TiO$_2$-ITO and TiO$_2$-ZnO nanocomposites: application on water treatment

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Abstract. One of the most promising ideas to enhance the photocatalytic efficiency of the TiO$_2$ is to couple this photocatalyst with other semiconductors. In this work, we report on the development of photo-catalytic properties of two types of composites based on TiO$_2$ – ITO (Indium Tin Oxide) and TiO$_2$ – ZnO deposited on conventional ceramic substrates. The samples were characterized by X-ray diffraction (XRD) and transmission Electron Microscopy (TEM). The photo-catalytic test was carried out under UV light in order to reduce/oxidize a typical textile dye (Cibacron Yellow). The experiment was carried out in a bench scale reactor using a solution having a known initial dye concentration. After optimization, we found that both nanocomposites exhibit better photocatalytic activity compared to the standard photocatalyst P25 TiO$_2$.

1 Introduction

In recent years, titanium dioxide has widely used as an environmentally photocatalyst, because of its various qualities, such as optical properties, low cost, high photocatalytic activity, chemical stability and non toxicity. However, it has been known that pure TiO$_2$ exhibits low photocatalytic property due to rapid recombination of photo-activated electrons and holes. [1]. Several studies show that the enhancement of the photocatalytic efficiency can be affected by means of composite TiO$_2$ materials. This promising approach consist of coupling other semiconductors with the titanium dioxide which can lead to more efficient charge separation, an increased lifetime of the charge carriers, and an enhanced interfacial charge transfer to adsorbed substrates. [2]. Recently, many studies have been devoted to the improvement of the photoactivity by adding the other semiconductor such as WO$_3$, ZnO, SnO$_2$, CdS, CuO, Fe$_2$O$_3$ etc [3, 4]. The aim of this study is to optimize the preparation for TiO$_2$ – ITO and TiO$_2$ – ZnO photocatalysts and to explore their photocatalytic activities. Their photocatalytic performance was evaluated using a well known textile dye. It will be shown that the photocatalytic properties of TiO$_2$ can be improved in the two cases. It is worth noting that both semiconductors ITO and ZnO were reported to act as photocatalysts[5-8].

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2 Experimental procedures

2.1 Preparation of nanocomposites based films

The TiO_2-based films were prepared from the P25 Degussa powder (80% anatase; 20% rutile) using the screen printing method. The P25 powder is composed of TiO_2 nanoparticles having a mean particle size of about 30 nm. The first nanocomposite ITO–TiO_2 were obtained by mixing the P25 TiO_2 powder with an organometallic paste of a dissolved combination of indium and tin ITO [9] and diluted in an organic solution. In order to prepare ZnO–TiO_2 nanocomposite, we have synthesized a colloidal solution based on Zinc Acetate as a precursor to which we added methanol. Different amounts of the obtained colloidal solution were mixed with the P25 powder to get the desired nanocomposite . A serie of TiO_2 – ITO and TiO_2 – ZnO nanocomposites with different ratios of ITO and ZnO to TiO_2 were prepared. For both cases, the obtained mixture was deposited on cheap conventional clay ceramics (10 - 15 cm^2); the latter were cleaned with acetone and dried in ambient air. The screen printed coatings were fired in air at 550°C during 15 min. These conditions enable to preserve the TiO_2 mean particle size (30 nm) and the anatase structure [10]. Films composed of pure P25 TiO_2 nanoparticles, pure ZnO and pure ITO were prepared separately in the same conditions for comparison.

2.2 Characterization of the prepared films

The same mixtures (used as a screen printed solutions) were sintered at 550 °C for 15 min in order to obtain TiO_2–ITO and TiO_2-ZnO powders. The samples were characterized by X-ray diffraction (XRD) using a Panalytical instrument model X'Pert Pro MPD and transmission electron microscopy (TEM) was used for morphological investigations.

