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## Photocatalytic Degradation of Methylene Blue by Cu Doped TiO<sub>2</sub> Thin Films under Visible Light Irradiation

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**Keywords:** Cu-TiO<sub>2</sub>, thin films, XRD, SEM, UV-Visible, photocatalytic activity.

**ABSTRACT.** Pure TiO<sub>2</sub> and Copper doped TiO<sub>2</sub> thin films of various concentrations (0.02–0.05 mol %) have been successfully deposited onto glass substrate by sol-gel dip coating technique and annealed at 400°C for 3 hours. The XRD results showed the presence of anatase phase for all the films and the crystallite size decreases with increasing doping concentrations. The morphological observations and compositional analysis were recorded with SEM and EDX. The UV-Visible study showed that the optical band gap energy decreases with increasing Cu content. It was also found that copper doping shifted the absorption edge of TiO<sub>2</sub> toward a visible regime depicting the possible modification in the electronic band structure. The photocatalytic activity was evaluated by monitoring the degradation of methylene blue under visible light illumination. It was found that the percentage of degradation was higher in 0.05mol% Cu-TiO<sub>2</sub> when compared with other films. The efficiency of the Cu-TiO<sub>2</sub> thin film was preserved even after the extended usage of the films which sustains the reusability nature of Cu-TiO<sub>2</sub> films.

**Introduction.** Titanium dioxide (TiO<sub>2</sub>) has been extensively studied because of its excellent photocatalytic activity, chemical stability, non toxicity, optoelectronic property and low cost. However, the wide band gap and intense electron-hole pair recombination limit its efficiency in photo electro chemical applications. Tailoring the band structure of TiO<sub>2</sub> is an effective method for widening its optical absorption range and improving its visible light photocatalytic activity [1, 2]. Catalytic activity of TiO<sub>2</sub> is dependent on its phase structure, crystallite size, specific surface area and pore structure. Doping additives were found successful in altering the photo electrochemical properties of TiO<sub>2</sub> [3, 4]. In particular, doping metal impurity in TiO<sub>2</sub> matrix has been found remarkable as the way it exploits the better photo catalytic activity [5, 6]. Cu is a potential metal dopant for photocatalytic mechanism since the visible light absorption of TiO<sub>2</sub> can be enhanced by the adding Cu [7]. Here the efforts have been made to prepare Cu doped TiO<sub>2</sub> film because the film shaped photocatalysts are convenient to use and recyclable. There are numerous methods to prepare Cu doped TiO<sub>2</sub> thin film but the sol-gel method shows more advantages over other methods [8]. By carrying out this method in solution, we can modify the few desired structural characteristics like compositional homogeneity, grain size, surface morphology and porosity is possible with this technique. Methylene blue is a harmful material existing in liquid coming from industries. Exposure to methylene blue causes various health issues such as increased heart beat rate, vomiting, shock, jaundice and tissue necrosis in human being. Cu doped TiO<sub>2</sub> thin film can be used to photo degrade the methylene blue in waste water. In this work, pure TiO<sub>2</sub> and Copper doped TiO<sub>2</sub> thin films with various Cu concentrations (0.02-0.05 mol %) were prepared by sol-gel technique. The structural and optical properties of the samples were reported. The photocatalytic activity of prepared films was evaluated by methylene blue degradation under visible light irradiation.

**Experimental methods.** The pure TiO<sub>2</sub> and Cu doped TiO<sub>2</sub> thin films were prepared by sol-gel method. Titanium tetra isopropoxide (Merk 95%) precursor was dissolved into ethanol and the mixture was stirred at room temperature for 15 minutes. To this mixture acetic acid was added as a chelating agent and stirred for 15 minutes. Titanium tetra isopropoxide, ethanol and acetic acid were used in the molar ratio of 1.5:10:0.3. In the process of copper doping, copper II nitrate trihydrate was dissolved in ethanol in the respective molar ratio (Cu/TiO<sub>2</sub> = 0.02, 0.03, 0.04 and 0.05 mol%) was mixed with TiO<sub>2</sub> gel and stirred in a magnetic stirrer for two hour for uniform dispersion. The Cu-TiO<sub>2</sub> sol were deposited on glass substrates by dip coating process at room temperature with the drawing speed of about 1.5 mm/s. The coated samples were dried at 100°C for 10 minutes and the process was repeated to obtain the desired thickness. The pure TiO<sub>2</sub> was also synthesized using the same procedure without the addition of copper precursor and all are annealed at 400°C for 3 hour.

