

COPPER DOPED TITANIUM DIOXIDE FOR ENHANCING THE PHOTOVOLTAIC BEHAVIOUR IN SOLAR CELL

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ABSTARCT : Pristine and Cu doped titanium dioxide (TiO_2) nanoparticles were prepared by chemical hydrolysis technique. Synthesized TiO_2 was characterized by XRD technique and it reveals that the samples are of tetragonal structure with anatase phase. The spherical morphology of the nanoparticles was observed from SEM. Optical absorbance and emissions were studied using UV–vis and photoluminescence spectra. The absorbance spectrum revealed the increase of band-gap for higher Cu doping from the un-doped TiO_2 leads to enhancing the V_{oc} . J-V measurements reveals that 3% Cu doped TiO_2 shows 18% of efficiency enhancement compared to bare TiO_2 .

Key Words : *Cu-TiO₂, Co-precipitation, X- ray diffraction, PL spectra, J-V measurements.*

1. Introduction

Many huge band gap semiconductors such as ZnO, TiO_2 , SnO_2 , and Nb_2O_5 etc, TiO_2 is the most famous semiconductor material used for the fabrication of dye sensitized solar cells. Due its relatively high reactivity, chemical stability and excellent charge transport ability [1,2] used for the fabrication of dye sensitized solar cells.

The main drawback of pure TiO_2 is its wide band gap (3–3.2 eV); because of which, it absorbs only the UV part of solar radiation that accounts for only 4% of the total solar radiation. Extension of visible portion of light is done through phosphors. Similarly doping is done to reduce the band gap. Here, Cu doped TiO_2 is considered for two reasons. (i) It can effectively alter the band gap of TiO_2 by creating defects and d-band states of Cu in TiO_2 and can act as active trap centre of electrons to reduce carrier recombination [3] and (ii) enhance the photo-catalytic/photo activity [4–6]. Even though lots of works are available in the literature for TiO_2 based dye sensitized solar cell (DSSC). Li Zhou et al. [7] have recently prepared Cu-doped TiO_2 semiconductor avoiding the formation of CuO during hydrothermal process and lowered the conduction band position of TiO_2 , which contribute to increase the short circuit current density of DSSCs. At the optimum Cu concentration of 1.0 at.%, the short circuit current density increased from 12.54 to 14.98

mA cm^{-2} , and full sun solar power conversion efficiencies increased from 5.58% up to 6.71% as compared to the bare DSSC.

Paruchai Pongwan et al. [8] have shown that the Cu-doped TiO_2 exhibited good photocatalytic activity in mineralization of oxalic acid and formic acid under visible light irradiation. Photo-mineralization of oxalic and formic acids under visible light irradiation greatly enhanced photo-activity of 2.0 mol% Cu-doped TiO_2 photo-catalyst compared to bare TiO_2 . The enhanced photocatalytic performance arises from copper ion doping in the TiO_2 structure, leading to an extended photo responsive range, enhanced photo generated charge separation, and transportation efficiency.

2. Experimental technique

A simple co-precipitation technique is followed to synthesize TiO_2 and Cu doped TiO_2 . Undoped and Cu doped TiO_2 nanoparticles (TCUOX where X is the doping concentration (X = 1, 3, 5%)) were prepared by chemical hydrolysis. Titanium (IV) iso-propoxide ($[\text{TiOCH}(\text{CH}_3)_2]_4$) was used as a starting precursor. Typically, 5 ml of $[\text{TiOCH}(\text{CH}_3)_2]_4$ was dissolved in 100 ml of isopropyl alcohol ($(\text{CH}_3)_2\text{CHOH}$) and solution was stirred continuously for 1 h at room temperature. Appropriate amount of $\text{Cu}(\text{NO}_3)_2$ (1, 3, 5%) was added to the TiO_2 precursor solution. After stirring, 400 ml of deionized water was added suddenly to the stock solution. The resultant solution was aged for 3 h, then centrifuged, washed several times with deionized water and ethanol and dried at room temperature for overnight. TCUOX nanoparticles were then obtained when the powder was annealed at 450°C for 2 h in air.

