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# Photocatalytic Activity of Cu Doped $TiO_2$ Synthesized by Sonochemical Method

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***ABSTRACT:*** *Undoped and cu doped $TiO_2$ nanopowders were synthesized by the sonochemical method. The physical and chemical properties of the prepared photocatalysts were characterized by XRD, FTIR and SEM. XRD analysis showed the formation of $TiO_2$ rutile phase in both cases. IR analysis indicated the involvement of hydroxyl groups on copper adsorption. Rods like shapes were inferred from SEM image. In addition, the prepared nanopowders were evaluated for photocatalytic activity. The photocatalytic tests indicated that the Cu doped $TiO_2$ nanoparticles showed high photocatalytic activity in degradation of methyl orange, which could be attributed to the creation of oxygen vacancies, increase the concentration of •OH radicals in the solution, which is beneficial for improving the photo degradation rate of organic compounds.*

## I. INTRODUCTION

Photocatalysis is a good potential method since it has a great potential for the energy conversion and for the decomposition of pollutants in air and water [1]. In recent years, various materials have been used for photocatalytic processes [2]. Titanium dioxide ($TiO_2$) as a photocatalyst has gained more importance because of its excellent capability of degrading a large variety of environmental contaminants [3]. Sonochemical reaction methods have been proven as a resourceful and capable technique for generating a various metal oxide. Karimipour *et al.* reported that the basic properties of $TiO_2$ powders doped with various transition metals such as Cu, Ni, and Fe [4]. In the present work, copper doped $TiO_2$ nanoparticles were synthesized by the sonochemical reaction method. Structural and morphological properties of the prepared copper doped $TiO_2$ nanoparticles were studied. In addition the photocatalytic activity of the prepared copper doped $TiO_2$ nanoparticles was also scrutinized.

## II. MATERIALS AND METHODS

### *2.1. Synthesis of Pure and Copper Doped $TiO_2$ nanoparticles*

All the glasswares were thoroughly washed with double distilled water prior to use. 1M pure $TiO_2$ and NaOH were grinded separately for 15 min in an agate mortar. The obtained fine powder were mixed with 6mL of PEG400 and subjected to further grinding for 30 min. The paste washed with double distilled water. Then the mixed solutions were kept in ultrasound irradiation for 30 min. After 30 min of ultrasonication, ethyl alcohol was added to remove the PEG400. Finally the solution was dried at 70°C for 1 h and calcined at 800 °C for 2 h. Copper doped sample was prepared by the same method mentioned above, with adding $TiO_2$. The synthesized product was subjected to different characterization.

### *2.2. Photocatalytic activity Measurement*

The photocatalytic activity of pure and copper doped $TiO_2$ nanopowders was studied by probing photocatalytic degradation of methyl orange (MO) in aqueous solution under UV irradiation (365 nm). The photo degradation of MO was employed to evaluate the photocatalytic activity. In this experiment 0.0164g of pure $TiO_2$ and copper doped $TiO_2$ was added in 10 ml of MO (0.0327g). Experiments were performed at a different UV irradiation time.

## III. RESULT AND DISCUSSION

### *3.1. Structural Study*

The XRD patterns of pure and copper doped $TiO_2$ nanoparticles synthesized using ultrasound irradiation were shown in Fig.1. Cu doped $TiO_2$ results agree well with the standard data (JCPDS 81-1612). The prominent peaks of Cu doped $TiO_2$ were observed at $27.3^{o}$, $33.5^{o}$, $35.5^{o}$, $38.7^{o}$, $48.7^{o}$, $53.3^{o}$, $53.9^{o}$, $56.5^{o}$ and $58.5^{o}$ that correspond to the reflections from (222), (400), (331), (422),(442), (533), (622), (444) and (711) crystal planes show the rutile phase and cubic structure. The peak in the copper doped $TiO_2$ is an increase in the intensity, slightly sharper when compared with pure $TiO_2$. This line width can be used to estimate the size of the particle by using the Scherrer formula. The XRD results show that the average crystalline size is 97.2nm and 99.2nm for pure and Cu doped $TiO_2$, respectively. The particle size of $TiO_2$ increases while doped with Cu.

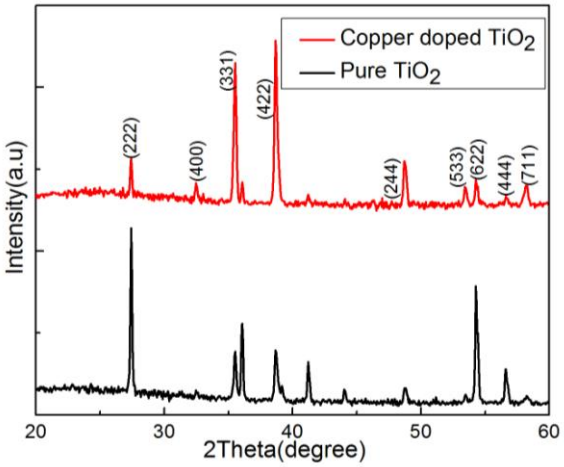


**FIGURE 1.** XRD spectra of pure and Cu doped $TiO_2$

### *3.2. Vibration Studies*

Fig.2 shows that the chemical bonding of the pure and Cu doped $TiO_2$ nanoparticles were scrutinized by mutually related the developed peaks in the spectrum to the vibration or stretching of various functional groups. The broad band around 3417cm$^{-1}$ and 1626cm$^{-1}$, which are observed in the copper doped $TiO_2$ samples were attributed to the stretching and bending vibration of the O-H group [5]. The absorption peak at 734 cm$^{-1}$ is associated with the Cu-O structure. The absorption peak at 476 cm$^{-1}$ and 537cm$^{-1}$ is associated with the Ti-O structure. The IR investigation confirmed that pure $TiO_2$ has a lower amount of surface OH groups than copper doped $TiO_2$.

