Co-Cu-codoped TiO$_2$ Nanoparticles for Photocatalytic Application under visible irradiation

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Abstract. Cobalt & Copper doped Co$_x$Cu$_{0.05}$Ti$_{1-x}$O$_2$; $x = 0.04$, $0.08$ & $0.12$ mol % nanoparticles have been prepared by sol-gel technique and characterized by X-ray diffraction, Electron dispersive X-ray spectroscopy, UV-visible spectroscopy, Fourier transform infrared and Field-emission scanning electron microscopy. The X-ray diffraction and EDXS measurements confirm the formation of anatase phase of TiO$_2$ nanoparticles. The average particle size of the prepared nanoparticles was calculated from X-ray diffraction using Debye Scherrer’s formula and found to be 16.4, 14.9, 13.1 nm respectively. The absorption edge in observed UV–Vis absorption spectra shifted to higher wavelength region correspond to blue shift indicates the decrease in band gap energy from 2.87eV to 1.90 eV on increasing cobalt concentration. The presence of strong chemical bonding and functional groups present at the interface of TiO$_2$ nanoparticles observed in FTIR spectra confirm the formation of stable anatase phase of TiO$_2$ nanoparticles. The photocatalytic activities of the prepared samples for methyl orange (MO) and congo red (CR) was investigated under visible light irradiation. It is observed that increase in dopant concentration enhance the photocatalytic activity is attributed to narrow band gap and increase in surface area of the synthesized nanoparticles.

1. INTRODUCTION

The industrial revolution is putting negative impacts on the entire globe due to increase in various hazardous compounds in waste water discharges by various printing, dyeing, textile and other chemical industries [1]. Azo dyes released from textile industries are one of the major pollutants disturbing the environment [2]. The presence of these Azo dyes in natural water is extremely harmful as these are non-biodegradable, toxic, and carcinogenic in nature and pose hazardous risk to environment [3]. Therefore these organic pollutants of industrial waste need to be treated before discharge to the water source [1]. Photocatalysis is emerges as an economical, environmental friendly and destructive technology in which solar energy converts into chemical energy leading to the total mineralization of organic contaminants [4–6]. In recent year’s titanium dioxide (TiO$_2$) as photocatalyst have received immense research interest because of its efficiency in decomposing and mineralizing the hazardous organic and inorganic pollutants from contaminated water [7]. A growing interest in synthesis of TiO$_2$ nanoparticles is due to the high surface to volume ratio that causes the structural and electronic changes responsible for enhance in other properties different from their bulk counterpart [8]. Several conventional techniques have been used for the synthesis of pure and doped titanium dioxide nanoparticles [9]. Sol–gel technique is one of the most preferable technique generally used for synthesis of nanomaterials at low temperature which permits tailoring of certain desired properties [10–11]. The use of TiO$_2$ for photocatalytic application is limited first due to its large band gap (Eg = 3.2 eV) which makes it active only under ultraviolet (UV) light available about 5% of the total solar spectrum and second due to the rapid recombination of photogenerated electron-hole pairs as a result a small part of the excited carriers can move to the surface of TiO$_2$ which further reduces photocatalytic efficiency [12–13]. To extend the photocatalytic response to visible region, transition metal (Cu, Fe, Cr, Mn, Co, Ni, etc.) are to be doped in TiO$_2$ nanoparticles to restrain electron-hole
recombination during migration from inside of the material to the surface [14]. The effect of Co and Cu co-doping in TiO₂ on photocatalytic activity have been investigated by several authors [8,14]. The synthesized nanocomposites exhibit excellent photocatalytic activity for degradation of methyl orange under UV and Visible light irradiation [15]. Cobalt doped TiO₂ nanoparticles were synthesized by incipient impregnation method and observed that the synthesized samples show higher photocatalytic activity under UV and visible light irradiation [16]. Cu doping in TiO₂ shifts the optical adsorption edge to higher wavelength region leads to decrease in band gap energy and enhance the photocatalytic activity under visible light irradiation [17]. Enhance in photocatalytic activity under visible light was observed in Co doped TiO₂ nanoparticles prepared by sol-gel technique [11]. In the present report we have synthesized Co-Cuo codoped TiO₂ nanoparticles by sol gel technique and characterized by X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDXS), UV-Visible absorption spectroscopy and Fourier transform infrared spectroscopy (FTIR). The photocatalytic degradation of synthesized nanoparticles for congo red and methyl orange dye was investigated under visible light source.

