Electrochemical Photocatalytic degradation of Brilliant Blue FCF as food dye by CuO–TiO$_2$ nanocomposite under visible and UV-light irradiations

Yuqi Li

Department of Life Science, Lvliang University, Lvliang, 033000, China

E-mail: yuqili30@yahoo.com, liyuqi7868@163.com

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In this work, a simple deposition technique was used to synthesize CuO/TiO$_2$ nanocomposites and their application as photocatalysts for the photodegradation of Brilliant Blue FCF (BBF) under visible and UV-light irradiations were studied. The prepared nanocomposites and their components were investigated in terms of structural, morphological, electrochemical, optical, and photocatalytic degradation properties. When UV–Vis absorbance spectra were used to characterize photocatalysts, it was revealed that the bandgap reduced as the CuO concentration increased. TiO$_2$, CuO-TiO$_2$-0.5, CuO-TiO$_2$-1.5, CuO-TiO$_2$-4 and CuO-TiO$_2$-8 had bandgap values of 3.36, 3.33, 3.31, 3.27, and 3.25eV, respectively, indicating that the band gap narrows with increasing CuO concentration. CuO supplied more electro-active on the surface of TiO$_2$ nanocomposites with greater conductivity, which can function as a catalyst in absorption and electrochemical processes, according to electrochemical tests. Photodegradation tests indicated that 100 mg/l of BBF was completely degraded in the presence of CuO/TiO$_2$ nanocomposites after 60 and 50 min of UV and visible-light irradiation, respectively. These findings suggest that the CuO-TiO$_2$ nanocomposites can be used to degrade BBF with great efficiency when exposed to visible and UV-light irradiation.

Keywords: Photocatalytic degradation; Brilliant Blue FCF; CuO–TiO$_2$ nanocomposite; UV–Vis absorbance; Cyclic voltammetry

1. INTRODUCTION

Photocatalytic degradation of organic and inorganic contaminants utilizing semiconductor metal oxides shows to have been a highly prominent issue in recent years [1, 2]. Dyes represent a key class of aquatic contaminants, which will have beginning to be a substantial cause of environmental pollution [3, 4]. According to the Food and Drug Administration, dye use has risen significantly between 1955 and 2009 [5, 6]. BBF (Bright Blue FCF) is really a food dye that is usually used in ice cream, dessert powders, baked goods, cereals, drinks, and blue raspberry-flavored products, a variety
of dairy products [7-9]. Human and animal health impacts of BBF have been widely recorded, including gastrointestinal cancers, neurological problems, and severe allergies [10, 11]. Since BBF's molecular structure contains three sulfonic acid groups, it is extremely soluble (200 g/L) [12, 13].

Advanced oxidation methods are promising technologies that use reactive radicals like the hydroxyl radical as a starting place. For the degradation of organic pollutants, the photocatalysis technique is recognized as a green approach [14, 15]. A semiconductor is activated via light-irradiation, and electrons migrate from the valence-bond to the conduction-bond while a hole remains in the valance bond, resulting in the generation of free radicals [16, 17].

Because of its appealing properties such as low cost, non-toxic, good safety, high chemical stability, and strong photo-oxidation potential, TiO$_2$ has been selected as an appropriate catalyst among semiconductors [18, 19]. TiO$_2$ has been used as a catalyst for prospective applications such as antibacterial agents, hydrogen generation, self-cleaning surfaces, dye sensitive solar cells, and photocatalytic degradation of dyes because of these capabilities [20-22].

To decrease recombination, the researchers placed the non-metallic semiconductor SiC on the TiO$_2$ surface [23, 24]. Non-metals, like N and C atoms, electron acceptors, and transition metals, have also been added to TiO$_2$ to improve solar light-absorbing [25-27]. CuO as a p-type semiconductor has proved to be an effective co-catalyst in photocatalytic water-splitting and also absorbed visible-light region, making it a suitable choice among metal oxides [28, 29].

In this work, CuO-TiO$_2$ was produced by a simple deposition approach wherein the CuO precursor was applied to TiO$_2$ slurry and placed in a photoreactor for 12 hours. SEM, XRD, CV, and UV-Vis spectroscopy were used to determine the significant difference between TiO$_2$ and CuO/TiO$_2$ nanocomposites. The CuO-TiO$_2$ nanocomposites were then considered for their performance in BBF degradation with a photodegradation experiment under a photoreactor.

