Chapter 6

**Efficiency Enhancement of DSSC using CuO nanoparticles**

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**Publication**

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6.1 Introduction

Among the oxides of transition metals, copper oxide (CuO) nanoparticles are of special interest. CuO is a semiconducting material with a narrow band gap and used for photoconductive and photo thermal applications. It is a p-type semiconductor with a band gap of 1.2–1.9 eV. TiO$_2$ is a semiconductor that crystallizes in eight polymorphic forms: anatase, rutile, brookite, TiO$_2$-B, TiO$_2$-R, TiO$_2$-H, TiO$_2$-II, and TiO$_2$-III. Anatase and rutile are the most common phases and much more research has been done on their synthesis and applications [1]. TiO$_2$ is one of the most common semiconductors used in DSSCs. The catalytic activity of this semiconductor is well known, focusing on the nature of the semiconductor, one way of achieving improvements in the properties of DSSC is by doping the semiconductor or using TiO$_2$ nanocomposites with different elements. For example, the following elements have been used as dopant e.g. chromium[2], carbon[3], bismuth[4], copper [5–7].

Copper oxide (CuO) is one of the thin films that can easily be deposited on substrates using a simple technique. The first photovoltaic cells observed by Becquerel in 1839 used copper oxide coated metal electrodes immersed in an electrolyte solution Copper oxide [CuO] is an inexpensive and non-toxic semiconducting material[8]. It is a p-type semiconductor with a narrow band gap (1.2 eV), which has interesting photovoltaic, electrochemical and catalytic properties [9]. Likewise, studies have reported the doping of TiO$_2$ for use in DSSCs, can lead to improvements in some of the photovoltaic properties of the cells. Wang and Teng enhanced electron transport in cells doped with zinc under low-intensity illumination [10]. Copper oxide (CuO) nanoparticles (NPs) were employed as electro
catalytic materials for the fabrication of counter electrode in dye sensitized solar cells (DSSCs). The cyclic voltammetry measurement revealed that CuO NPs based thin film showed reasonably good surface for the reduction of triiodide ions in redox electrolyte, suggesting its good electro catalytic activity toward the iodide ions. Moderately high solar to electrical energy conversion efficiency of $\sim 3.4\%$ along with high short circuit current density ($J_{sc}$) of $\sim 8.13$ mA/cm$^2$, open circuit voltage ($V_{oc}$) of $\sim 0.676$ V and fill factor (ff) of 0.62 was recorded in the DSSC fabricated with synthesized CuO NPs based counter electrode [11]. In this chapter, CuONPs, TiO$_2$NPs and CuO-TiO$_2$ nanocomposites were synthesized using sol-gel method, the newly synthesized nanoparticles and nanocomposites were characterized using standard analytical techniques such as X-ray diffraction, UV-Visible Spectroscopy, Scanning Microscopy. The photovoltaic properties were studied in standard conditions.

### 6.2 Experimental details

#### 6.2.1 Synthesis of CuO nanoparticles

The CuO nano particles were synthesized using sol-gel technique. In the typical synthesis, copper nitrate was dissolved in distilled water with a molar ratio of 1:1. The solutions were stirred on magnetic stirrer at 100°C till the formation of gel in 2hrs. The gel was allowed to burn at 200°C. A light fluffy mass was obtained as a result of combustion, which was further annealed at 400°C for 1 hr to obtain crystalline CuO nanoparticles. The synthesized CuO nanoparticles were characterized by XRD, FT-IR, SEM, and UV- Vis. Crystallinity structure and crystallite size were determined by XRD using Rigaku (Tokyo Japan) Miniflex X-ray diffractometer with Cu-K$_\alpha$ radiations ($\lambda = 0.15406$) in the $2\theta$ range from 20° to 80°. FT-IR spectra of the samples were obtained using Perkin Elmer (Waltham, MA) FT-IR spectrophotometer in the KBr matrix. SEM analysis was carried out using a JEOL (Tokyo Japan) scanning electron microscope and UV-Visible spectroscopy was done by Perkin Elmer (lambda – 35) spectrophotometer.