3. Results and discussion

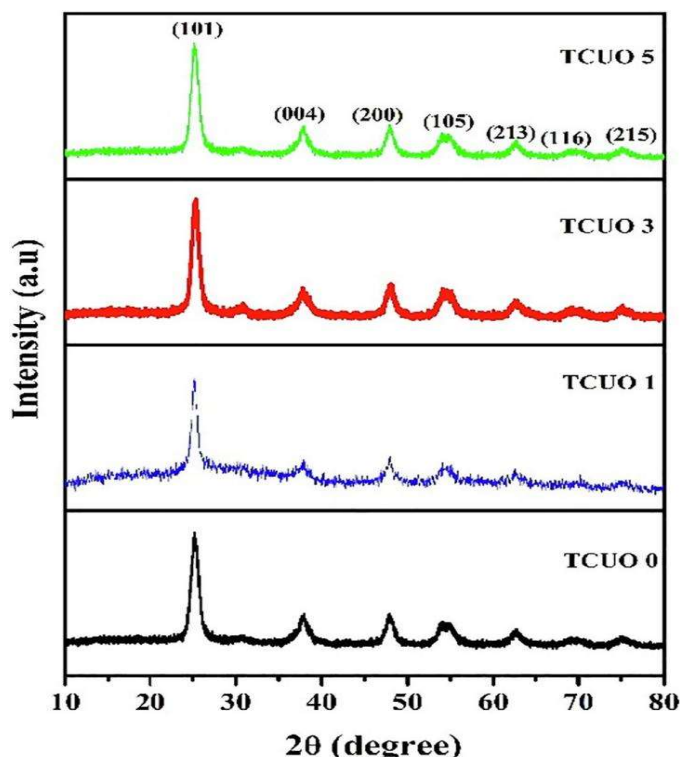


Fig. 1 : XRD spectra for undoped and Cu doped TiO_2 nanoparticles. XRD picture of the TCUOX is shown in **Fig. 1**. The dominant peak is obtained at 25.32°

corresponding to (1 0 1) plane of TiO₂ in anatase phase (JCPDS No.89–4921). The diffraction peaks at 25.32°, 37.7°, 48.0°, 53.9°, 62.3°, 69° and 75.1° are assigned to (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 3), (1 1 6) and (2 1 5) are the crystal planes of TiO₂. The crystallite size of TiO₂ increases when doped with Cu. Furthermore, no characteristics peaks belonging to copper related phase structure are seen, showing that Cu was successfully incorporated into the TiO₂ lattice. This is thermodynamically favourable for these ions to reside in the interstitial positions of TiO₂ lattice [9]. The average crystallite size was in the range 5–7 nm. It is to be noted that there is no signature of CuO in the XRD.

SEM image of the synthesized TiO₂ and TCUO₃ nanoparticles show the particles are spherical in shape which is shown in (Fig.2(a)–(c)) respectively. Moreover, EDAX spectrum is clearly depicts there are no other impurities are presented except Ti, O and Cu which is shown in Fig.2(b) and (d).

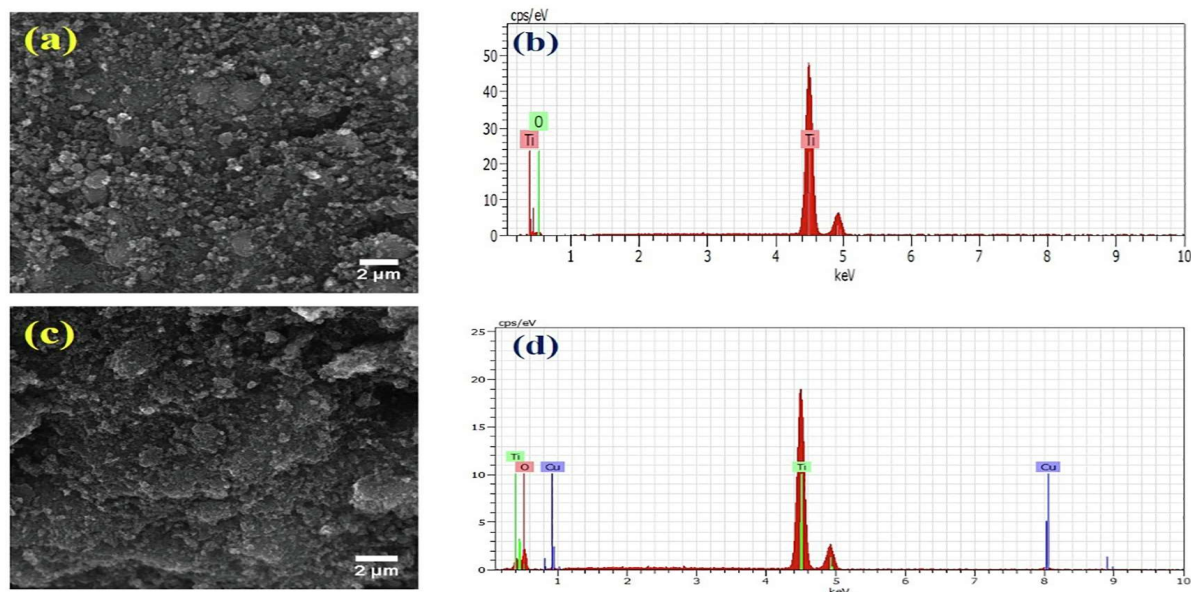


Fig. 2 : SEM images for pure TiO₂ nanoparticles.

Fig. 3(a) shows the UV–Vis spectra of the TCUOX samples. Initially for TCUO1 sample, the absorbance peaks are shifted to higher wavelength side compared to pristine and when to increasing the Cu concentration the peak shifts to lower side means increase in band-gap. The PL spectra of the TCUSX samples are displayed in Fig. 3(b) where a major peak at around 380 nm (violet region) is found, due to the band-to-band recombination. The spectrum of TCUO also shows other small PL peaks at 423 nm (violet emission) and 486 nm (blue emission), which are attributed to the transition from localized surface states to the valence band of TiO₂. The peaks appeared in PL spectra of the TCUOX are observed at the higher wavelength side in TCUO means Cu doping improves the luminescence process.