## Results and discussions.

### Structural analysis.

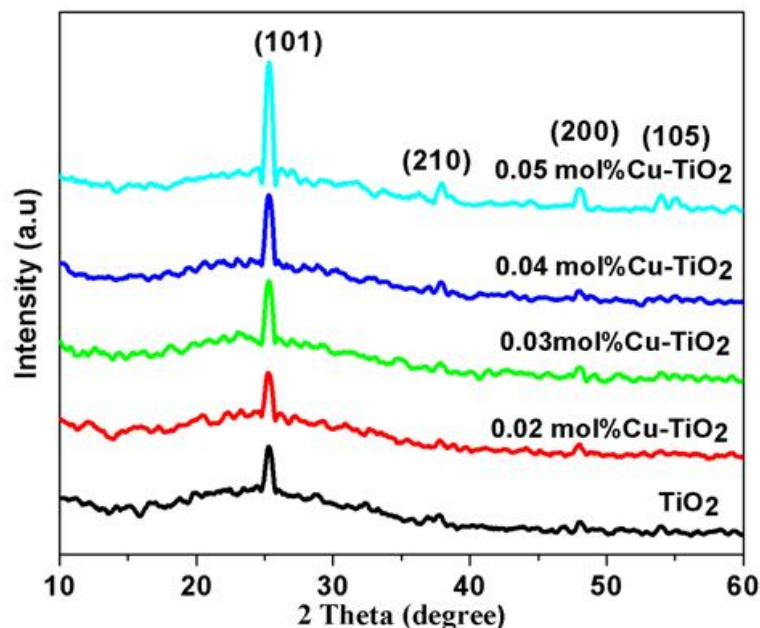


Fig. 1. XRD pattern of Cu-TiO<sub>2</sub> films with various Cu doping concentrations.

The XRD pattern of pure and Cu doped TiO<sub>2</sub> thin films with different concentrations are shown in Fig.1. Both undoped and Cu-doped TiO<sub>2</sub> films show pure anatase phase with strong peak (1 0 1) at  $2\theta=25.5^\circ$  which is in agreement with JCPDS card no 89-4203 [9]. However, no peaks related to Cu impurities are found due to the low doping concentrations of Cu or the Cu metal ions have been well dispersed into the TiO<sub>2</sub> matrix in the form of small cluster [10]. The crystallite size of as-synthesized samples were estimated from Scherrer's equation using the full width at half maximum of the (1 0 1) peak of anatase TiO<sub>2</sub>. It was perceived that the crystallite size decreases with the increased Cu proportions [11] as the stress created by the difference in ionic radii of Ti<sup>4+</sup> (0.75Å) and Cu<sup>2+</sup> (0.87Å). Furthermore a large number of dislocations were initiated when Cu ions occupying interstitial sites within Ti lattice which led to decrease in crystallize size [12].

**Surface morphological analysis.** The microstructure and chemical composition of Cu-TiO<sub>2</sub> thin films were characterized using SEM and EDX. Fig.2 shows the SEM and EDX images of 0.04mol% Cu-TiO<sub>2</sub> thin films. The SEM image illustrates a few localized agglomerations with cracked patterns [13]. The crack formation was possibly by the repeated process done to make thicker coatings of films

(7-layered) [14]. The energy dispersive spectrum (EDX) exposes the presence of titanium, copper and oxygen in appropriate proportions.