2. EXPERIMENTAL DETAILS

All AR grade materials; Titanium tetraisopropoxide (Ti(OCH(CH₃))₄), Cobalt(II)Nitrate (Co(NO₃)₃·6H₂O) and Copper(II) Sulphate pentahydrate (CuSO₄·5H₂O) were purchased from Sigma Aldrich and taken as source for titanium precursor, cobalt, Copper respectively and distilled water was used as solvent throughout the experiment. Co-Cu- codoped TiO₂ nanoparticles were synthesized via a conventional sol–gel technique. For the synthesis of nanoparticles, 13 ml of titanium tetra isopropoxide (TTIP) was added into 50 ml of methanol under constant stirring, after 1 hour 0.8 ml of Nitric acid was added as to prepared mixture and stirred continuously for 30 min. The obtained solution was named as solution I. Solution II was prepared by dissolving 0.5 gm of Cobalt (II) Nitrate (0.04 mole %) in small amount of DI water. Solution II was then added slowly to Solution I under vigorous stirring for 30 minutes at room temperature the as obtained mixture was Solution III. For the preparation of Solution IV, which consists of 0.6 gm of CuSO₄·5H₂O dissolved in small amount of DI water was also added slowly to solution III to form a homogeneous mixture. The resulting mixture was vigorously stirred for 3 hour at room temperature to yield a wet gel. The Co- Cu- codoped TiO₂ sol was obtained after a certain time of aging. The precipitate obtained were filtered and washed with DI water for several times to get neutral solutions. The gel was dried in an oven for 24 hr at 100°C to remove the solvents. The dried powder was ground in an agate mortar and finally annealed at 400°C, for 4 hour in a muffle furnace for stable nanoparticles. The step wise detail procedure of synthesis of 0.04 mole% Co - codoped TiO₂ nanoparticles is Figure 1 (a). Other concentrations of Co- Cu- codoped TiO₂ nanoparticles were prepared adopting the similar procedure by adding appropriate amount of dopant. X-ray diffraction pattern of synthesized nanoparticles were recorded at room temperature on X-ray diffractometer using Cu-Kα radiation of wavelength 1.5406 Å. Elemental analysis of the synthesis samples was carried out using Energy dispersive X-ray spectrometer attached to SEM. The band gap energy was calculated using UV-visible absorption spectroscopy in the spectral range 200 – 800 nm. The structural formation of Co-Cu-codoped TiO₂ nanoparticles was verified using Fourier transform infrared spectroscopy in the spectral range 400-4000 cm⁻¹. The photocatalytic degradation of synthesized samples was carried out with 0.05 gm of the Co-Cu-codoped TiO₂ nanoparticles, added in 100 ml of 10⁻⁵ M congo red solution in different beakers at room temperature under vigorous stirring for 1 hr kept in dark for establishment of an adsorption/desorption equilibrium. Then solution was subjected to irradiation with a phosphor coated 160 W high-pressure mercury vapor lamp as a visible light source for 120 minutes having wavelength in range 420-520 nm. 3 ml of mixture was withdrawn at periodic time intervals of 20 min, during the irradiation and after centrifugation for 3 min at a speed of 11,000 r/min the absorption maxima for each solution was measured by using Perkin Lambda 20 UV-Spectrophotometer taking DI water as reference. All the photocatalytic results were checked twice to ensure the accuracy of the data. Same procedure is followed for degradation of methyl orange.