2.3 Photo-catalytic degradation

2.3.1 Pollutant

The selected pollutant model is the Cibacron Brillant Yellow 3GP, an azo dye used in textile industry (Figure 1) and supplied by Aldrich. Based on the given molecular weight of 873 g mol^{-1},40 mM (35 mg L^{-1}) of dye solution was prepared for photocatalytic tests. The final pH is neutral. No significant color removal was observed in the test experiments in the presence of UV illumination (without catalysts) and in the presence of thin film catalysts (in the dark). This is to say that the dye cannot undergo photo-degradation without the presence of light and semiconductor nanoparticles.
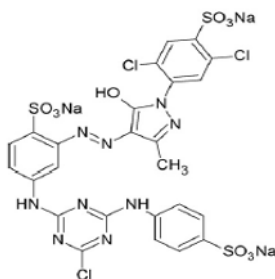
Fig. 1. Chemical structure of the Yellow Brillant Cibacron 3G-P azo dye molecule.

2.3.2 Photo-catalysis set up

Small thin film fixed bed reactor (TFFBR) [11] was used for photo-catalytic experiments. The reactor is south oriented to the sun with an inclination angle of 20°. The total surface covered with the ceramic-supported TiO_2—ITO film is equal to 600 cm^2. A flow rate of 18 L/h is chosen to feed the reactor with the dye solution from a reservoir tank ($V_0 = 2$ L). The photo-catalytic degradation of the dye (discoloration) was monitored by withdrawing 10 ml of samples at selected times, from the outlet of the reactor, and by measuring the absorbance in the UV–Vis range.

3 Results and discussion

3.1 X-ray diffraction

Figure 2 shows X-ray diffraction (XRD) patterns of the TiO_2–ZnO powder. The intense line at $2\theta \approx 25°$ is assigned to the anatase structure, while that peaking at $2\theta \approx 27°$ corresponds to the rutile phase. The XRD analysis shows clearly that ZnO structure can be obtained. For photocatalysis the crystalline structure and particle size of the catalyst have been proven to have a strong influence on photocatalytic activity. It was observed that the coupled composites consist of both well crystallized TiO_2 (anatase and rutile) and wurtzite ZnO. The peaks related to ZnO become more intense as the proportion of ZnO increases in the nanocomposite.
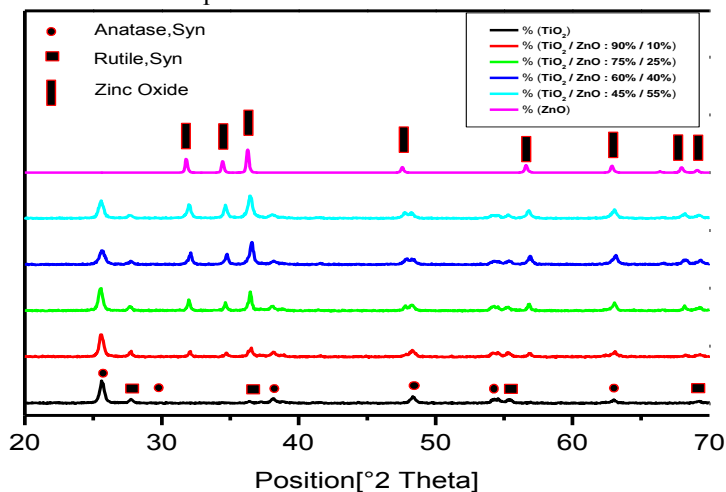
Fig. 2. XRD patterns of the synthesized TiO_2–ZnO powders.

Figure 3 shows X-ray diffraction (XRD) patterns of the TiO_2–ITO powder. The intense line at $2\theta \approx 25°$ is assigned to the anatase structure, while that peaking at $2\theta \approx 27°$ corresponds to the rutile phase.

The peak at $2\theta \approx 30°$ corresponds to the In_2O_3 phase. Like the TiO_2–ZnO nanocomposite, the peaks related to ITO become more intense as the proportion of ITO increased in the TiO_2–ITO nanocomposite.

