Effect of Additives on Characterization and Photocatalytic Activity of TiO$_2$/ZnO Nanocomposite Prepared via Sol-Gel Process

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TiO$_2$/ZnO nanocomposites were prepared by the sol-gel method with and without additives such as carboxy methyl cellulose (CMC), poly(ethylene glycol) (PEG), polyvinylpyrrolidone (PVP), and hydroxylpropylcellulose (HPC). The characteristics of the prepared TiO$_2$/ZnO nanocomposites were identified by IR spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) methods. The additives have a significant effect on the particle size distribution and photocatalytic activity of TiO$_2$/ZnO nanocomposites. The photocatalytic activity of the synthesized nanocomposites was investigated for decolorization of methyl orange (MO) in water under UV-irradiation in a batch reactor and the results showed that the photocatalytic activity of the nanocomposites have been increased by CMC, PEG, PVP, and HPC, respectively. SEM has shown that the particle size distribution of TiO$_2$/ZnO nanocomposite in the presence of HPC was better than the other samples.

1. Introduction

Azo dyes constitute the largest group of coloring materials in the textile industry [1–3]. Release of these substances in nature is the largest source of pollution for natural ecosystems. In recent decades, semiconductor photocatalyst TiO$_2$ has been investigated as one of the most promising candidate for a photocatalyst and it has been attracted due to its potential application in removing of all types of organic pollutants in water [4–6]. In order to improve the photocatalytic activity and the response into visible part of the spectrum, TiO$_2$ doping with metal ions or metal oxides has been applied [1, 2]. Several methods on the preparation of TiO$_2$/ZnO were reported, such as solid-state method, impregnation method, and chemical coprecipitation method [7–9]. Another method is the sol-gel method that has significant advantages such as, high purity, good uniformity of the powder microstructure, low-temperature synthesis, and easily controlled reaction condition and therefore it has been used for preparing of TiO$_2$/ZnO nanocomposite [4, 7, 10–12]. In this work, TiO$_2$/ZnO nanocomposites were prepared by the sol-gel method in presence and absence of CMC, PEG, PVP, and HPC as additives. The synthesized nanocomposites were characterized by means of XRD, SEM, EDS, and IR spectroscopy. Since the particle size is an important parameter in photocatalytic activity, the effects of mentioned additives have been surveyed on the particle size distribution. The photocatalytic activity of TiO$_2$/ZnO nanocomposites were assessed for decolorization of methyl orange (MO) in water under UV irradiation in a batch reactor.

2. Materials and Methods

2.1. Materials. The chemicals used in this study were Tetra isopropyl orthotitanate (TTIP) (for synthesis), zinc nitrate tetrahydrate, diethanolamine (DEA) (for synthesis), Glacial acetic acid, methyl orange (MO), absolute ethanol, deionized water from Merck Chemical Company, and carboxymethyl cellulose (CMC), poly(ethylene glycol) (PEG), poly vinyl pyrrolidone (PVP), and hydroxylpropyl cellulose (HPC) from Sigma-Aldrich Company.
2.2. Preparation of Nanocomposites. In this study, TiO$_2$/ZnO nanocomposite powders were prepared by the sol-gel process. The TiO$_2$ sol was made at room temperature, and TTIP was used as a precursor as follows. In the first stage, additive (CMC or PEG or PVP or HPC = 30 g/L) was dissolved in ethanol under fast stirring for 5 minutes. Then TTIP was added into ethanol with a 1:9 molar ratio of TTIP to ethanol and was stirred for 15 minutes, to obtain a precursor solution. After that, a mixture of absolute ethanol, acetic acid, and deionized water with the molar ratio of 10:6:1 was added slowly into the precursor by a fast stirring and it was continuously stirred for 15 minutes to achieve a yellow transparent sol. Here, acetic acid was used as an inhibitor to reduce quick hydrolysis of TTIP, and so the pH value was adjusted on 5.

In the second stage, ZnO sol was prepared as follows. Firstly, zinc nitrate tetrahydrate was dissolved in absolute ethanol with the molar ratio of 0.1:110. After that, stirred for 5 minutes, then a mixture of absolute ethanol, diethanolamine, and deionized water with the molar ratio of 10:2:1 was added slowly into the precursor by a fast stirring and it was continuously stirred for 15 minutes to achieve transparent sol.

The prepared ZnO sol was directly added into the TiO$_2$ acidic sol with the molar ratio of 1:50 to get TiO$_2$/ZnO sol. This sol aged for 24 hours. After that, the prepared sol was dried in the air, then heat treated at 350°C for 10 minutes and at 500°C for 5 hours. During this process, the temperature was raised at speed of 5°C/Sec. The samples were naturally cooled after the heat treatment (Table 1) [2, 5, 11, 13, 14].

