

SYNTHESIS OF Cu/TiO₂ NANOCOMPOSITE BY GAMMA IRRADIATION FOR ENHANCED PHOTOCATALYTIC ACTIVITY

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ABSTRACT

TiO₂ doped with copper nanoparticles (Cu/TiO₂) was prepared by γ -irradiation method. The Cu/TiO₂ nanoparticles were characterized using X-ray diffraction, transmission electron microscopy (TEM) and diffuse reflectance spectra (DRS). The photo-catalytic degradation of rhodamine B (RB) in the aqueous suspensions of TiO₂ and Cu/TiO₂ under visible light was carried out. Results showed that Cu/TiO₂ catalysts was found to enhance photo-degradation efficiency of rhodamine B compared to pure TiO₂. At 3.0% Cu content, the Cu/TiO₂ photocatalyst exhibited the highest visible light photocatalytic activity. The higher activity of copper doped TiO₂ is due to the enhancement of electron-hole separation by the electron trapping of copper particles.

Keywords: TiO₂; copper; nanoparticles; photocatalytic; γ -irradiation; rhodamine B.

1. INTRODUCTION

The nano-TiO₂ photocatalyst is a well-known photocatalyst among the metal oxides recognized for its high efficiency, low cost, physical and chemical stability, widespread availability, and noncorrosive property [1]. However, its band gap (3.0–3.2 eV) can capture UV light only. One of the most efficient ways to improve photocatalytic activity of TiO₂ is the generation of defects in the lattice through selective metal or nonmetal doping which decreases the band gap energy, and as a result shifts the absorption band to the visible range [2, 3].

Recently, different routes have been used to enhance the photocatalytic activity of TiO₂. One of routes is to modify the surface of TiO₂ by doping it with another metal. In this case, the doping metal acts a trap to collect photogenerated electrons from the conduction band of the TiO₂ semiconductor, and hence it preven the recombination of photogenerated electrons and holes by increasing the charge separation.

Metal dopants have been used to improve the morphology and photocatalytic activity of nano-doped-TiO₂. In previous

studies, various metal dopants, including cobalt (Co) [4], barium (Ba) [5], manganese (Mn) [6], nickel (Ni) [7], copper (Cu) [8], zinc (Zn) [9], and iron (Fe) [9] have been analyzed for their abilities to enhance the photocatalytic performance of nano-doped-TiO₂.

Many methods have been developed to synthesize metal doped TiO₂ included precipitation [10], hydrothermal, solvothermal [11], chemical vapour deposition [12], and electrospinning [13]. There is no report regarding the synthesis of Cu/TiO₂ by gamma irradiation. Compared with other methods, gamma irradiation has many advantages: radiolysis is a powerful method to synthesize nanoparticles of controlled size and shape in solutions and on supports [14, 15], which can be carried out at room temperature by simply using there reducing agent in a one pot reaction, having no further treatment requirement for the product [16].

Because of the above reasons, this study focused on the doping of Cu nanoparticles on TiO₂ using gamma irradiation. The structure and photocatalytic activity under simulated visible light irradiation of Cu/TiO₂ are also discussed.

2. EXPERIMENTAL

2.1 Material

Titanium dioxide nanoparticle used in experiments was TiO₂ with a particle size of 21 nm, was purchased from Degussa chemical company, Germany. Copper (II) sulfate pentahydrate were used as dopant from China and ethanol, rhodamine B dyes was purchased from China.

2.2 Catalyst preparation

Copper doped TiO₂ was prepared by γ irradiation method. Firstly, 4 g TiO₂ was added to 170 mL of distilled water and 30 mL ethanol, CuSO₄ were then added to TiO₂ suspension with different concentrations of dopant (1.0; 2.0 and 3.0 wt%). The mixture was irradiated by γ -irradiation on a γ -⁶⁰Co for reduction of Cu²⁺. After that, the TiO₂ doped with Cu photo-catalyst was separated by centrifugation, washed by distilled water and dried at 60°C.

2.3 Characterization of Cu/TiO₂

The XRD pattern of TiO₂ and Cu/TiO₂ was measured on D8 Advanced, Bruker, Germany using a Cu K α ($\lambda = 0.15418$ nm), recorded in the $2\theta = 20-70^\circ$. The size of Cu/TiO₂ catalyst was measured by TEM images on a JEM 1010, JEOL, Japan. The DRS of the samples was obtained using JASCO V550 model UV-vis spectrometer to determine the optical band gap (E_g) of catalysts.