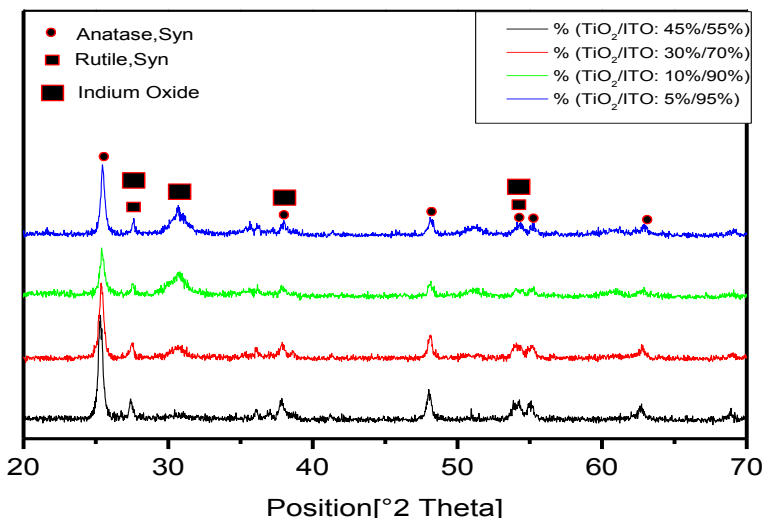**Fig. 3.** XRD patterns of the synthesized TiO_2–ITO powders.

3.2 Transmission electron microscopy (TEM)

For TEM observations, we choose the samples that give the best photocatalytic activities, namely the TiO_2–ITO (45%:55%) and TiO_2–ZnO (45%:55%). Figure 4 shows TEM views of pure P25 TiO_2 powder (Figure 4a) , pure ITO powder (Figure 4b) , pure ZnO powder (Figure 4c) , TiO_2–ZnO (45%:55%) nanocomposite powder (Fig. 4d) and TiO_2–ITO (45%:55%) nanocomposite powder (Fig.4e). The mean particle size of pure TiO_2 (Figure 4a) seems to be in agreement with the well known particle size of the P25 powder (i.e., 30 nm).

However, the mean particle size of the TiO_2–ITO powder is larger than that of pure TiO_2. In previous work, we have demonstrated that the TiO_2–ITO powder is composed of ITO-coated TiO_2 particles. The ITO nanocrystallites may be considered as a binder for the TiO_2 particles [12].

Concerning the TiO_2–ZnO nanocomposite, it is clear that the powder is composed by microspheres irregularly shaped as aggregates. The average size of the microspheres ranged from 10 nm to 50 nm.

(a)   (b)   (c)

(d)   **(e)**
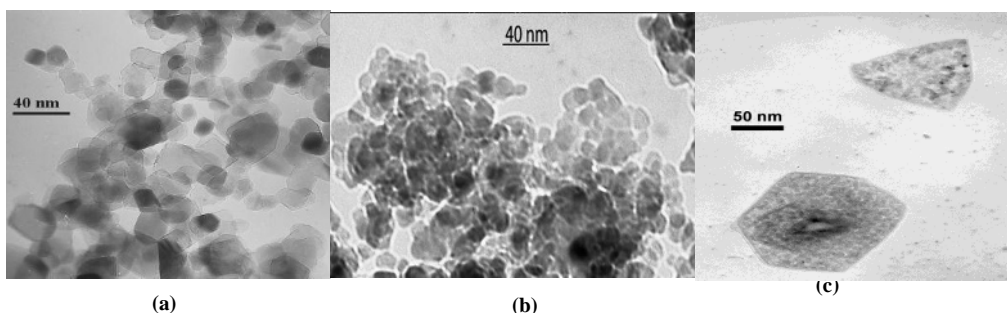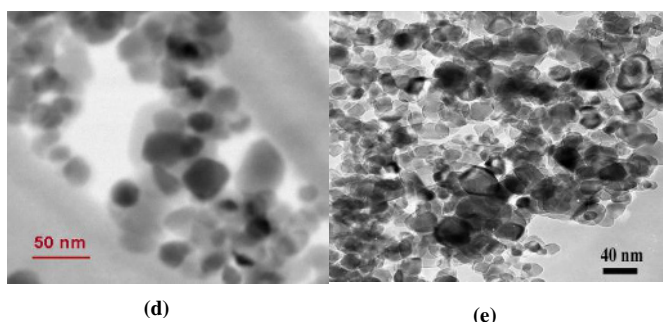
Fig. 4. TEM micrographs of (a) pure P25 TiO2 powder, (b) pure ITO powder, (c) pure ZnO powder, (d) TiO2-ZnO (45%:55%) nanocomposite, (e) TiO2-ITO (45%:55%) nanocomposite obtained after calcinations of the deposited solutions at 550°C for 15 min.