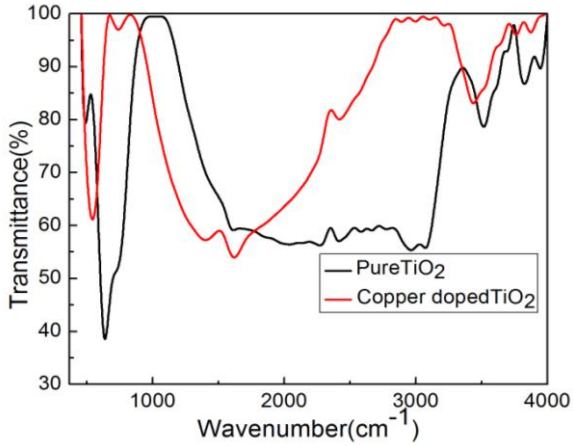


**FIGURE 2.** FTIR spectra of pure and Cu doped $TiO_2$

### *3. 3. Morphological Studies*

Fig. 3(a) and (b) shows SEM images of pure and Cu doped $TiO_2$ respectively. The figure shows the morphology of the prepared photocatalysts. Pure $TiO_2$ is spherical like structure. It shows that the Cu doped $TiO_2$ microstructure has been totally changed and transforms to irregular cylinder rod-like structures and also spherical structures are formed. It clearly indicates that the Cu doped $TiO_2$ shows large crystalline size when compared to pure $TiO_2$.

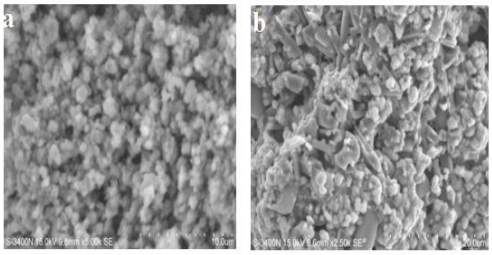


**FIGURE 3.** SEM morphology of (a) pure $TiO_2$ and (b) Cu doped $TiO_2$ nanoparticles.

### *3.4. Photocatalytic Studies*

The photocatalytic activity of Cu doped $TiO_2$, degradation experiments of methyl orange was studied under UV light irradiation. The photocatalytic activity of prepared pure $TiO_2$ and Cu doped $TiO_2$ samples with methyl orange solution at various time intervals for irradiation are not shown in Figure. In our previous articles also reported this type of irradiation method [6]. The photocatalytic degradation of dye with reaction time is a first order as confirmed by using the linear transforms equation

$$\ln (A_t / A_o) = k_{app} \times t \qquad (1)$$

Where $A_o$ is the absorbance value of MO at t=0 and $A_t$ is the absorbance of MO at different irradiation time. Fig. 4 show the plot of rate of decomposition of MO using pure and copper doped $TiO_2$ nanoparticles vs. irradiation time. The $K_{app}$ values of pure $TiO_2$ copper doped $TiO_2$ with MO solution at various time intervals are 0.089 and 0.5 $min^{-1}$respectively. In both cases, pure $TiO_2$ nanoparticles shows a low decomposition rate compared with copper doped $TiO_2$ nanoparticles. Cu dopant could promote the better formation of Cu based oxides. These oxides play a highly potential role in the catalytic process. The photocatalytic activity of copper doped $TiO_2$ has been enhanced, and the formation of oxygen vacancies. These oxygen vacancies directly involved in the photocatalysis processes. These irradiations provide more energy to excite the electrons of Cu doped $TiO_2$ nanoparticles and generates more electron–hole pairs, which improve photocatalytic activity. It can capture the photo-generated holes ($h^+$) and transform to $^{\bullet}OH$ radicals, which are the main reactive species for the decomposition of organic molecules. Therefore, the Cu doped $TiO_2$ nanoparticles were producing more $^{\bullet}OH$ radicals which greatly improve the photocatalytic degradation. The Cu doped $TiO_2$ nanoparticles shows improved photocatalytic activity compare to the undoped $TiO_2$ in direct irradiation.

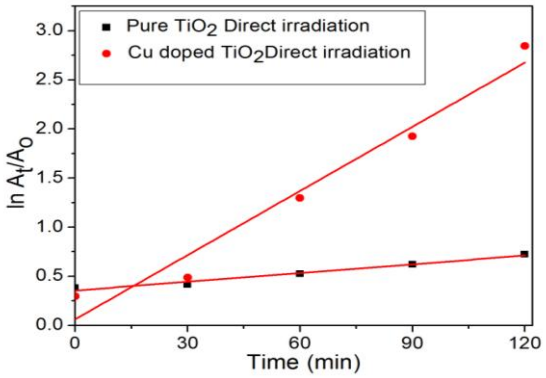


**FIGURE 4.** Rate of decomposition of pure and Cu doped $TiO_2$ nanoparticles **vs.** irradiation time.

## IV. CONCLUSION

Cu doped $TiO_2$ nanoparticles were successfully synthesized by the sonochemical reaction method. XRD, FT-IR and SEM studies proved the prepared $TiO_2$ is doped with Cu. XRD result confirmed that the particle size of the $TiO_2$ increased due to copper doped. Cu doped $TiO_2$ nanoparticles could be attributed to well crystalline rutile phase. The enhanced photocatalytic degradation performance for Cu doped $TiO_2$, it can be attributed to the higher level of surface hydroxyl groups, increased crystallinity and low recombination rate of photogenerated electron - hole pairs. The higher photocatalytic activity has been observed for Cu doped $TiO_2$ irradiation. Copper doped $TiO_2$ nanoparticles were effective in dealing with the environmental problems.

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