The band gap energies (E_g) of all samples were calculated by the following equation Eq. (1)

$$E_g \text{ (eV)} = 1240 / \lambda \text{ (nm)} \quad (1)$$

2.4 Photocatalytic degradation activity of the catalysts

Photocatalytic degradation process occurred in glass reactor using 500 W halogen lamp as a visible light source. In the experiment, 50 mg of catalysts were added to 50 mL dye solution (10⁻⁵M). The suspension was stirred for 1 hour in darkness to achieve the adsorption – desorption

equilibrium of dye. Then, it was irradiated by halogen lamp. At certain time intervals, the aqueous suspension was centrifuged for 15 min and 6000 rpm to separate photocatalyst and dye solution. Dye concentration was analyzed by a UV-vis spectrophotometer (UH5300, HITACHI).

The degradation of rhodamine B was measured by UV-vis spectrophotometer at 554 nm.

3. RESULTS AND DISCUSSION

3.1 Characterization of the photocatalysts

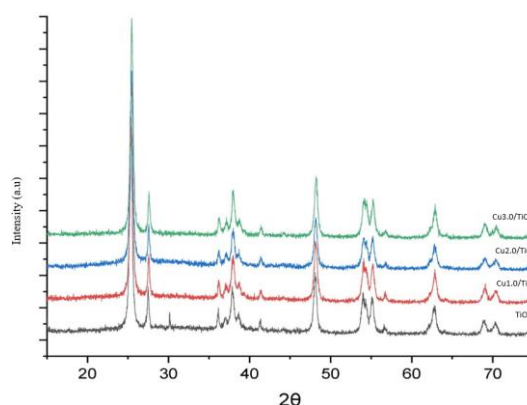


Fig. 1. XRD patterns of TiO₂; Cu1.0/TiO₂; Cu2.0/TiO₂; Cu3.0/TiO₂

Figure 1 shows the XRD spectrum of TiO₂ and Cu/TiO₂. The peaks at 2θ value of 25.3°, 37.8°, 48.0°, 55.1°, 62.6°, 68.7° and 70.2° corresponding to the crystal planes of (101), (004), (200), (211), (204), (220) and (220), respectively indicates formation of anatase titanium dioxide. The standard peaks of rutile can be observed at 2θ values of 27.45°, 36.09°, 54.32°, corresponding to the crystal planes of (110), (101), (211), respectively [JCPDS card no 21-1272]. In addition, there are no typical peaks for Cu, because of the low content of Cu below the detection limit.

Figure 2 indicates TEM image of TiO₂ and Cu3.0/TiO₂ catalyst, the TEM images of TiO₂ (Fig.2a) showed that the morphology of the TiO₂ was uniform and the average diameter of TiO₂ was ~20–40nm. The morphology of TiO₂ did not change after the irradiation process. TEM of Cu3.0/TiO₂ sample indicated small, black and uniform

dots corresponding to Cu nanoparticles, loaded on the TiO_2 surface.

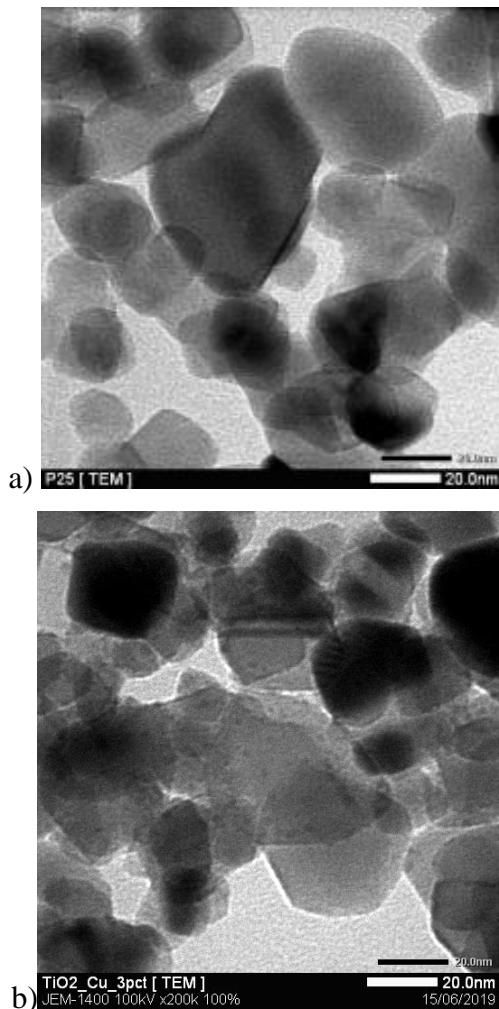


Fig. 2. TEM image of TiO_2 (a) and $\text{Cu}_{3.0}/\text{TiO}_2$ (b)