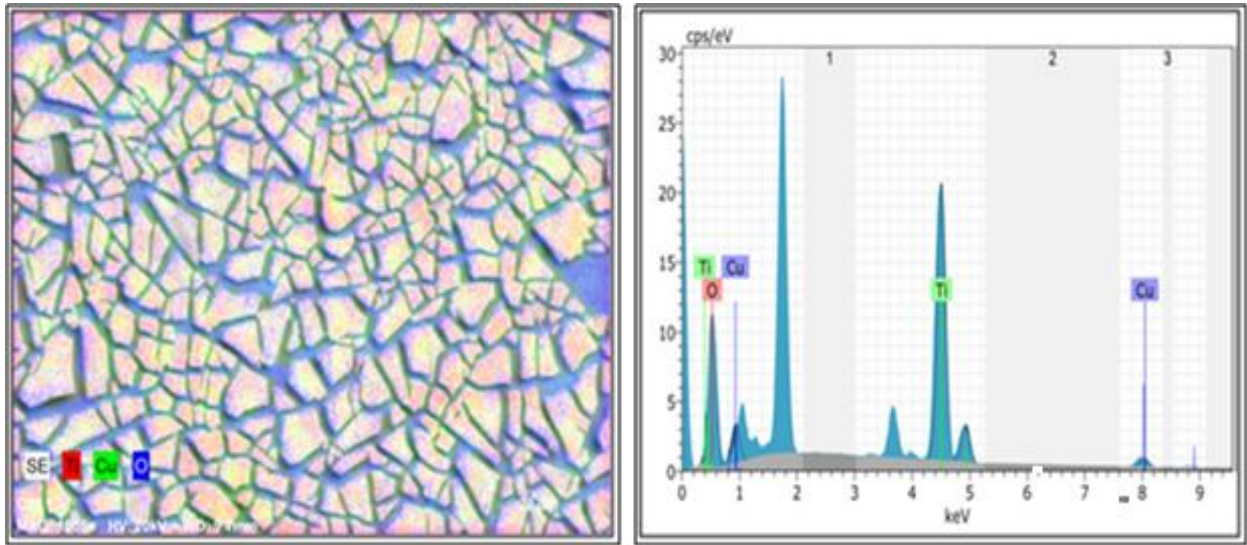


Fig. 2. SEM and EDX spectrum of Cu-TiO<sub>2</sub> (0.04mol %) thin film.

### Optical Analysis

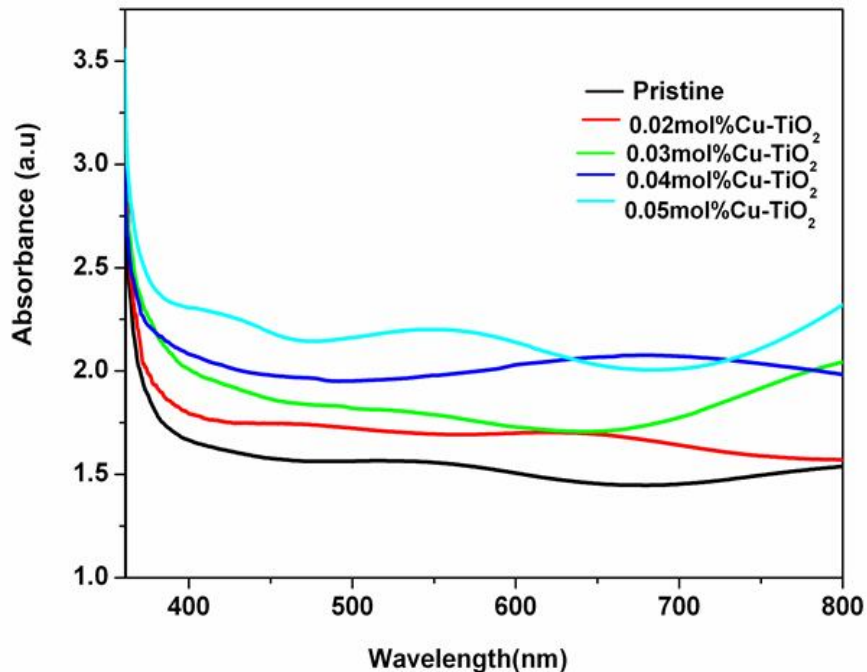


Fig. 3. Absorption spectra of Cu-TiO<sub>2</sub> films with various Cu doping concentrations.

The UV-visible absorption spectra of pure TiO<sub>2</sub> and Cu-TiO<sub>2</sub> films are shown in Fig.3. It was viewed that the pure TiO<sub>2</sub> shows UV light absorption as it requires maximum energy for the transition of electrons from the top of the valence band to the bottom of the conduction band (wide band gap). Conversely Cu-TiO<sub>2</sub> demonstrates enhancement in visible light absorption as Cu doping creates new electronic levels and reduces the band gap energy requirement. Accordingly the absorption edge of

TiO<sub>2</sub> was shifted towards visible light region [15]. Widening the absorption edge to the visible region can upraise the photocatalytic activity reasonably [16].

