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# Photocatalytic mineralization of methylene blue from water by a heterogeneous copper-titania nanocomposite film

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ABSTRACT

Copper-doped nanostructure titania film was successfully prepared using the sol–gel method. The phase structure, thermal, microstructure, and surface properties were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy, scanning electron microscopy, reflectance spectroscopy (Ultraviolet Diffuse Reflectance [UV-DRS]), and thermal analysis (Thermal gravimetric differential thermogravimetry [TG-DTG]). XRD showed that titania consisted of 92% anatase and 8% rutile crystalline phases. The results obtained have shown that these systems can degrade methylene blue (MB) as a model environmental pollutant in wastewater. The degradation rate of MB in the presence of copper-doped titania at optimized conditions was higher than that for bare titania. MB is almost completely mineralized to carbon dioxide, nitrate, and sulfate ion by the photocatalytic method. The results showed that no significant fraction of copper-titania residues was released from the film in water. This investigation will give a new insight into understanding the industrial textile dye photodegradation in aquatic environment.

*Keywords:* Dye removal; Photocatalytic degradation; Copper-doped titania film; Photocatalyst; Environmental pollutant; Methylene blue

## 1. Introduction

Titania is one of the most important photocatalysts and many researches have been devoted to the modification of this semiconductor [1–3]. It is the most efficient and environmentally benign photocatalyst for photodegradation of various pollutants. Titania has been used as photocatalyst for the three classes of water contaminants: organic, inorganic, and microbiological with minimal risk of the production of harmful byproducts [4–7]. Titania absorbs UV light to generate electron hole pairs. These separated electrons and holes are then available to drive reduction and oxidation reactions, respectively. The generated valence band holes and conduction electrons recombination in the bulk decreases the catalytic efficiency of titania [8–10]. The improvement of titania is an important task to ensure that more photo-generated electrons and holes can move to the surface of the semiconductor particles before they recombine in bulk. Researches into the enhancement of photocatalytic activity have been carried out [11–13]. The need of UV light for titania excitation restricts the use of easily available sunlight. In order to improve the response into the visible part of the spectrum, $TiO_2$ doping with transition metals has been employed [14,15]. The improved photocatalytical reactivity is related to the efficiencies of the doping in trapping charge carriers and interceding in the interfacial transfer. Trapping either an electron or hole alone is

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ineffective for photodegradation because immobilized charge species quickly recombine with the mobile counterpart. Doping of titania with metal ions can provide charge trapping sites and reduce electron–hole recombination rate [16–18]. Besides the effect of doping, structural, morphological parameters, the method of doping, the type, and the concentration of dopant affect the photocatalytic activity of a semiconductor [19–21]. There are reports on the improved activity of semiconductor by doping noble metal ions, but they are very expensive [22]. The textile industry produced dye pollutants as a major source of environmental contamination. Metal oxide photocatalysts such as titania are promising materials for degradation of organic pollutants by utilizing solar and/or UV light [23–28]. Recently, we have reported the fabrication and characterization of copper nanoparticles using thermal reduction [29]. On the basis of the above-mentioned background, to further improve the titania photooxidation for water and wastewater treatment, this study was aimed at modifying the pure titania film by doping with Cu to hinder the recombination of electron/hole pairs and to modify the surface properties by enlarging the specific surface of titania photocatalyst.

The aim of this study is to investigate the influence of copper on the structural and photocatalytic properties of titania. In this research for the first time, copper dopant is used for titania film with relative abundance and low cost. The copper-doped $TiO_2$ was characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR), and UV-DRS techniques. The photocatalytic activity was studied by monitoring the decomposition process of methylene blue (MB), used as a model substance.

## 2. Experimental

### 2.1. Materials

Hydrochloric acid, hydrogen peroxide ($H_2O_2$, AR), MB, and copper nitrate were purchased from Merck. Titanium isopropoxide ($Ti(OC_3H_7)_4$, Aldrich) was chosen as a precursor. The water used in the experiments was double distilled and deionized.