2. MATERIALS AND METHODS

Synthesis of CuO-TiO$_2$ nanocomposites was done by the photo-assisted deposition technique. In the first step, TiO$_2$ slurry was made by dissolving 2 grams of TiO$_2$ powders into 150 mL of distilled water and addition of the nitric acid (96%) to reduce the slurry pH to 3 prior sonicating for 35 minutes. In the second step, CuCl$_2$.2H$_2$O was dissolved into 100mL of distilled water with changing mass variations for every sample (0wt%, 0.5wt%, 1.5wt%, 4wt% and 8wt%) and then mixed the solution into TiO$_2$ slurry, mixing it for 40 minutes before adding 50 mL of pure methanol (96%) to the slurry which is indicated as TiO$_2$, CuO-TiO$_2$-0.5, CuO-TiO$_2$-1.5, CuO-TiO$_2$-4 and CuO-TiO$_2$-8, respectively. The slurry is then placed in the photoreactor, where it will be continually irradiated and churned for 5 hours. The slurry is then rinsed until the pH reaches 5 before being separated using a 4000rpm centrifuge for 20 minutes. Finally, the product was kept at 200°C for one hour before being calcined at 300°C.

All photocatalysis tests were carried out in a quartz cylinder reactor with a diameter of 8 cm and a height of 20 cm. The BBF solution was put into the reactor at a volume of 300 mL. KOH and H$_2$SO$_4$ (0.1 M) were used to adjust the pH value of the solution. The solution was mixed using a
mechanical stirrer. The solution was held at 24°C for the duration of the experiment. Two low-pressure lamps (6W) were employed as the UV source in light irradiation, and they were set 2 cm apart on opposite sides of the reactor. Before beginning the photodegradation, the UV lamps were warmed up for 15 minutes. A UV-Vis spectrometer was used to record the BBF's absorption spectra. Monitoring variations in the absorption peaks at 550 nm was used to measure the BBF concentration.

The electrochemical analysis was carried out on an AUTO LAB electrochemical workstation utilizing a traditional three-electrode electrochemical cell with Ag/AgCl as a reference, Pt as a counter, and the produced CuO-TiO₂ nanocomposites on glassy carbon electrodes as working electrodes. In phosphate buffer solutions including 5mM [Fe(CN)₆]³⁻/⁴⁻, CV measurements were performed. The surface morphology of CuO-TiO₂ nanocomposites was studied using scanning electron microscopy (SEM). The samples' X-ray diffraction (XRD) measurements were performed using a Shimadzu, Japan, D/max 2550Pc automated diffractometer of polycrystalline (CuKα radiation) that worked at 40keV and 100mA at 0.02°/s scanning rate.

3. RESULTS AND DISCUSSION

Figure 1 indicates the SEM images of TiO₂ and CuO-TiO₂-4 nanocomposites which indicate the closely uniform morphology of both samples. Because charge carriers have little effect on the particle size and aggregate of every nanocomposite specimen, the surface area of the CuO-TiO₂ must not change considerably. In particular, it can be deduced that the larger amount of CuO precursors added to the nanocomposites, the further CuO is deposited in TiO₂, resulting in a slight reduction in the nanocomposite's surface area [30].

![Figure 1. SEM images of (a) TiO2 and (b) CuO-TiO2-4 nanocomposites](image)

Figure 2 shows the XRD patterns of the as-synthesized samples. The powder materials' peaks are linked to their corresponding crystal planes. The anatase TiO₂ can be accurately ascribed to all diffraction peaks since they are well dunned (JCPDS-21-1272). The photoactivity of anatase TiO₂ nanoparticles was previously known to be high, making them useful for water treatment and
purification [31]. The XRD pattern revealed no distinctive peaks associated with other crystalline forms, suggesting that the product is anatase phase-pure. As shown in Fig. 2, the primary structure of TiO2 is anatase and rutile, with the CuO peak appearing at a loading of 8wt% at 2Ө about 36° [32].