#### 6.2.2 Synthesis of CuO-TiO$_2$ nanocomposite

TiO$_2$ nanoparticles were synthesized using sol-gel method described earlier. The CuO-TiO$_2$ was synthesized by adding 2 mg of CuO nanoparticles to 1.0 g of TiO$_2$ nanoparticles
followed by grinding in mortar for 30 min. The composite was added to 50 ml ethanol and sonicated for 30 min the nanocomposite sample was again grinded till it dries. The same procedure was repeated by varying copper percentage.

6.3 DSSC fabrication

All the samples were stored under dry conditions and in the dark. All experiments were conducted at room temperature (295 K).

To fabricate the photo electrode of the DSSC, 6 g of synthesized TiO₂ nanoparticles were mixed with a solution containing 0.1ml of Triton X-100 (Sigma-Aldrich, USA), 0.2ml of acetyl acetone (Fluka), and 10ml of ethanol to yield a TiO₂ paste. Three drops of the TiO₂ paste were spread on fluorine-doped tin oxide substrate (10 Ω/cm²) masked with the Scotch magic tape (3 M) for an area of 1 cm² by the doctor-blade method. The as-coated glass was preheated at 70°C for 15 min and sintered at 450°C for 30 min. The TiO₂ coated glass was immersed in ruthenium N-719 (Sigma Aldrich) anhydrous ethanol solution for 24 hr in dark. The stained photo electrodes was dried in air for assembling the DSSC. The counter electrode was prepared by distribution of three drops of H₂PtCl₆·6H₂O (Alfa Aesar, USA) on the conducting tin oxide electrode (10 Ω/cm²) with a spin coating at 1500 rpm for 15 sec. The electrodes were preheated at 70°C for 10 min and sintered at 450°C for 10 min. The photo electrode (anode) and counter electrode (cathode) were tied together with a 60 μm thick hot-melt thermal foil as a spacer after introducing iodide/triiodide electrolyte into the cell. A 100mW/cm² solar simulator (Oriel, USA) conjugated with an AM 1.5 Global and Keithley 2450 source meter was employed to measure the I-V characteristics of the DSSC. The illumination was fixed at 100 mW/cm² using a reference solar cell and meter. The same procedure was adopted for CuO-TiO₂ nanocomposite anode. In each experiment, at least five solar cell measurements per sample were carried out to ensure the acceptable data being obtained.
6.4 Results and Discussion

6.4.1 X-ray Diffraction (XRD)

The XRD patterns of pure TiO$_2$ and CuO-TiO$_2$ nanocomposite powders are shown in Figure 6.2. The synthesized nano powders were characterized for crystal phase identification by X-ray diffraction (XRD) in the 2θ range of 20°–80° Rigaku MiniFlex X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu K$_\alpha$ radiations (λ = 1.5418Å) operated at voltage of 30 kV and current of 15 mA. The peaks were indexed by using Powder-X Software. The diffraction peaks for all samples match well with the anatase TiO$_2$ (JCPDS No. 21-1271). The diffraction patterns of all nanocomposite show only the dominant anatase phase of TiO$_2$. The average anatase crystallite size was determined by Debye-Scherer equation as given by,

$$D = \frac{K \lambda}{\beta \cos \theta}$$
Where, \( D = \) crystallite size, \( K = \) shape factor (0.9), \( \lambda = \) wavelength, \( \theta = \) diffraction angle, \( \beta = \) full width at half maximum. The mean size of the crystallites in samples was estimated by the FWHM of the XRD peak (101) using the Debye-Scherer equation.

The strong and sharp diffraction peak at 34.8°, 37.9° indicates the high crystalline quality of CuO, the indexed peak show the Pattern of monoclinic CuO with lattice constant \( a = 4.69 \) Å, \( b = 3.42 \) Å, \( c = 5.13 \) Å, which is in good agreement with the literature values for JCPDS cardno (JCPDS-410254) no crystalline impurity peaks were observed. The average crystallite size was calculated as, 15.4 nm for (111) plane.