### 2.2. Preparation of the undoped titania sol

The undoped titania sol was prepared by the sol–gel method. Titania sol was prepared by dissolving titanium isopropoxide (4.4 mL) in 1-butanol (15 mL). The solution mixture was stirred for 5 min resulting in a transparent solution. This solution is stable for several months at room temperature when kept in a closed glass recipient.

### 2.3. Preparation of the copper-doped titania film

Copper-doped titania (CDT) film was deposited on square 1-mm thick borosilicate glass substrates (75 × 25 mm) by sol–gel spin-coating. Glass substrates used were pre-coated with six copper-doped $TiO_2$ film layers deposited by the sol–gel spin-coating technique. For the synthesis of the CDT film, titanium isopropoxide (4.4 mL) was dissolved in a mixture of copper (II) nitrate (0.243 g), deionized water (1.8 mL), and 1-butanol (4.4 mL). The solution pH was adjusted to 3 by addition of diluted nitric acid and stirred for 4 h mixing. The sol was converted to gel by heating in 70° C for 24 h. This gel was calcined at 500°C under aerated conditions and a white powder called CDT was obtained.

### 2.4. Characterization techniques

Thermal analysis (TG-DTG) measurements were carried using a Mettler TA 4000 system. The crystalline phase of colloids was studied by X-ray diffractometer (XRD) technique with a D8 Advanced Bruker X-ray diffractometer at room temperature with monochromated Cu Kα ($\lambda = 1.54$ Å) in the scan range of $2\theta$ between 4° and 100° with a step size of 0.03 ($2\theta\, s^{-1}$). Measurements were taken under beam acceleration conditions of 40 kV/35 mA. Philips XL-30 SEM was used to image the size and morphology of the CDT nanopowder. An elemental composition analysis of the films was performed using energy-dispersive X-ray spectroscopy (EDAX) connected to the SEM. FT-IR spectra were obtained using KBr disks on a FT-IR 6300, JASCO. UV-DRS spectra were recorded on a V-670, JASCO spectrophotometer.

### 2.5. Photoreactor and photocatalytic measurements of MB using undoped titania and CDT films

Undoped titania or CDT film was placed in 25 mL sample of water containing MB (10 ppm) and subjected to UV irradiation using two 8 W lamps (Philips; $\lambda = 365$ nm) having an intensity of about 20 mW/cm$^2$ placed 5 cm above the solutions. All photodegradation experiments were conducted in a batch reactor with the UV lamp placed in a cooling silica jacket in a constant pH of 6.8. The degradation process was monitored by measuring the UV–vis absorbance. All photocatalytic tests were performed at a constant stirring rate

(500 rpm) at room temperature (25˚C). Control experiments without UV light were also performed (the reaction system was kept in the dark). In a typical experiment, 10 mL of each MB solution with initial concentration of 10 ppm was used. The solution was stirred continuously and a constant-temperature water bath was maintained at 25˚C. Two millilitres of the sample was taken at regular time intervals during irradiation and analyzed by a double-beam UV–vis spectrophotometer (Varian Cary 500 Scan) to measure the concentration of MB ($\lambda_{max} = 654$ nm). In order to compare their catalytic activities, the reactor was filled up to the same amount of undoped and CDT ($TiO_2$ or Cu–$TiO_2$). In addition to this, thermal-blank degradation experiments of MB were performed without light, with and without the catalysts. No degradation was observed in any of these controls.

## 3. Results and discussion

CDT film was deposited on borosilicate glass substrates by sol–gel spin-coating. The sol was converted to gel and calcined at 500˚C under aerated conditions. The photocatalytic activity of undoped titania and CDT films was measured using MB in which the chemical structure is shown in Fig. 1.

### 3.1. Thermal study

The thermal behavior of nanostructure undoped $TiO_2$ and copper-doped $TiO_2$ samples prepared from sol–gel route is depicted in Figs. 2 and 3, respectively. Peaks regarding the elimination of solvent and removal of physically adsorbed water were observed in the temperature range of 50–190˚C. In the last step, $TiO_2$ crystallization occurred at 398˚C. The weight loss of the powder was approximately 37% during process up to 600˚C.