Figure 2. XRD patterns of the as-synthesized samples

Figure 3a shows the UV-visible absorption spectra of CuO-TiO2 nanocomposites with different CuO content at wavelengths ranging from 300 to 900 nm. Because of electrical transitions from the valence band to the conduction band in TiO2, the absorption spectra show an absorption edge of about 330 nm [33]. When the absorption spectra of TiO2 and CuO-TiO2 nanocomposites are compared, the redshift of the absorption edge may be attributed to the decreasing band gap value of CuO-TiO2 due to CuO's lower Fermi level than TiO2 [34]. Furthermore, when the amount of CuO in the TiO2 matrix grows, the redshift rises, which is consistent with other studies [35, 36]. Additionally, increasing the CuO concentration in TiO2 increases the absorption value, which could be attributed to additional photon absorption sites.

Figure 3b displays the Tauc plots of nanocomposites for determining their optical bandgap (Eg) using the UV-vis absorption spectrum measured and the Tauc equation as follows [37]:

\[(\alpha h\nu)^2 = A(h\nu - E_g)\]  \hspace{1cm} (1)

Where \(\alpha\) shows absorption coefficient, \(A\) represents constant, and \(h\nu\) indicates the photon energy. Extrapolating the linear portion of the curve toward the x-axis gives the Eg values. From the Tauc curves in Figure 3b, the Eg values are found TiO2, CuO-TiO2-0.5, CuO-TiO2-1.5, CuO-TiO2-4 and CuO-TiO2-8 nanocomposites are found at 3.36, 3.33, 3.31, 3.27, and 3.25eV, respectively. As a result, as the concentration of CuO increases, the Eg values of CuO-TiO2 nanocomposites decrease. CuO may be incorporated into the TiO2 structure, resulting in orbitals with intermediate energy levels and electronic interaction between Cu orbital states and O 2p and Ti 3d bands in TiO2. CuO-TiO2 nanocomposites with high electronic coupling might generate strong bonds between CuO atoms and
TiO\textsubscript{2} oxygen [38]. CuO-TiO\textsubscript{2} nanocomposites have lower Eg values, making them better choices for photocatalytic activity in visible light.

![Figure 3](image)

Figure 3. (a) UV-visible absorption spectrum and (b) Tauc plots of TiO\textsubscript{2}, CuO-TiO\textsubscript{2}-0.5, CuO-TiO\textsubscript{2}-1.5, CuO-TiO\textsubscript{2}-4 and CuO-TiO\textsubscript{2}-8.

Figure 4 shows the CVs of CuO-TiO\textsubscript{2} nanocomposites with various CuO contents in 0.1M PBS (pH 7) with 5mM [Fe(CN)\textsubscript{6}]\textsuperscript{3−/4−} as redox-active material at 20 mV/s scan rate. As shown, the cathodic and anodic peak currents are 0.03 and 0.08V for CuO-TiO\textsubscript{2} nanocomposites, respectively. Because conductivity improves with increasing CuO content in TiO\textsubscript{2}, the current of redox peaks rise, resulting in greater electron transport and charge separation [39, 40]. The decreased charge-transfer resistance can significantly improve the interfacial charge-transfer procedure and contribute more to increased photocatalytic activity by facilitating charge transfer. As a result, as compared to pure TiO\textsubscript{2}, the CuO-TiO\textsubscript{2} nanocomposites may have higher photocatalytic activity.
Figure 4. CVs of CuO-TiO$_2$ nanocomposites with various CuO contents in 0.1M PBS (pH 7) with 5mM [Fe(CN)$_6$]$_{3/4}^-$ as redox-active material at 20 mV/s scan rate.

Figure 5. The photocatalytic degradation of 100 mg/l BBF in solution containing KOH and H$_2$SO$_4$ (0.1 M) by CuO-TiO$_2$ nanocomposites with various CuO contents under (a) UV-light and (b) visible-light irradiations in at room temperature.