3.3 Photo-catalytic degradation

The photo-catalytic test was carried out under UV light in order to reduce/oxidize a typical textile dye (the Yellow Brillant Cibacron 3G-P) in water. The experiment was carried out in a TFFBR reactor using a solution having a known initial dye concentration (C0 = 40 mM/L). The reaction process was followed by systematic sampling. It should be mentioned that at the end of experiment a complete removal of the dye color was observed. Figure 5a shows the concentration C of the dye solution as a function of irradiation time in presence of the TiO_2–ITO nanocomposites; measurements made on pure TiO_2 as well as on ceramic-supported ITO are given for comparison. It is worth noting that ITO presents limited photocatalytic degradation towards the dye, as compared to pure TiO_2 or to TiO_2–ITO nanocomposites. However, the photo-catalytic activity of the ceramic-supported TiO_2–ITO-based films is better than that of pure TiO_2. Figure 5b depicts the photo-catalytic efficiency of ceramic supported TiO_2–ITO and pure P25 TiO_2 given for comparison.

The degradation of the textile dye solution follows a first-order kinetic model (Figure 5b) according to Eq. (1).

$$r = -\frac{dC}{dt} = KC \qquad (1)$$

The constant rate k was obtained by fitting the linear plot of ln(C0/C) versus time (Fig. 5b). From Fig. 5b, one can point out that the ceramic-supported ITO–TiO_2 nanocomposite has a larger reaction rate constant (k = 0.027 min^{-1}) with respect to ceramic-supported TiO_2 (k = 0.014 min^{-1}).

The photo-catalytic activity of the ceramic-supported TiO_2–ZnO-based films is better than that of pure TiO_2. Fig.6b depicts the photo-catalytic efficiency of ceramic supported TiO_2–ZnO and pure P25 TiO_2 given for comparison. One can point out that the ceramic-supported ZnO–TiO_2 nanocomposite has larger reaction rate constant (k = 0.017 min^{-1}) as compared with ceramic-supported TiO_2 (k = 0.008 min^{-1})

This enhancement may be explained by the fact that both TiO_2–ZnO and ITO–TiO_2 interfaces would have efficient photo-catalytic effects than ITO, ZnO or TiO_2 used separately. The positive influence of ITO and ZnO on dye degradation is explained by the improvement of charge separation and increase in the lifetime of the charge carrier. The efficiency of electron transfer from ITO or ZnO to TiO_2 for each samples, was taken as the ability to degrade the Cibacron Yellow dye under UV irradiation.

(a)

(b)
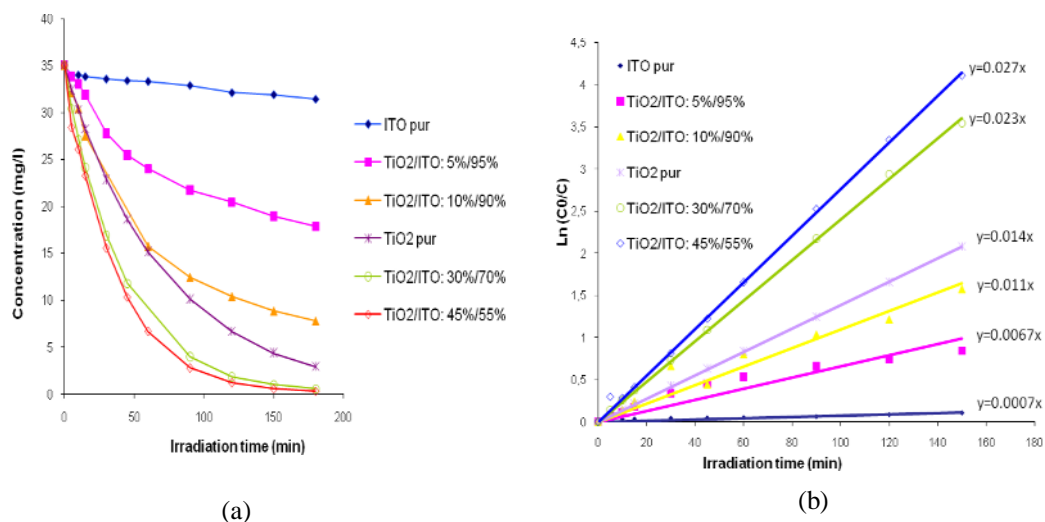
Fig. 5. (a) Evolution of the dye concentration versus irradiation time in presence of ceramic-supported TiO$_2$–ITO nanocomposites with different proportions; ceramic-supported pure P25 TiO$_2$ and ceramic-supported ITO. The tests were made at an excitation wavelength of 405 nm. (b) Linear transform ln(C0/C) versus irradiation time.