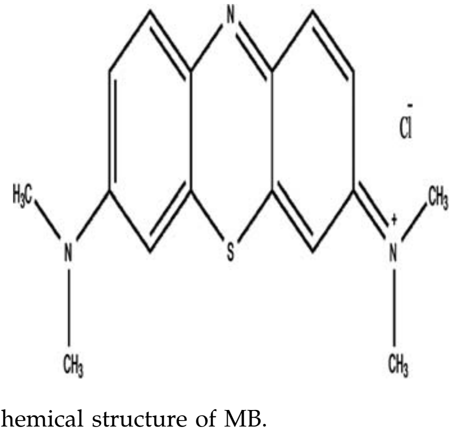

Fig. 1. Chemical structure of MB.

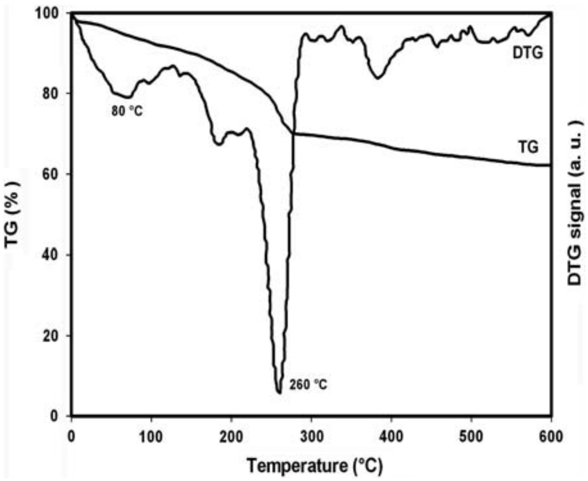

Fig. 2. TG-DTG curves of pure titania prepared by sol–gel method annealed at 500˚C.

### 3.2. Structural and compositional study

The synthesis of undoped titania and CDT samples was carried out using the sol–gel method. The XRD spectra of the undoped titania and CDT samples, which were calcined at 500˚C, are shown in Figs. 4 and 5, respectively. The phases are identified as anatase (0 0 4), (2 0 0), (2 0 4) and rutile (1 0 1) peaks. The results for undoped titania sample produced from the sol–gel titania (Fig. 4) were very similar to those of CDT (Fig. 5). The main peaks are at two-theta angle of 25.44, 37.7, 48.03, and 62.7, which are ascribed to anatase and rutile crystalline phases. The XRD pattern of the undoped titania and CDT samples reveals that the

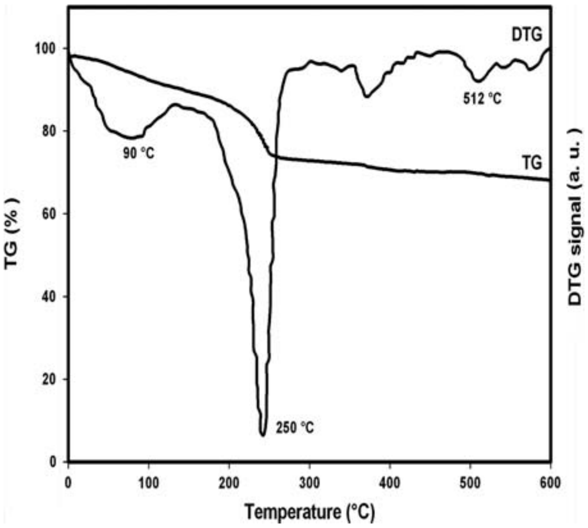

Fig. 3. TG-DTG curves of CDT (5% copper) prepared by sol–gel method annealed at 500˚C.