The XRD of nanocomposite with varying quantity of CuO as: 0.2%, .5%, 1.0%, 3.0%, 5.0% and 7.0% was recorded. The particle size of pure TiO\(_2\) was 17 nm and increases to 20.1 nm for the nanocomposite up to 3% CuO. Also the decrease in FWHM indicates increase in crystallite size for the nanocomposite the peak corresponding to CuO and TiO\(_2\) were observed. With further increase in , the particle size decreases. Furthermore, peaks were observed at approximately 34.68° and 38.08°. These peaks can be assigned to copper oxide (CuO). It can be seen how the relative intensity of the two diffraction peaks of CuO increases in relation to the main peak of anatase when the percentage of Cu incorporated into the semiconductor increases [12]. It was observed that the crystal structure of TiO\(_2\) remained unchanged after the addition of copper nanoparticles. The nanocomposite have crystallite size ranging from 17 to 20 nm [13] as shown in Table 6.1.
Figure 6.2. XRD pattern of TiO$_2$, CuO and CuO-TiO$_2$ nanocomposites.

Table 6.1. Crystallite size of TiO$_2$, CuO and CuO-TiO$_2$ nanocomposite.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of CuO (%)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0</td>
<td>17.0</td>
</tr>
<tr>
<td>2.</td>
<td>0.2</td>
<td>17.8</td>
</tr>
<tr>
<td>3.</td>
<td>0.6</td>
<td>18.7</td>
</tr>
<tr>
<td>4.</td>
<td>1.0</td>
<td>19.5</td>
</tr>
<tr>
<td>5.</td>
<td>3.0</td>
<td>20.1</td>
</tr>
<tr>
<td>6.</td>
<td>5.0</td>
<td>19.0</td>
</tr>
<tr>
<td>7.</td>
<td>7.0</td>
<td>18.9</td>
</tr>
</tbody>
</table>
6.4.2 Fourier Transform Infrared spectroscopy (FT-IR):

FT-IR analysis was performed to characterize the surface nature of the synthesized CuO nanoparticles and CuO-TiO$_2$ nanocomposite, as depicted in Figure 6.3. A strong absorption peak at 502 cm$^{-1}$ related to the vibrations of the Cu–O functional group. This confirmed the presence of CuO nanoparticles. Peaks appear at 1382 and 1612 cm$^{-1}$ corresponding to CO stretching of Carboxylate ion bond to the CuO nanoparticles [14]. An intense and broad band appeared in the region 3400–3550 cm$^{-1}$ corresponding to the stretching mode of the hydroxyls of adsorbed water molecules since the nanocrystalline materials exhibit a high surface to volume ratio and thus absorb moisture.

![Figure 6.3. FT-IR pattern of TiO$_2$, CuO and CuO-TiO$_2$ nanocomposites.](image)
6.4.3 UV-Vis Spectroscopy

The absorption peak of CuO and TiO$_2$ were observed as 288 nm and 320 nm respectively as shown in Figure 6.4, red shift was observed for CuO-TiO$_2$ nanocomposite.  

The band gap energies of TiO$_2$ and the CuO-TiO$_2$ nanocomposite with varying wt. percent of CuO were estimated from the intersection of the extrapolated linear portion of the curve of $(\alpha h\nu)^2$ vs. photon energy (h\nu), as shown in Figure 6.5. Band gap of TiO$_2$, CuO and CuO-TiO$_2$ nanocomposites

