature of the nanocomposites was evaluated with the average optical bandgap, E_{gap}, value of 2.14 eV, calculated from UV–Vis spectra. This value is lower than those reported for ZnS (3.56 eV) and CdS (2.37 eV). The decrease can be associated to an enhancement of activated states at the forbidden band promoted at the metal–semiconductor interphase improving the photoactivity [14].

To determine the photocatalytic performance we evaluated hydrogen potential (pH), sensitizer (acetone) concentration, photocatalyst (Ag-CdZnSO/ZM) concentration, and compared with standard photocatalysts. The pH value was set at 7 due to the negligible photodegradation observed along experimental pH values of 5, 6, 7, 8, and 9. Fig. 3(a) shows that acetone concentration promotes photolysis reactions due to the sensitization of DO30 that has been described elsewhere [16]. However,

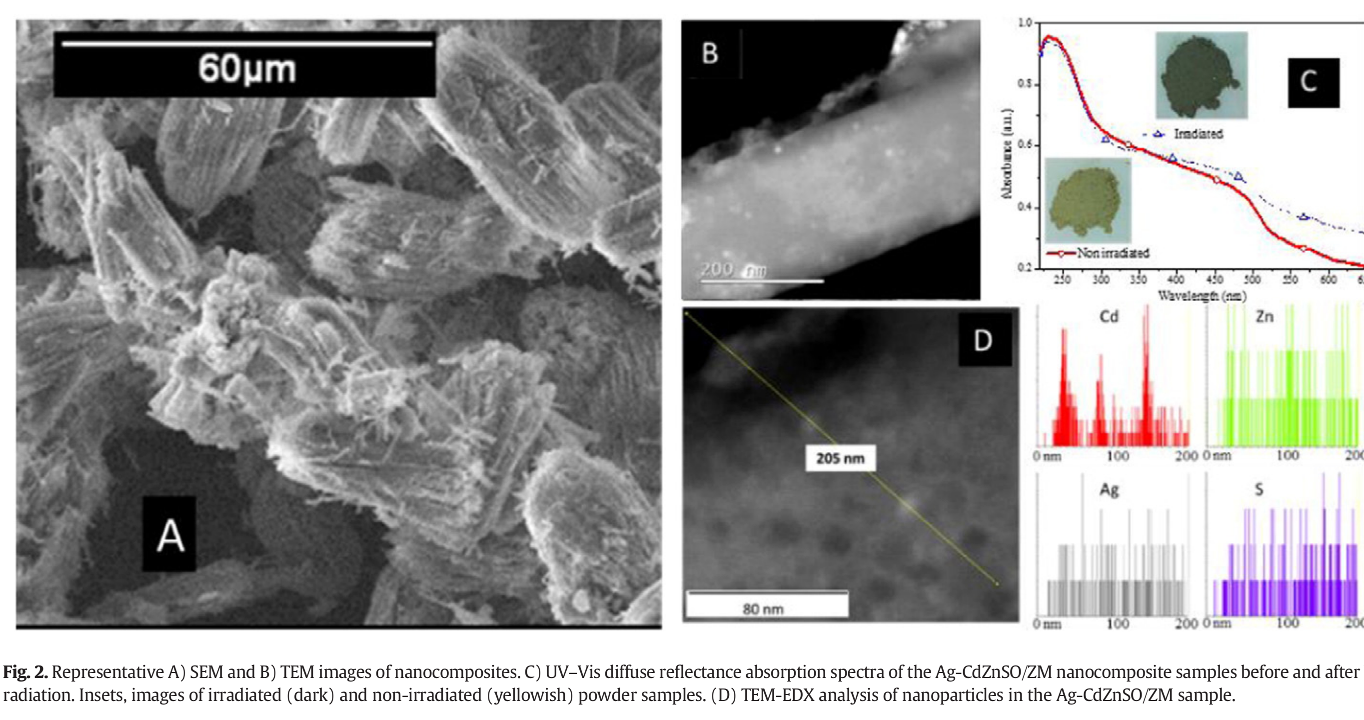

Fig. 2. Representative A) SEM and B) TEM images of nanocomposites. C) UV–Vis diffuse reflectance absorption spectra of the Ag-CdZnSO/ZM nanocomposite samples before and after UV radiation. Insets, images of irradiated (dark) and non-irradiated (yellowish) powder samples. (D) TEM-EDX analysis of nanoparticles in the Ag-CdZnSO/ZM sample.