**Photocatalytic activity.** Photocatalytic activity of TiO<sub>2</sub> and Cu doped TiO<sub>2</sub> thin films was analyzed by examining the degradation of aqueous solution of methylene blue (MB) under visible light irradiation using 500-W halogen lamp. In order to carry out the process, 3 μl of the methylene blue was mixed with 30ml water in a 50-ml beaker. The thin films were soaked into this and kept under visible light irradiation for 0,1,2,3 and 4 hour. After that the 5ml of the degradation solution was taken to measure the absorbance using Shimadzu-1800 UV-Vis spectrometer.

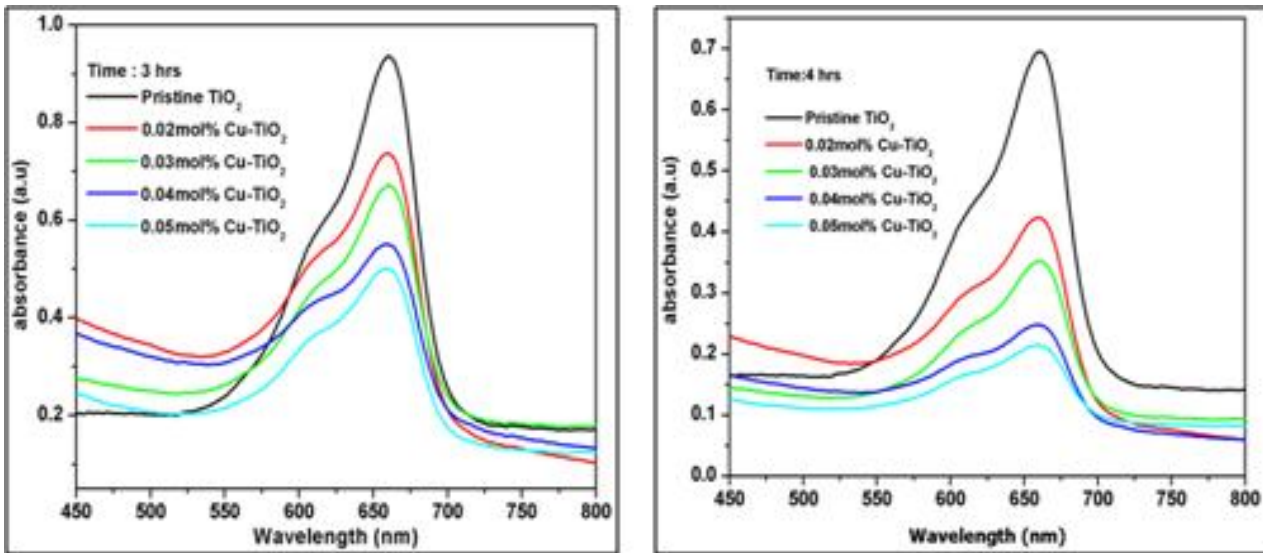


Fig. 4. Optical absorption spectra of degradation of MB dye for Cu-TiO<sub>2</sub> thin films.

Fig. 4 show the absorbance spectra of degraded MB with different time periods (3 hr and 4hr) of pure TiO<sub>2</sub> and Cu-TiO<sub>2</sub> thin films. It was observed that the doped TiO<sub>2</sub> films depict enhanced catalytic activity than undoped film. The interpretation is that due to illumination, the generated electron-hole pair is transferred to the surface of photo catalyst which excites electrons of the pollutant to the conduction band of TiO<sub>2</sub> [17, 18]. Here Cu doping delays electron-hole recombination and thus by promotes the photo induced interfacial charge-transfer between Cu ion and TiO<sub>2</sub> energy levels. This leads to the production of more reactive species.

