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## Preparation and Photocatalytic Effect of Cu<sup>2+</sup>-Doped TiO<sub>2</sub> Nanoclusters

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### ABSTRACT

Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoclusters are prepared by the sol-gel method. Scanning electron microscopy and X-ray diffractometry are applied to characterize their structural properties. The photocatalytic analysis is done by UV-Vis absorption spectrum. The results of X-ray diffraction (XRD) shows the presence of rutile peak with a strong orientation along (1 1 0) plane. Scanning electron microscopy (SEM) study shows the uniform distribution of agglomerated nanoclusters. EDS spectrum confirms the presence of doped metal ion Cu<sup>2+</sup> in the TiO<sub>2</sub> crystal lattices. In this work, the photocatalytic effect of Cu<sup>2+</sup>-doped TiO<sub>2</sub> on the degradation of methyl orange dye is studied. TiO<sub>2</sub> doped with 5 wt% Cu<sup>2+</sup> gives an excellent result in the degradation of methyl orange.

### 1. Introduction

In this modern world, wastewater treatment is a challenging task by the textile industries. The most common effluents used by the textile manufacturers are synthetic organic compounds, such as dyes. Due to the stability of modern dyes, it is difficult to remove them from wastewater and may require tertiary and further treatments [1]. Semiconductor nanoparticles used in disposing of environmental pollutant by a method called Heterogeneous photocatalysis [2]. TiO<sub>2</sub> is a well-known photocatalyst for removing effluents from wastewater [3-5]. The photocatalytic efficiency of TiO<sub>2</sub> nanoparticles is improved by doping Cu<sup>2+</sup> metal ions with TiO<sub>2</sub> [6]. In this article, we present a simple method to synthesize Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles and investigate the decolorizing effect on degradation of methyl orange (MO) dye under UV light irradiation.

### 2. Experimental Methods

#### 2.1 Preparation of TiO<sub>2</sub> Nanoparticles

Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles are prepared by hydrolysis of TTIP (titanium tetra-isopropoxide) by deionized water. In this procedure, the suitable amount of doping material (Cu<sup>2+</sup>, 1 & 3 wt%) dissolved in 10 mL of deionized water is added to 100 mL of ethanol taken in a beaker under room temperature. The mixed solution is stirred well up for ten minutes. Now the pH of the solution is adjusted in the acid range by using nitric acid. Then 15 mL of TTIP is added dropwise to the mixed solution of precursor and metal ions. During the addition TTIP hydrolysis reaction takes place and TiO<sub>2</sub> nanoparticles are obtained in the form of a gel in the beaker. The gel is filtered, dried and calcinated to 500 °C to get rutile crystalline phase TiO<sub>2</sub> nanoparticles. Fig. 1 shows the photograph of the synthesis method of Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles.

#### 2.2 Characterization

The synthesized materials are characterized by various sophisticated techniques. Powder X-ray diffraction (PXRD) is carried out using XPERT PRO diffractometer with diffraction angle 2θ in the range 20-80° using Cu-Kα radiation of wavelength 1.54060 Å. Surface morphology is carried out

using Carl Zeiss SUPRA 55VP model Scanning Electron Microscopy (SEM) instrument. EDS spectra are recorded using JEOL Model JED-2300 Energy Dispersive Spectrometer.



Fig. 1 Photograph of Synthesizing Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

#### 2.3 Study of Photocatalytic Activity

The photocatalytic activity of the Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles is evaluated by the photodegradation of MO aqueous solution with an initial concentration of 1 mg/L. Two UV-A (18 W) fluorescent lamp is used as the light source. The degradation of the solution is analyzed by recording UV-Vis absorption spectra of MO. According to the standard curve between concentration and absorption, the value of  $\left(\frac{C_0 - C_t}{C_0} \times 100\%\right)$  is calculated, denoted as the degradation percentage. Fig. 2 shows the image of the experimental reactor.