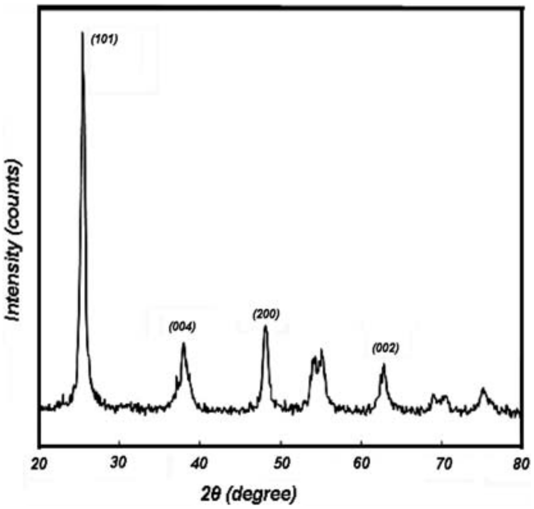

Fig. 4. XRD pattern of pure titania prepared by sol–gel method annealed at 500℃.

titania composition is a mixture of 92% anatase and 8% rutile crystalline phases. The two phases of anatase and rutile could be identified clearly from the XRD pattern in Figs. 4 and 5 [30]. No significant differences could be observed indicating that undoped $TiO_2$ and copper-doped $TiO_2$ samples have the same crystalline phase. It has been reported that a small amount of transition metal decreases the crystallization temperature of the anatase titania. That no characteristic peaks of copper oxides were showed in the XRD patterns of the sample implies that the Cu is incorporated into the lattice of anatase $TiO_2$ or copper oxide is very small and highly dispersed [31]. Fig. 6 shows the SEM image of the CDT calcified at 500℃.

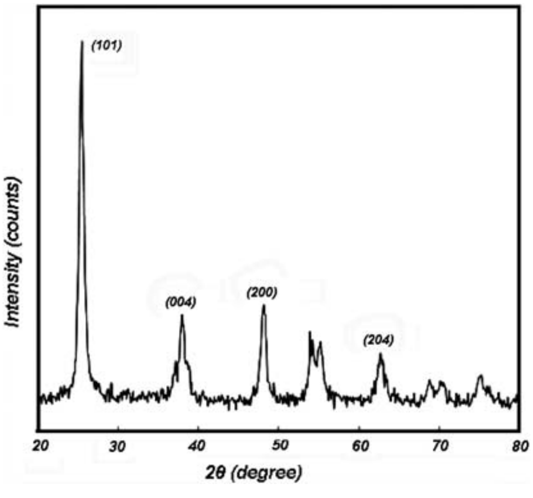

Fig. 5. XRD pattern of CDT prepared by sol–gel method annealed at 500℃.

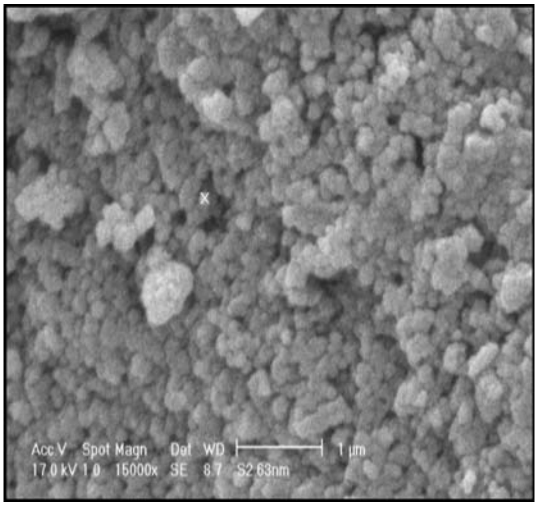

Fig. 6. SEM image of CDT prepared by sol–gel method annealed at 500℃.