The UV-Vis spectral of the pure TiO_2 and Cu/TiO_2 catalysts shown on figure 3. It was found that absorption spectrum of Cu/TiO_2 samples has shifted to visible light compared to TiO_2 . Hence, the reduction of the TiO_2 band gap was due to the Cu-doped into the lattice of TiO_2 , and consequently enhanced the visible-light absorption capability of the photocatalysts. On the other hand, the band gap energy (E_g) of TiO_2 and Ag nano/ TiO_2 are shown in table 1. E_g of Cu/TiO_2 catalysts were lower than pure TiO_2 , which allow the delay in recombination rate and enhance the photocatalytic activity. Thus, nanosized metal colloids such as copper show a very intense surface plasmon absorption band in

the visible region. As the results, the addition of Cu to the TiO_2 effectively improved the activity of the catalyst in the visible light irradiation.

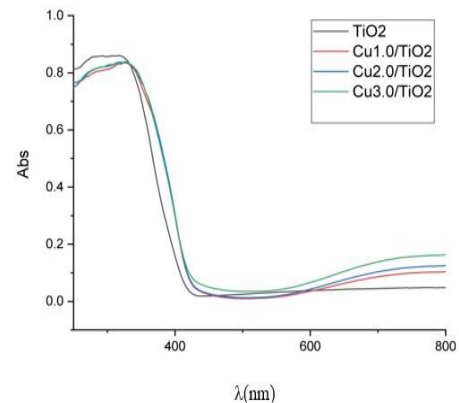


Fig. 3. UV-vis diffuse reflectance spectra (DRS) of pure TiO_2 and Cu/TiO_2 photocatalysts.

Table 1. Band gap (E_g) of original TiO_2 and modified TiO_2 catalysts.

Sample	Band gap E_g (eV)
TiO_2	3,4220
$\text{Cu}_{1.0}/\text{TiO}_2$	3,1822
$\text{Cu}_{2.0}/\text{TiO}_2$	3,1125
$\text{Cu}_{3.0}/\text{TiO}_2$	3,1204

3.2 Photodegradation studies

Figure 4 shows that Cu-doped TiO_2 exhibits photocatalytic activity much efficiently than pure TiO_2 in the visible region. It was found that rhodamine B dye undergoes decolorization effectively in the presence of Cu doped TiO_2 with 3.0 wt.% dopant when compared to 1.0 and 2.0 wt.% Cu dopant. The end conversion of RB is 76%. $\text{Cu}_{3.0}/\text{TiO}_2$ sample has photodegradation efficiency of RB higher than the original TiO_2 sample about 18%. The photocatalytic activity was found to be strongly influenced by the amount of Cu. Because, under the gamma radiation, Cu^{2+} has been reduced to metal Cu and incorporated into the TiO_2 lattice structure, thereby reducing the band gap energy. A part of the metal Cu on the TiO_2 surface will form electron traps that prevent the recombination of the photogenerated electron-hole pair.

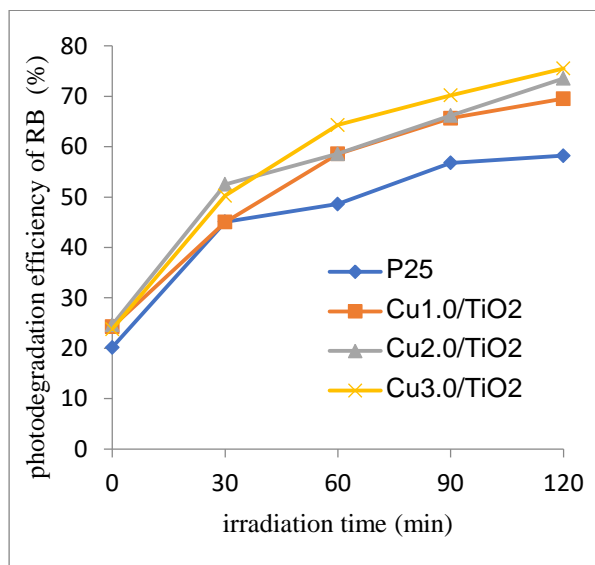


Fig. 4. Comparison of the Rhodamine B photodegradation with pure TiO₂ (P25), and Cu/TiO₂ under visible light irradiation.

4. CONCLUSION

Cu/TiO₂ were successfully synthesized by gamma irradiation. The Cu/TiO₂ catalysts synthesized had the band gap smaller than original TiO₂, which lead to having a higher photocatalytic activity than TiO₂. Among all synthesized catalysts, the TiO₂ modified with 3.0% Cu (w/w) showed the highest photocatalytic activity under visible light, eliminated 76% RB after a 120-min irradiation.

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