(a)

(b)
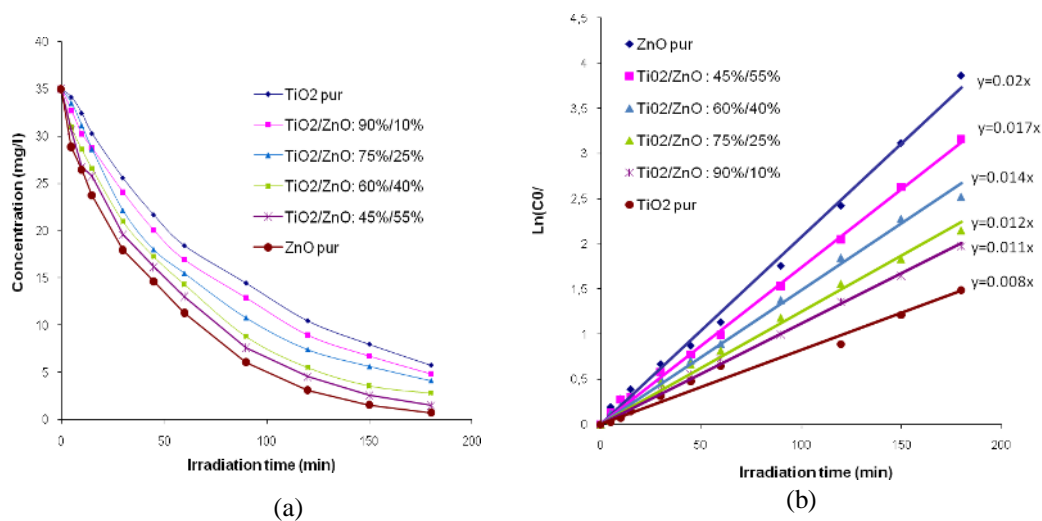
Fig. 6. (a) Evolution of the dye concentration versus irradiation time in presence of ceramic-supported TiO$_2$–ZnO nanocomposites with different proportions; ceramic-supported pure P25 TiO$_2$ and ceramic-supported ZnO. The tests were made at an excitation wavelength of 405 nm. (b) Linear transform ln(C0/C) versus irradiation time.

It is well known that the photocatalytic activity of the TiO$_2$ is mainly due to its anatase phase [13]. On the other hand the photocatalytic activity depends on the specific surface area of the catalyst and essentially on the surface defect density. In the case of a TiO$_2$–ITO and TiO$_2$–ZnO nanocomposite, the interfaces may play an important rate regarding the photocatalytic activity. Indeed the perturbation of the surface of TiO$_2$ nanoparticles by other nanoparticles may induce a variation of the adsorption sits leading to a variation in the photocatalytic activity.

Generally the ability of the semiconductors to improve the photodegradation of the organic pollutant is attributed to their electronic structures. The electronic structure is characterized by the filled valence band and the empty conduction band. In TiO_2–ZnO composites, the electron transfers from the conduction band of ZnO to the conduction band of TiO_2 under illumination and conversely, the holes transfers from the valence band of TiO_2 to the valence band of ZnO, decreasing the pairs' recombination rate; this charge separation effectively increases the lifetime of the charge carriers and enhances the efficiency of the interfacial charge transfer to adsorbed substrates [8].

4 Conclusions

Compared to P25 TiO_2, both TiO_2 – ITO and TiO_2 – ZnO nanocomposites showed a significant high photocatalytic activity under UV irradiation. The enhancement of the photocatalytic activity was investigated as a function of added amount of other mixed semiconductors such as ITO and ZnO. The positive influence of ITO or ZnO on dye degradation is explained by the improvement of charge separation and increase in the lifetime of the charge carrier.

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