The SEM images of the samples annealed at 500℃ showed that the crystalline phase of titania is formed. A representative SEM-image-doped titania (Fig. 6) shows that the titania particles are compact with a particle size of 63 nm. The $TiO_2$ particles shown in the SEM images tend to stack with random orientations with geometrical considerations. SEM was equipped with energy-dispersive X-ray spectrometers to identify the elemental composition of the CDT. Fig. 7 shows the EDAX spectra of CDT. EDAX shows strong Ti peaks and weak Cu peaks of the CDT sample. The EDAX analysis of CDT shows the $TiO_2$ (95%) and Cu (5%) content of the sample. FT-IR spectroscopy was used to confirm the formation of CDT (Fig. 8). The

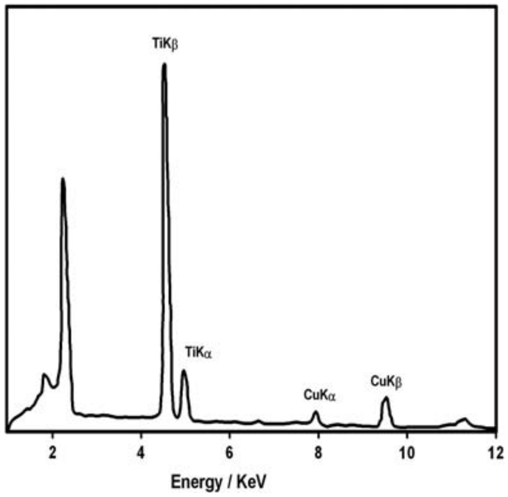

Fig. 7. EDAX of the CDT prepared by sol–gel method annealed at 500℃.

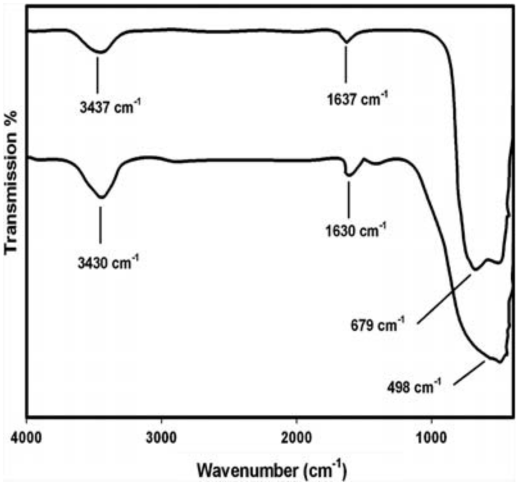

Fig. 8. FT-IR spectrum of (a) pure titania and (b) CDT prepared by sol–gel method annealed at 500˚C.

FT-IR spectrum of CDT (Fig. 8) presents a peak at 3,429 $\text{cm}^{-1}$ assigned to the OH stretching of Ti–OH. The new bands at 679 and 497 $\text{cm}^{-1}$ were assigned to the Ti–O stretching vibration.

### 3.3. MB degradation

CDT film was applied for the photodegradation of MB in wastewater. Fig. 9 represents the decay of MB with the irradiation time using CDT catalyst. MB considerably degrades with time and the concentration is reduced to more than 98% within 2 h. Optical absorption spectra of MB after UV-light irradiation at different exposure times in the interval of 450–750 nm were recorded in order to quantify the photocatalytic activity. The MB concentrations were determined following the Beer–Lambert's law. To determine the quantity of MB degradation, the maximum absorbance for every spectrum according to Beer–Lambert's law is calculated. The lower the concentration of MB, the higher the MB degradation and hence the higher photocatalytic activity is reached. Fig. 10 shows the photocatalytic degradation of MB solution using $TiO_2$–Cu (copper load 5 at.%). From these curves, it is evident that degradation of MB becomes higher as the exposure time increases. The improved photocatalytic activities may be explained by the injection of electrons from copper into titania. The plot of $C/C_0$ with time of irradiation compares the photocatalytic degradation of pure titania (curve a), CDT (curve b), pure titania with hydrogen peroxide (curve c), and CDT with hydrogen peroxide (curve d) on photocatalytic degradation of MB dye. Additionally, it is worth mentioning that pure $TiO_2$ presented a lower degradation. This result proves the catalytic effect of the copper on the degrading properties of the titania prepared by the sol–gel technique. The degradation of MB was investigated under four different experimental conditions viz. pure $TiO_2$, $TiO_2$–Cu (copper load 5%), pure $TiO_2$–$H_2O_2$, and $TiO_2$–Cu–$H_2O_2$ with UV irradiation. Adsorption of the MB with CDT film under dark conditions was negligible. The degradation of MB under UV alone under the same condition was negligible. The degradation of MB