2.3. Characterization of Nanocomposites. The characteristics of TiO$_2$/ZnO nanocomposites were investigated as follows.

2.4. Photocatalytic Activity Measurement. Photocatalytic activity of the nanocomposites was investigated for the decolorization of MO. All of the experiments were accomplished in a rectangular cube glass reactor with 1 liter capacity. A 15 W UV lamp (Osram) was applied as a light source and it was placed in a quartz tube, which was installed inside the reactor (Figure 1). Initially, 1 g of photocatalyst was added into a 1 liter solution of MO with initial concentration of 5 ppm. Before irradiation, the suspension was stirred for 24 hours in darkness, due to elimination of absorption effect of the solution in the catalyst. After that, the lamp was switched on for starting the reaction. During irradiation, the suspensions were sampled at regular intervals and immediately centrifuged to remove catalyst particles [3, 4, 15–17].

3. Results and Discussion

3.1. FT-IR Spectra. FT-IR spectra of samples have been presented in Figure 2 in the wave number range from 400 to 4000 cm$^{-1}$. Four significant peaks were observed around 650, 800, 1450, and 3450 cm$^{-1}$. The peak around 650 and 800 cm$^{-1}$ can be ascribed to symmetric stretching vibration of the Ti-O-Ti and vibration mode of Zn-O-Ti groups [8–10]. The peak around 1450 cm$^{-1}$ was ascribed to the vibration mode of Ti-O and Ti-O-C that the Ti-O-C may result from the interaction between the Ti-O network and
the organic polymers (CMC, PEG, PVP, or HPC). The wide peak around 3450 cm\(^{-1}\) which observed in sample b has been assigned to the OH stretching vibration of surface hydroxyl group. During the hydrolysis of TTIP, a large amount of ethanol lead to the appearance of hydroxyl bond [2, 4, 18, 19].

3.2. SEM. The SEM images and EDS analysis on the prepared nanocomposites were carried out and the results were shown in Figure 3.

Sample a without any additives, contains scattered particles which have different sizes. Sample b with CMC, is almost similar to sample a. In sample c, in presence of PEG, particle size becomes small and its distribution is more monotonous than previous samples [5, 9, 11, 20]. In sample d, with PVP the number and density of particles are increased but the aggregation and the sticking together of the particles are observed. The last sample, e, which contains HPC has the most uniform particle distribution and it shows no agglomeration in comparison with other samples [7, 8, 21].

Figure 3. also demonstrates EDS analysis of TiO\(_2\)/ZnO nanocomposites in absence and presence of additives. In all of samples, the nanoparticles were composed of Ti and Zn. This proves that Zn was incorporated into the TiO\(_2\) nanoparticles to form nanocomposite [9, 14].

3.3. XRD. XRD patterns of all samples have been shown in Figure 4. The peaks were observed at \(2\theta = (25), (27), (31, 48, 57, 63)\) and \((35, 39, 43)\) which were related to anatase, rutile, zincite, and zinc phases, respectively. As can be seen, anatase
phase as the dominant phase has observed in all samples. In all samples, TiO$_2$ and ZnO were not doped, however, separate crystallization of them was observed [5, 18, 20].

The calculated anatase phase percentages of the samples with different additives are between 80–90%. Sample e with 85% anatase phase and 15% rutile phase has showed a good catalytic activity [21–23].

3.4. Photocatalytic Activity. Figure 5 displays photocatalytic activity of the nanocomposites for decolorization of MO as a function of time at $\lambda = 465$ nm. The photocatalytic activity of the synthesized nanocomposites was investigated for decolorization of MO (5 mgL$^{-1}$) in water under UV irradiation in a batch reactor. According to Figure 5, the photocatalytic activity is enhanced by using additives [6–8]. Sample e with HPC has the best photocatalytic activity in comparison of other samples and about 3.5 h after starting the reaction, the absorbance of MO solution has been reached to 0. It indicates that organic polymers have been used as a dispersed factor to avoid accumulation of nanocomposite particles [23–25].

4. Conclusions

Five samples of TiO$_2$/ZnO nanocomposites have been prepared with and without CMC, PEG, PVP, and HPC by the sol-gel method. The XRD results exhibit that in all samples anatase phase has observed as the dominant phase and sample e with 85% anatase phase and 15% rutile phase has showed the best photocatalytic activity. The SEM images indicated that in presence of HPC, density of particles and their size distribution have been improved. It is important for photocatalytic activity that the particle size of the photocatalyst be homogeneous. Finally, all studies show that photocatalytic activity of the nanocomposites has
been enhanced in presence of additives and HPC was more
effective than others.

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