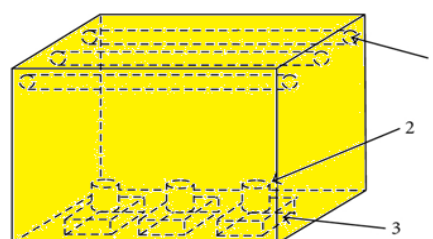


Fig. 2 Image of the Photocatalytic Experimental Reactor (1. UV- lamp, 2. MO solution and 3. stand)

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### 3. Results and Discussion

#### 3.1 Powder X-Ray Diffraction Analysis

Figs. 3 and 4 show the PXRD patterns of 1 and 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles calcinated at 500 °C. Both the samples show similar peaks with various intensities. Sharpening of peaks indicates that the degree of crystallinity is high and the crystallites are higher in size due to calcination [7, 8]. All the peaks are identified and indexed in accordance with the JCPDS file JCPDS 21-1276 of a rutile crystalline structure [9]. Peaks of CuO is not found due to the lower content of Cu. The average crystal size of the Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles have been found out using the most intense reflection (1 1 0) by Debye – Scherrer formula,  $D = 0.89\lambda/b\cos\theta$ , where  $D$  is the mean crystallite size,  $\lambda$  is the wavelength of X-ray,  $\theta$  is the Bragg angle, and  $b$  is the half width of the full maximum [11, 12]. The crystallite size of Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles are found to be 40 and 61 nm for 1 and 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles, respectively which is agrees with the earlier report of Gorska et al. [13].

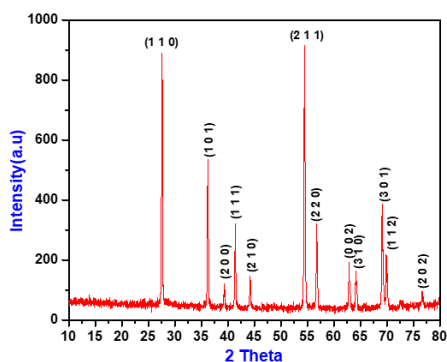


Fig. 3 PXRD pattern of 1 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

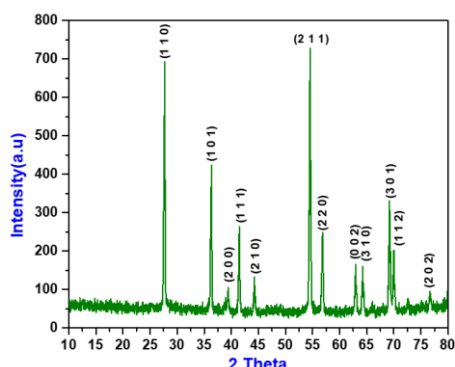


Fig. 4 PXRD pattern of 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

#### 3.2 Scanning Electron Microscopy (SEM) Analysis

Figs. 5 and 6 show the SEM micrograph of 1 and 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles. SEM micrographs show that the synthesized nanoparticles are spherical in shape and are agglomerated nanoclusters. Such a morphology is formerly obtained by Hamadian et al. by the Sol-Gel method [14].

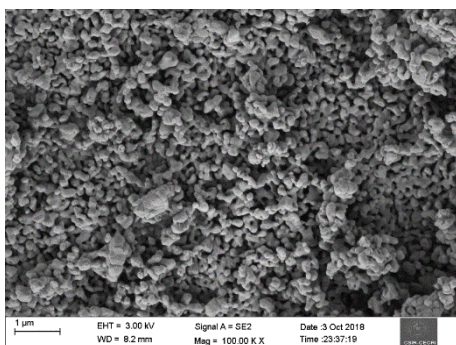


Fig. 5 SEM micrograph of the 1 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

#### 3.3 EDS Analysis

In order to prove the existence of Cu<sup>2+</sup> in the TiO<sub>2</sub> crystal lattice, the EDS spectrum is recorded for 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles. Fig. 7 shows the EDS spectrum of 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles. The <https://doi.org/10.30799/jnst.208.19050110>

peaks of copper exist at 0.9, 8.0 and 8.8 keV. This confirms the incorporation of copper in the TiO<sub>2</sub> crystal lattice. In addition to these high and low intense peaks of Ti and O are clearly arising in the spectrum suggests bulk surface of TiO<sub>2</sub> [14].

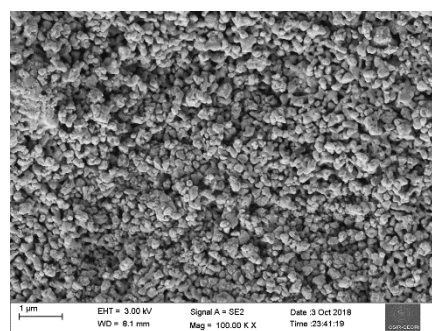


Fig. 6 SEM micrograph of the 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