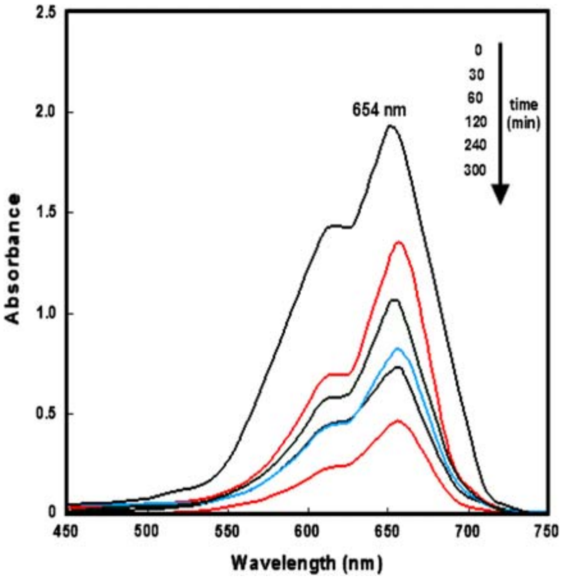

Fig. 9. Optical absorbance spectra of MB solution before (a) and after UV irradiation, in different reaction time using CDT film prepared by sol–gel method annealed at 500˚C.

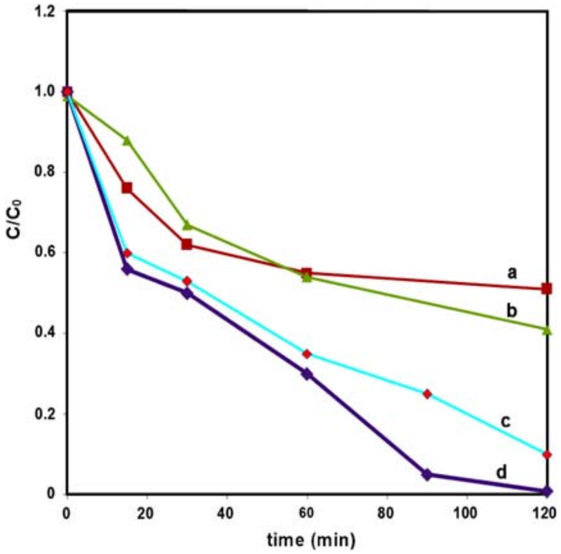

Fig. 10. Photocatalytic degradation of MB solution using (a) pure $TiO_2$, (b) $TiO_2$–Cu(copper load 5%), (c) pure $TiO_2$–$H_2O_2$, (d) $TiO_2$–Cu–$H_2O_2$ and after UV irradiation, in different reaction times.

using CDT film showed better results (62%) than pure titania film (45%) under the same condition. The highest degradation of MB (98%) was observed using a CDT film with $H_2O_2$.

## 4. Conclusion

CDT films have been deposited by sol–gel spin-coating on glass substrates. The films deposited at room temperature are predominantly amorphous and upon thermal annealing at 500˚C crystalline phases are developed. Uniform and adherent thin films with a smooth surface were obtained by this simple and economical method. This paper demonstrates that photocatalytic removal of MB was dramatically enhanced using CDT film as compared to an undoped titania film. The CDT film fabricated using the sol–gel spin-coating method exhibited better photocatalytic capacity with hydrogen peroxide for the removal of MB in aqueous solution. An increase in photocatalytic degradation indicates that the copper is substituted in the titania lattice. The promotion of degradation rate for MB in the presence of hydrogen peroxide should be attributed to the formation of **.**OH radicals by $H_2O_2$ photolysis. MB is almost completely mineralized to carbon dioxide, nitrate, and sulfate ion by the photocatalytic method. The results showed that no detectable amount of copper–titania residues was released from the film in water. The photocatalytic process shows that CDT film deposited on glass plate is attractive for applications in water cleaning.

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