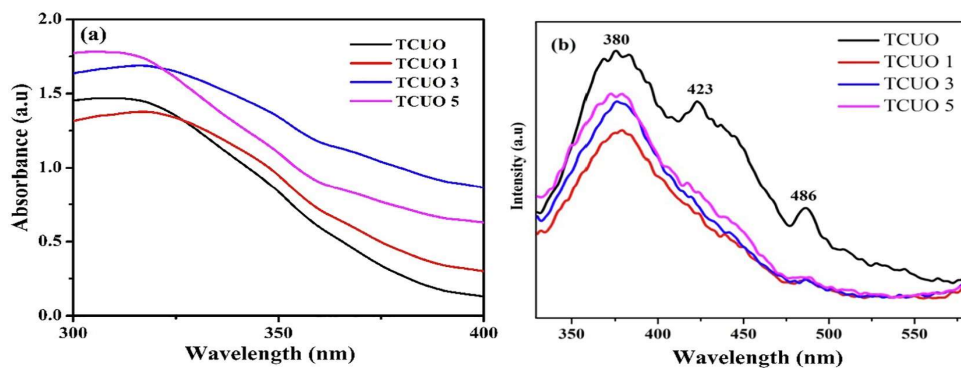


Fig. 3 : (a) UV–vis (b) photoluminescence spectra of synthesized undoped and Cu doped TiO₂ nanoparticles

[Fig. 4](#) shows the current density–voltage curve for TCUOX nanoparticles based solar cells. From the J-V plot the solar cell parameters such as short circuit current (J_{sc}), open circuit voltage (V_{oc}), field factor (FF) and efficiency (η) are calculated and summarized in [Table 1](#). From [Fig. 4](#) it can be seen that, open circuit voltage decreases for 1% Cu doping and increases for 3% and 5% of copper concentration which is due to increases the bandgap leads to increase in Fermi energy which in turn increase V_{oc} . V_{oc} of the DSSCs depends on the energy level of the electrons in the oxide film and the redox potential of the electrolyte [\[10\]](#).

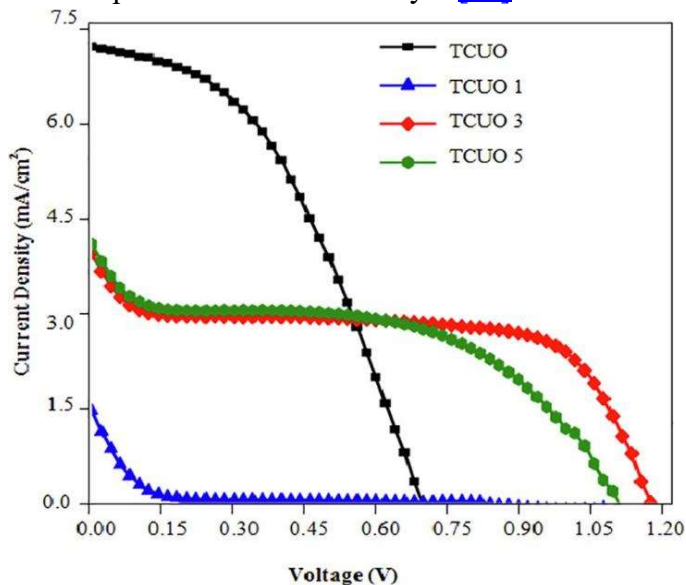


Fig. 4. J-V characterization spectrum of undoped and Cu doped TiO₂ nanoparticles.

If Cu^{2+} ions substitute Ti^{4+} ions at the Ti-lattice sites in TiO₂, the electronic energy level of the oxide film is elevated, which leads to an increase of V_{oc} [\[11\]](#) but there is a decrease in short circuit current which is due to other defects in the oxide film, which causes the recombination of photo induced holes and electrons [\[12\]](#).

Table : 1

Solar cell parameters for un doped and Cu doped TiO₂ nanoparticles.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Efficiency (%)
TCUO	7.215	0.70	0.31	1.75
TCUO 1	0.046	0.90	0.49	0.02
TCUO 3	2.957	1.19	0.62	2.18
TCUO 5	3.053	1.12	0.46	1.57

The slight increase in J_{sc} for TCUO 3 and TCUO 5 samples is mainly due to the conversion luminescence of copper, which facilitates the harvest of more incident light [13]. The optimized 3% Cu doped TiO₂ shows the best power conversion efficiency than pure TiO₂. It again shows that Cu doping could enhance the luminescence process, which the dye N719 can absorb effectively, thereby increasing the sun-light harvesting and the efficiency of DSSC.

4. Conclusion

As Cu could enhance the photo-catalytic activity, an attempt is made here to fabricate a DSSC based on Cu doped TiO₂. Here it is found that even a very simple chemical preparation of this system could yield a good efficiency in line with the works of Li Zhou et al. Now work is in progress to include a phosphor in this system to enhance the efficiency.

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