In room temperature visible and UV-light irradiations, the photocatalytic degradation of 100 mg/l BBF in solution containing KOH and H$_2$SO$_4$ (0.1 M) by CuO-TiO$_2$ nanocomposites with various CuO contents were examined. CuO-TiO$_2$ nanocomposites have a greater degradation efficiency than pure TiO$_2$, as shown in figure 5a. After 60 minutes of UV irradiation, the CuO-TiO$_2$-8 sample had a maximum degradation efficiency of 100%. Figure 5b indicates that increasing CuO content in
nanocomposites increases sample degradation efficiency under visible light irradiation. After 50 minutes of visible irradiation, the CuO-TiO$_2$-8 nanocomposites were completely degraded. The results indicate that CuO-TiO$_2$-8 sample has higher photocatalytic activity ~37% and 41% compared to that of pure TiO$_2$ under UV and visible-light irradiations, respectively. These results show that CuO can enhance the photocatalytic activity of BBF degradation under UV and visible-light irradiations. CuO has a lower Fermi level than TiO$_2$, meaning that it serves as an accumulation center for photo-induced electrons in TiO$_2$ [41]. For CuO-TiO$_2$-8 specimen, the number of CuO is optimal and the photo-induced electrons remarkably transfer to the CuO. Because photo-generated electrons and holes may be held by adsorbed oxygen to create reactive species superoxide, these accumulation sites can operate as routes for electron separation, lowering the recombination rate of photo-generated holes and electrons [42, 43]. Furthermore, these electrons may react with Ti$^{4+}$ onto a photo-catalyst surface, forming Ti$^{3+}$ reactive sites.

**Table 1.** Comparison of the obtained results for degradation efficiencies of BBF in CuO-TiO$_2$ nanocomposites with other reported photocatalysts

<table>
<thead>
<tr>
<th>Material</th>
<th>BBF content (mg/l)</th>
<th>Light source</th>
<th>Degradation time (min)</th>
<th>Degradation efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-TiO$_2$</td>
<td>100.00</td>
<td>UV visible</td>
<td>60</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Persulfate/zero valent iron</td>
<td>20.00</td>
<td>visible</td>
<td>30</td>
<td>98.9</td>
<td>[44]</td>
</tr>
<tr>
<td>Ag-doped ZnO</td>
<td>70.00</td>
<td>UV visible</td>
<td>70</td>
<td>49.8</td>
<td>[45]</td>
</tr>
<tr>
<td>Ag$_2$O-decorated ZnO</td>
<td>100.00</td>
<td>visible</td>
<td>30</td>
<td>94</td>
<td>[46]</td>
</tr>
<tr>
<td>Tungsten doped TiO$_2$</td>
<td>100.00</td>
<td>sunlight</td>
<td>180</td>
<td>93.25</td>
<td>[47]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>20.00</td>
<td>visible</td>
<td>200</td>
<td>88</td>
<td>[48]</td>
</tr>
</tbody>
</table>

In Table 1, the findings of this study was compared to those of other photocatalysts for BBF degradation efficiency. The comparison reveals that CuO-TiO$_2$ nanocomposites have high photocatalytic activity for the degradation of BBF under visible-light irradiation, which can be ascribed to the synergistic effect of porous structure, which helps facilitate electron-transfer inside the interface between CuO and TiO$_2$, as well as oxygen vacancies and plentiful anatase, which can enhance charge separation in CuO-TiO$_2$ nanocomposites [49].

4. CONCLUSIONS

This research focused on a simple deposition method for synthesizing CuO/TiO$_2$ nanocomposites and their application as photocatalysts for the photodegradation of Bright Blue FCF (BBF) under visible and UV-light irradiations. The prepared nanocomposites and their components
were studied in terms of structural, morphological, electrochemical, optical, and photocatalytic degradation properties. When UV–Vis absorbance spectra were used to characterize photocatalysts, it was revealed that the bandgap reduced as the CuO concentration increased. TiO$_2$, CuO-TiO$_2$-0.5, CuO-TiO$_2$-1.5, CuO-TiO$_2$-4 and CuO-TiO$_2$-8 had bandgap values of 3.36, 3.33, 3.31, 3.27, and 3.25eV, respectively, indicating that the band gap narrows with increasing CuO concentration. CuO supplied more electro-active on the surface of TiO$_2$ nanocomposites with greater conductivity, which can function as a catalyst in absorption and electrochemical processes, according to electrochemical tests. Photodegradation tests revealed that 100 mg/l of BBF was completely degraded in the presence of CuO/TiO$_2$ nanocomposites after 60 and 50 min of UV and visible-light irradiation, respectively. These findings suggest that the CuO-TiO$_2$ nanocomposites can be used to degrade BBF with great efficiency when exposed to visible and UV-light irradiation.

References

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