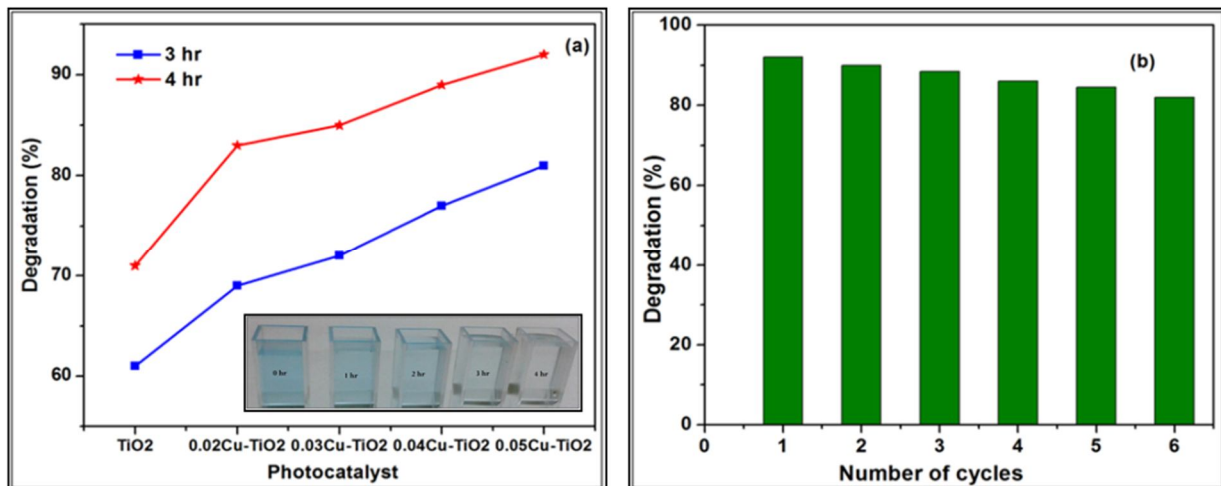


Fig. 5. (a) Percentage of degradation of MB (b) Reusability of the film.

The produced OH and O<sub>2</sub><sup>-</sup> radicals oxidize and decompose the molecules of MB photo reactor. As a result, the characteristic color of MB dye was degraded with time. The photo catalytic mechanism is influenced by the degradation time too. Hence the absorption peaks corresponding to the MB decreases further to a minimum value with increase in time. The percentage of degradation of MB is shown in Fig. 5a. The 0.05 mol% Cu doped TiO<sub>2</sub> thin films show the highest percentage of degradation (92%) than that of pure TiO<sub>2</sub> (68%). This is attributed to that the smaller particle size of 0.05 mol% Cu-TiO<sub>2</sub> compared to that of pure TiO<sub>2</sub> as the photo bleaching process rely upon particle size, crystallinity and surface area. Also, the larger surface area facilitates the films to have more adsorption site and enhances the surface contact between photo reactor MB and Cu-TiO<sub>2</sub> catalyst. Consequently fast degradation process has taken place under visible light irradiation. Thus with 0.02 to 0.05 mol% stoichiometric range, Cu dopant promotes the reaction rate and increases decolorisation efficiency appreciably.

One of the important features of thin film catalyst is its reusability. This catalyst could be easily recovered by cleaning with water and reused without loss of its catalytic activity [19]. Hence to calculate Cu-TiO<sub>2</sub> catalyst stability, the film was undergone with 6 cycles of photo degradation in MB dye under visible light irradiation. Here, we report the reusability of 0.05 mol% of Cu-TiO<sub>2</sub> thin film. After each cycle, the film was washed with distilled water, dried in air and reused in same conditions. The catalytic efficiency was evaluated in each cycle. It was noticed that it maintains its excellent catalytic efficiency even after 6 cycles with a small loss which is shown in Fig. 5b. The Cu-TiO<sub>2</sub> thin film (0.05mol %) was preferred for testing the reusability since it showed the improved catalytic performance than all other prepared films in degradation of dyes.

**Summary.** Pure TiO<sub>2</sub> and Cu doped TiO<sub>2</sub> with different concentrations were deposited on glass substrates by sol-gel dip coating technique. The presence of anatase phase and decreasing crystallite size with the increasing Cu ratio were spotted from the recorded XRD pattern. The morphology study reveals that the surface of the film was comprised with agglomerated flakes like structure and the existence of Cu, Ti and O elements are confirmed from EDX measurements. Copper doping shifted the absorption edge of TiO<sub>2</sub> towards the visible light region. The TiO<sub>2</sub> thin film doped with 0.05 mol % Cu exhibits strong photo catalytic activity thus by drawing higher percentage of methylene blue degradation. The aptness of the Cu-TiO<sub>2</sub> thin film as a photo catalyst with the repeated usages was found to be excellent.

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