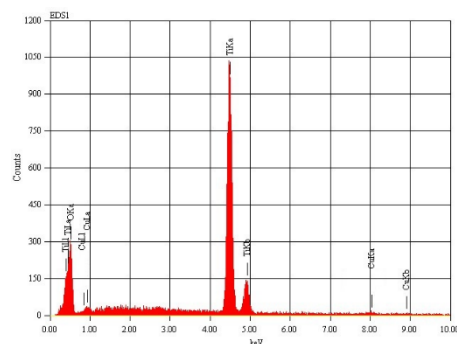


Fig. 7 EDS spectrum of 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

#### 3.4 Photocatalytic Activity Results

The photocatalytic activity of Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles is evaluated by examining the degradation of MO under UV light (18 W, UV-A fluorescent lamp) irradiation. For this typical study, 50 mL of 10 ppm aqueous MO solution is taken in a 100 mL beaker. 100 mg of powdered TiO<sub>2</sub> nanoparticles was dispersed in this solution. The solution is irradiated with UV light up to 210 min. Every 30 min, 5 mL of MO solution is taken out and is centrifuged immediately to remove the catalyst. The degradation efficiency of Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles is viewed through UV-vis absorption spectra of MO solution.

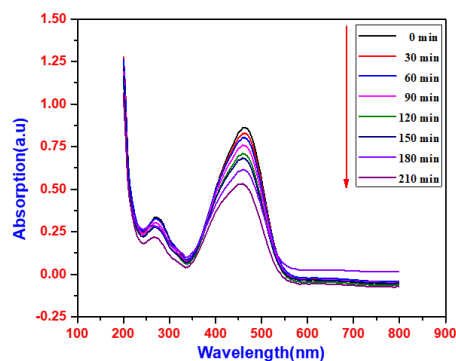


Fig. 8 Absorption spectra of methyl orange in photodegradation assisted by 1 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

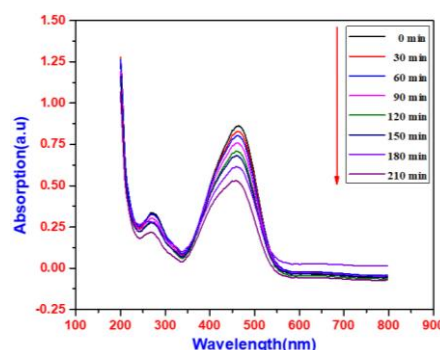


Fig. 9 Absorption spectra of methyl orange in photodegradation assisted by 3 W% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

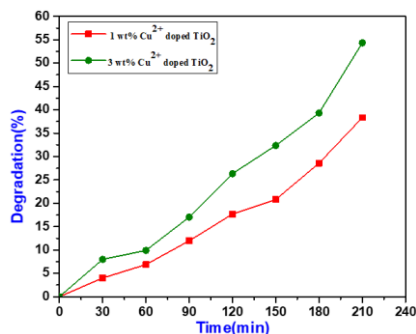
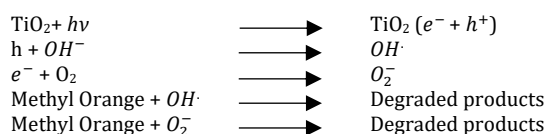


Fig. 10 Photocatalytic efficiency of 1 and 3 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles

Figs. 8 and 9 show the UV-Vis absorption spectra of MO excited with a UV lamp at different intervals of time. Photocatalytic performance of the Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles is tested by the UV light excitation and the results are shown in Fig. 10. It is found that both the Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles show average photocatalytic efficiency. But, 5 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles shows higher degradation of 54%, which is 16% higher than 1 wt% Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles. The photodegradation mechanism of MO by using Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles are proposed as follows [15,16].



UV irradiation of light energy greater than or equal to its band gap falls on Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles excites electrons from a filled valence band to an empty conduction band, supplying electron-hole pairs. The holes in the valence band react with adsorbed OH<sup>-</sup> to produce hydroxyl radicals (OH<sup>·</sup>), whereas the electrons (e<sup>-</sup>) in the conduction band react with O<sub>2</sub> and produce superoxide O<sub>2</sub><sup>-</sup> radicals. The hydroxyl and superoxide radicals react with MO giving rise to degraded products.

According to the earlier report of Hamadani et al. [10] doping with Cu<sup>2+</sup> causes suppression of the electron-hole pair recombination. Furthermore, which could be induced sub-band levels near the bottom of the conduction band and easily trapping photoinduced electrons. Hence, the separation of photoexcited charges could be enlarged, resulting in the enhancement of the photocatalytic activity of TiO<sub>2</sub> under UV irradiation. Thus, the efficiency is improved in our prepared Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles.