![Absorbance spectra of TiO$_2$, CuO and CuO-TiO$_2$ nanocomposites](image-url)
The band gap observed was 3.2eV for pure TiO$_2$, 2.60 eV and 2.52 eV for 3wt% and 5wt%, CuO, respectively. These results indicate the reduction of the band gap energy with the addition of CuO in TiO$_2$. Similar results pattern were observed by [15]. The red shift of the absorption peak of the CuO-TiO$_2$ nanocomposites shows the dependence on the Cu concentration [16]. It can be inferred that CuO-TiO$_2$ composites present higher photocatalytic activity than pure TiO$_2$ [13]. Since CuO-TiO$_2$ has a relatively smaller band gap than TiO$_2$, active species such as HO, and H$_2$O$_2$ can be generated more easily for CuO–TiO$_2$ under the same UV irradiation. It indicates that CuO–TiO$_2$ has better ability of light absorption when compared with TiO$_2$ [17].
Table 6.2. Band gap of TiO$_2$, CuO and CuO-TiO$_2$ nanocomposites

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Concentration of Cu (%)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0% (Pure TiO$_2$)</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>1.0%</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>3.0%</td>
<td>2.6</td>
</tr>
<tr>
<td>4</td>
<td>5.0%</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>100% Pure Cu</td>
<td>1.6</td>
</tr>
</tbody>
</table>

6.4.4 Photovoltaic Characterization of DSSC

The J-V characteristics of the DSSC is enhanced with the addition of CuO nanoparticles in TiO$_2$ the results are shown in Figure 6.6. The DSSC containing 3.0 % of the CuO exhibits a maximum short-circuit photocurrent density $J_{sc}$ of 10.7 mA/cm$^2$, moderate open-circuit photo voltage $V_{oc}$ of 0.76V and the conversion efficiency of $\eta = 6.52\%$ , i.e. an enhancement of about 20% in as compared to DSSC with pure TiO$_2$ nanoparticles.

The results are shown in Table 6.3.
Figure 6.6. J-V characteristics of DSSC for TiO$_2$ and CuO-TiO$_2$ anode

Table 6.3. Performance parameters of DSSC for CuO-TiO$_2$

<table>
<thead>
<tr>
<th>Anode material</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>Vm (mV)</th>
<th>Im (mA/cm$^2$)</th>
<th>Efficiency (%)</th>
<th>Fill factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO$_2$</td>
<td>0.76</td>
<td>9.6</td>
<td>0.60</td>
<td>7.78</td>
<td>4.67</td>
<td>0.63</td>
</tr>
<tr>
<td>1.0% CuO-TiO$_2$</td>
<td>0.77</td>
<td>10.7</td>
<td>0.68</td>
<td>7.68</td>
<td>5.22</td>
<td>0.63</td>
</tr>
<tr>
<td>3.0% CuO-TiO$_2$</td>
<td>0.76</td>
<td>12.8</td>
<td>0.63</td>
<td>10.35</td>
<td>6.52</td>
<td>0.67</td>
</tr>
<tr>
<td>5.0% CuO-TiO$_2$</td>
<td>0.78</td>
<td>10.0</td>
<td>0.67</td>
<td>7.9</td>
<td>5.53</td>
<td>0.68</td>
</tr>
</tbody>
</table>
6.5 Conclusions:

This study has investigated the effect of addition of CuO in TiO$_2$ for its use as a semiconductor in DSSCs. The particle size of pure TiO$_2$ was 17 nm and increases to 20.1 nm for the nanocomposite up to 3% CuO. Also the decrease in FWHM indicates increase in crystallite size for the nanocomposite the peak corresponding to CuO and TiO$_2$ were observed. It was observed that the crystal structure of TiO$_2$ remained unchanged after the addition of copper nanoparticles. The absorption peak of CuO and TiO$_2$ were observed as 288 nm and 320 nm respectively. The band gap observed was 3.2 eV for pure TiO$_2$, 2.60 eV and 2.52 eV for 3wt% and 5wt%, CuO, respectively. These results indicate the reduction of the band gap energy with the addition of CuO. The presence of CuO leads to decreases in the band gap energy of the semiconductor. The presence of CuO gives appreciable increase in short circuit current, as a result the DSSC efficiency increases from 4.67% to 6.52%.
References:


