Photocatalytic Evaluation of Bi-doped TiO/TiO_2 under Solar Irradiation

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Abstract. Abstract. The photocatalytic properties of TiO2 have been studied in the last decade due to its a high capacity to degrade organic compounds which dangerous for the human health. In order to increase its degradation efficiency, we propose the doping of TiO_2 with Bi dopant using concentrations from 0 to 5 at%. A simple and fast (40 min) combustion method was used to synthesize Bi doped TiO_2. According to the X-ray diffraction patterns, we obtained a mixture of TiO/TiO_2 phases with Bi dopant concentrations below 0.5 at.%. Above this value, the Bi7.68O12.16Ti0.32 compound was obtained. The morphological studies by Scanning electron microscopy demonstrated that a porous material is obtained for Bi concentrations below 0.5% but highly coalesced particles appeared for higher concentrations. The Bi doped materials were used to degrade Methylene blue dye under solar exposure and found a maximum degradation percentage of 96% for the sample doped with 0.1 at% of Bi.

1. Introduction

The water contamination problem has increased during the last years due to the use of dyes, herbicides and phenol derivatives in industrial processes, which are difficult to degrade. These contaminants are found in rivers and water effluents produced by the textile industry, fertilizer industry etc. [1]. Photocatalysis is considered a reliable alternative for the degradation of various organic and inorganic compounds in industrial wastewater through oxidation and reduction reactions. In this process, a photocatalyst is irradiated by light with energy equal or greater than its band gap [2–4], it absorbs the light and electrons are excited from the valence band (VB) to the conduction band (CB), which produces electron-hole (e-h) pairs. These ones react with water to produce OH- and O^{-2} radicals, which in turn, attack the dye or pharmaceutical contaminant, producing its degradation [5].

The industrial factories are looking for innocuous photocatalysts that can be activated with sunlight [6], [7]. In this sense, TiO_2 (Titania) photocatalyst could be an option because previous works demonstrated that it can degrade dyes and organic contaminants under Ultraviolet (UV) irradiation (λ < 385 nm) and this radiation could come from the sunlight. The Bi has been introduced as dopant in TiO_2 host to enhance its degradation efficiency, obtaining total degradation times of 30-180 min. An advantage of Bi doped materials such as TiO_2:Bi is their easy preparation using simple methods such

as sol-gel [8], [9]. Due to the advantages of Bi to enhance the photocatalytic degradation of dyes and the capacity of titania to absorb the UV component of the sunlight. We doped TiO_2 with Bi and evaluated its performance for the photocatalytic degradation of MB under sunlight irradiation.

2. Experimental

2.1. Combustion Synthesis of Bi-doped TiO_2 samples

The reagents were purchased from Sigma Aldrich and used as received. In a typical synthesis, Titanium isopropoxide [$C_{12}H_{28}O_4Ti$ (99.999%), Sigma Aldrich], bismuth nitrate pentahydrate [$Bi(NO_3)_2$ $5H_2O$ (98.0%) Sigma Aldrich], and glycine as fuel [$C_2H_5NO_2$ (99.0%), Faga Lab] were dissolved in a quartz beaker with 20 ml of distilled water under continuous stirring at 500 rpm. After this, a transparent blend was observed. Next, the beaker was introduced into a preheated furnace at 350 ℃ to achieve the combustion process. After 10 minutes, a gray crystalline foam was produced from the combustion. Finally, the gray foam was grinded to obtain a photocatalyst powder. Several Bi-doped TiO_2 samples were synthesized with Bi dopant concentrations of x=0, 0.1, 0.3 and 0.5 at.%.

Photocatalysis experiments

The photocatalytic experiments were achieved for each Bi-doped TiO2 sample as follows: 30 mg of photocatalysts was added in 100 ml of aqueous methylene blue (MB) solution (25 ppm initial concentration). The MB was purchased from Sigma Aldrich with a 99.99% of purity. Immediately, the beaker was placed into a dark room for 1 h to allow adsorption of MB molecules at the surface of the photocatalyst. Subsequently, the solution was exposed to natural sunlight. Next, aliquots were extracted in regular periods of time for 240 minutes and their absorbance was measured using a UNICO SQ4802 UV-Vis spectrophotometer in the range of 200-800 nm. The MB degradation was observed by monitoring the decrease of the absorption peak at 665 nm, which is attributed to the MB dye. Thus, the degradation percentage of MB was calculated by:

$$\text{Degradation}=[(A_t-A_o)/A_o\ ]*100\% \quad , \tag{1}$$

where A_t is the absorbance at the time "t" and A_0 is the initial absorbance of the initial MB solution. In addition, the solar irradiance was monitored by using a Davis photodiode solarimeter detector each 30 minutes and the maximum value of the irradiance during the experiments was: 958 ± 10 W/m^2. The solar photocatalysis experiments were made at the astronomic observatory of Autonomous University of Coahuila in Saltillo México, which coordinates are Latitude: 25° 26' 0″ North Longitude: 101° 0′,0'' West, Height: 1581 m. in a sunny day starting at 12:14 h and finishing at 16:15 h.

3. Results and discussion

The X-ray diffraction patterns of TiO_2:Bi samples are shown in figure 1. Two phases appear in x = 0.0at%, 0.1at% and 0.3at% Bi-doped samples, that, this, TiO and TiO_2 (marked with α letter and PDF #96-900-8750). The sample with 0.5 at% of Bi dopant showed another phase, corresponding to the Bismuth titanium oxide: $Bi_{7.68}O_{12.16}Ti_{0.32}$ with PDF #96-200-5006 and labeled with β in figure 1. Thus, the increase of the Bi content provokes the phase change from TiO_2 – TiO to $Bi_{7.68}O_{12.16}Ti_{0.32}$.

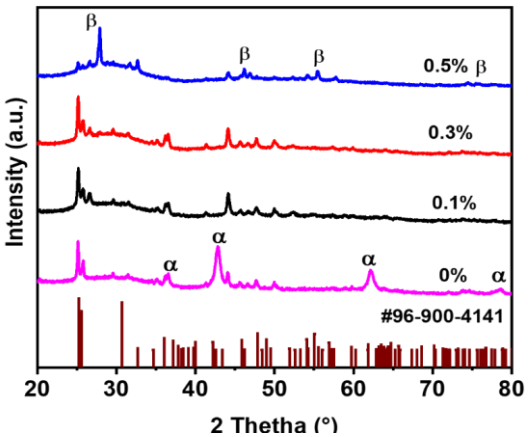

Figure 1. a) X-ray diffraction patterns of Bi-doped TiO_2 samples.

The SEM micrographs of Bi-doped TiO_2 samples are shown in figure 2. Figure 2a shows the typical porous morphology of undoped TiO_2 where grains with sizes from 0.2 to 1 μm are observed. The sample corresponding to x = 0.1at% is depicted in figure 1b, the morphology is similar, but it has bigger grains with sizes from 0.25 μm to 1.2 μm. The SEM images show coalesced grains in the sample with 0.3 at% of Bi dopant, see figure 1c. It shows irregular grains without the same porosity than the samples above and sizes from 0.6 μm to 6 μm. The most notorious change occurs in the sample with x=0.5at% in figure 1d, where conglomerated particles with sizes in the range of 1 μm to 15 μm are observed. The porosity was drastically reduced, and the particles have irregular shape.

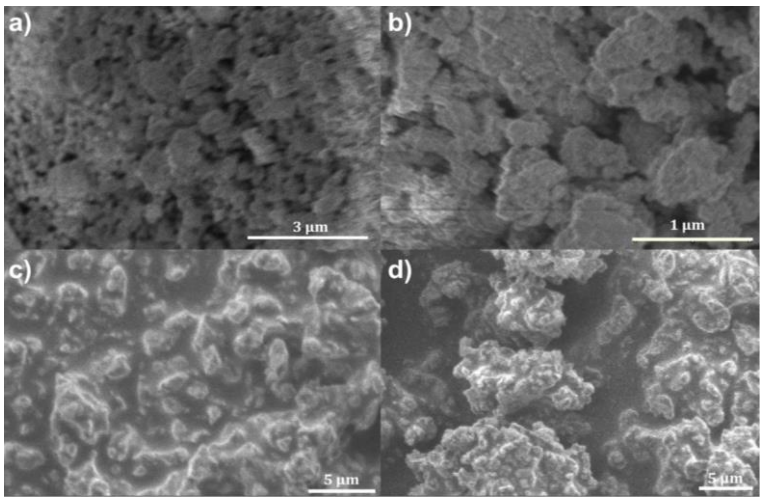

Figure 2. SEM micrographs of the Bi-doped TiO/TiO_2 samples: a) x = 0.0%, b) x = 0.1% and c) x = 0.3% as well as for $Bi_{7.68}O_{12.16}Ti_{0.32}$ (x = 0.5%).

Figure 3a shows the absorbance spectra obtained from the MB solution with the 0.1 at% photocatalyst, these spectra were obtained each 30 minutes for 4 hours. The absorption peak of MB is located at 665 nm. The solution changes its coloration from blue to transparent liquid after 240 min, as observed in the inset of figure 3a. The peak at 665 nm disappeared after 180 min, see figure 3a. The MB degradation percentage values corresponding to x = 0.1, 0.3 and 0.5% samples were calculated taking into account the degradation of the peak at 665 nm and the equation (1). Figure 3b shows the MB degradation percentage produced by the Bi-doped samples as a function of time. The 0.1% Bi-doped sample was the most efficient photocatalyst, because it produced a degradation percentage of 96% after 240 min, followed by the 0.3at% sample with 91% of degradation for the same time. The 0.0% sample reached a maximum degradation of 84%. The blank solution presented 66% of degradation after 240 min. The sample 0.5at% Bi-doped sample showed a degradation of 76% [10]. We tried to

make TiO_2: Bi but we obtained TiO/TiO_2:Bi instead. However, we obtained degradation results similar to these reported in reference [8], where the authors employed a complex method of sol-gel to make the TiO_2:Bi Powders and degrading Rhodamine B in aqueous solutions.

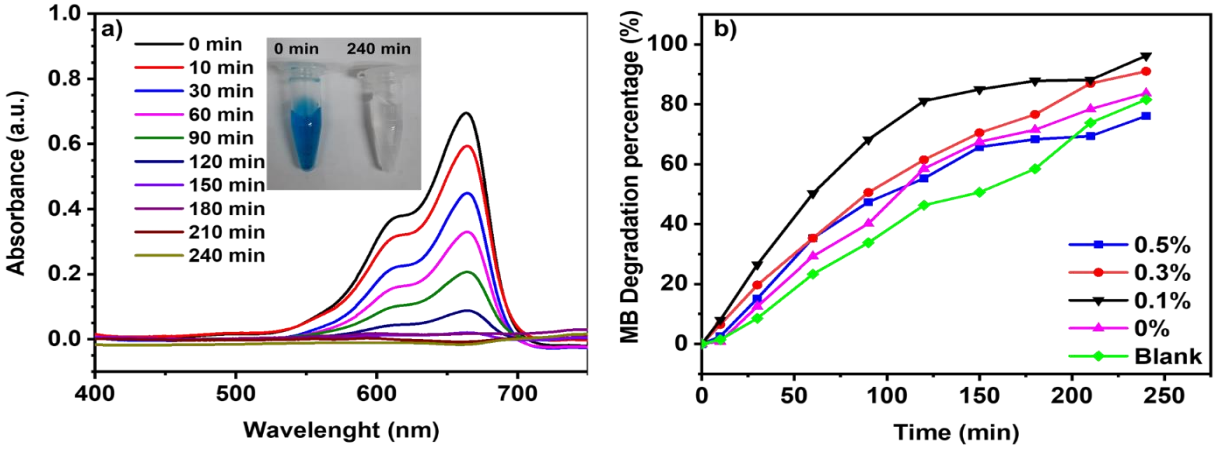

Figure 3. a) Absorbance spectra of the undoped TiO_2. b) Graph of MB degradation under sunlight irradiation.

4. Conclusions

The XRD patterns demonstrated that the crystalline structure of Bi doped titania changed with the content of Bi. If the Bi dopant is higher than 0.5at %, the composition changes from Bi doped TiO/TiO_2 to $Bi_{7.68}O_{12.16}Ti_{0.32}$ phase. The morphology presented in the undoped and Bi-doped samples (x=0.1 at%) showed coalesced grains and some porosity most similar to the typical morphology of the TiO_2. Samples doped with x=0.3 and 0.5 at% presented a more coalesced morphology. The highest MB degradation percentage was observed in the sample doped with 0.1 at%, which means that doping with bismuth is useful to enhance the degradation of MB. Due to the 91% of MB degradation in aqueous solutions, the TiO_2:$_x$Bi (x= 0.1at%) photocatalysts could be used in water-cleaning applications.

5. References

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