#### 4. Conclusion

In summary, rutile phase Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoclusters are successfully prepared by the Sol-Gel method. The result of photocatalytic study proves

the improvement in the photodegradation of MO under UV irradiation for both Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles. Hence, the Cu<sup>2+</sup>-doped TiO<sub>2</sub> nanoparticles synthesized by the Sol-Gel method are the efficient and superior photocatalyst for wastewater treatment.

#### References

- [1] S. Saxena, A.S.M. Raja, A. Arputharaj, Challenges in sustainable wet processing of textiles and clothing sustainability, Textile science and clothing technology, Springer, 2017.
- [2] M.N. Rashed, A.A. El-Amin, Photocatalytic degradation of methyl orange in aqueous TiO<sub>2</sub> under different solar irradiation sources, Int. J. Phys. Sci. 2(3) (2007) 073-081.
- [3] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and TiO<sub>2</sub> assisted degradation of textile dye reactive blue 4, Chemosphere 46 (2002) 1173-1181.
- [4] Z. He, Q. Cai, H. Fang, G. Situ, J. Qiu, S. Song, J. Chen, Photocatalytic activity of TiO<sub>2</sub> containing anatase nanoparticles and rutile nanoflower structure consisting of nanorods, J. Environ. Sci. 25(12) (2013) 2460-2468.
- [5] B.A. van Driel, P.J. Kooyman, K.J. van den Berg, A. Schmidt-Ott, J. Dik, A quick assessment of the photocatalytic activity of TiO<sub>2</sub> pigments-From lab to conservation studio, Microchem. J. 126 (2016) 162-171.
- [6] D.V. Raorane, P.S. Chavan, S.R. Pednekar, R.S. Chaugule, Green and rapid synthesis of copper-doped TiO<sub>2</sub> nanoparticles with increased photocatalytic activity, Adv. Chem. Sci. 6 (2017) 13-20.
- [7] V. Mathew, J. Gim, M.H. Alfaruqi, S. Kim, J. Song, et al., Porous TiO<sub>2</sub> electrode prepared by an energy efficient pyro-synthesis for advanced lithium-ion batteries, J. Electrochem. Soc. 162(7) (2015) A1220-A1226.
- [8] J.T. Moon, S.K. Lee, J.B. Joo, Controllable one-pot synthesis of uniform colloidal TiO<sub>2</sub> particles in a mixed solvent solution for photocatalysis, Beilstein J. Nanotechnol. 9 (2018) 1715-1727.
- [9] D.V. Aware, S.S. Jadhav, Synthesis, characterization and photocatalytic applications of Zn-doped TiO<sub>2</sub> nanoparticles by sol-gel method, Appl. Nanosci. 6 (2016) 965-972.
- [10] Y. Zhao, C. Li, X. Liu, F. Gu, H.L. Du, L. Shi, Zn-doped TiO<sub>2</sub> nanoparticles with high photocatalytic activity synthesized by hydrogen-oxygen diffusion flame, Appl. Catal. B: Environ. 79 (2008) 208-215.
- [11] Q. Zhang, L. Gao, J. Guo, Effects of calcination on the photocatalytic properties of nanosized TiO<sub>2</sub> powders prepared by TiCl<sub>4</sub> hydrolysis, Appl. Catal. B: Environ. 26 (2000) 207-215.
- [12] R. Mohammadi, M. Mohammadi, Photocatalytic removal of methyl orange using Ag/Zn-TiO<sub>2</sub> nanoparticles prepared by different methods, Desal. Water Treat. 2015 (2015) 1-9.
- [13] P. Gorska, A. Zaleska, E. Kowalska, T. Klimczuk, J.W. Sobczak, E. Skwarek, et al., TiO<sub>2</sub> photoactivity in visibility and UV light: The influence of calcination temperature and surface properties, Appl. Catal. B: Environ. 84 (2008) 440-447.
- [14] M. Hamadani, A. Reisi-Vanani, A. Majedi, Synthesis, characterization and effect of calcination temperature on phase transformation and photocatalytic activity of Cu, S-Co doped TiO<sub>2</sub> nanoparticles, Appl. Surf. Sci. 256 (2010) 1837-1844.
- [15] Y. Su, Y. Yang, H. Zhang, Y. Xie, Z. Wu, et al., Enhanced photodegradation of methyl orange with TiO<sub>2</sub> nanoparticles using a triboelectric nanogenerator, Nanotechnol. 24 (2013) 295401.
- [16] P.P. Subha, M.K. Jayaraj, Solar photocatalytic degradation of methyl orange dye using TiO<sub>2</sub> nanoparticles synthesised by sol-gel method in neutral medium, Jour. Exp. Nanosci. 10(14) (2015) 1106-1115.