3. RESULTS AND DISCUSSION

X-ray diffraction pattern of Co-Cu-codoped TiO₂; CoₓCu₀.₈₅Ti₀.₉₅₋ₓO₂; x = 0.04, 0.08 & 0.12 mol % nanoparticles recorded at room temperature are shown in Figure 1 (b). The diffracted peaks observed at 20 angles 25.41°, 37.95°, 48.12°, 54.17°, 55.19°, 62.86°, 68.91°, 70.41°, and 75.26° respectively were assigned to (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal plane of TiO₂ anatase phase which is perfectly match with JCPDS card no. 84-1285 of TiO₂ anatase phase. No impurity peak was observed in X-ray diffraction confirms the single phase.
formation of prepared nanoparticles. The average crystallite size of the synthesized samples was calculated using Debye-Scherrer equation [18]

\[ D = \frac{K\lambda}{\beta \cos \theta} \quad (1) \]

Where \( D \) is the crystal size; \( \lambda \) is the X-ray wavelength (0.154 nm); \( \beta \) is the FWHM of the diffraction peak (rad); \( K \) is the shape factor (0.89) and \( \theta \) is the diffraction angle of most intense peak. The observed values of particle size vary from 16.4 nm to 13.1 nm and are tabulated in Table 1. The decrease in crystallite size is attributed to the replacement of TiO\(_2\) by copper concentration (x). The elemental composition of prepared samples was determined from energy dispersive X-ray spectroscopy. The absence of any impurity peak confirms the formation of stable TiO\(_2\) anatase phase. On doping the absorption edge is slightly shifted to higher wave length region as observed in UV-visible absorption spectra Figure 2 (a) clearly indicate the reduction in optical band gap energy of the synthesized nanoparticles. The optical band gap energy of as prepared samples were determined using relation [19]

\[ \alpha h\nu = B (h\nu-E_g)^n \quad (2) \]

Where \( \alpha \) represents optical absorption coefficient, \( h\nu \) is the energy of incident photon, \( E_g \) represents the optical band gap energy and \( n = 1/2 \) for indirect transitions occurred in TiO\(_2\) semiconductor. The calculated values of band gap energy of prepared nanoparticles with different molar concentration found to be 2.87, 2.61 & 1.90 eV respectively and are listed in Table 1. The observed valves of band gap energy decreases with increase in Co content (x) is responsible to reduce the photo excited electro-hole pair and enhance the photocatalytic activity.
FIGURE 2. (a) UV-Visible absorption spectra of synthesized nanoparticles. 
(b) Tauc’s plot of Co$_{x}$Cu$_{0.05}$Ti$_{0.95}$O$_2$; $x$ = 0.04, 0.08 & 0.12 mol % synthesized nanoparticles.

FIGURE 3. (a) FTIR transmission spectra of Co$_x$Cu$_{0.05}$Ti$_{0.95}$O$_2$; $x$ = 0.04, 0.08 & 0.12 mol % nanoparticles. 
(b) Mechanism of the photo excited electron-hole separation and transport process of nanoparticles.

The Fourier transform infrared spectra of Co-Cu-codoped TiO$_2$ nanoparticles recorded at room temperature are shown in Figure 3(a). The following peaks observed at 623.15, 987.8, 1101.4, 1145.10, 1147.03, 1624.53 and 3376.93 cm$^{-1}$ are assigned in the FTIR spectra of the prepared samples. The absorption band observed at 623.15 cm$^{-1}$ corresponds to stretching vibration of Ti-O in TiO$_2$ network. A low intense absorption band observed at 987.8 cm$^{-1}$ is assigned to Ti-O-Ti bending vibration in TiO$_2$ anatase. Absorption bands observed at 1101.4 and 1147.03 cm$^{-1}$ is due to symmetric and asymmetric vibration of C-O-C group [20]. On increasing Co concentration these bands convert into single band observed at 1145.10 cm$^{-1}$ is attributed to C-O vibration suggest that Co cations effectively enter into TiO$_2$ lattice [21]. The absorption band observed at 1624.53 cm$^{-1}$ in all the composition correspond to the bending vibrations of (H–O–H) representing physically adsorbed water as the moisture [9,21]. Besides these observed vibration bands one broad absorption band is located at 3376.93 cm$^{-1}$ is attributed to the stretching vibration of O–H hydroxyl groups and is persistent in all the samples under study. The mechanism of the
Photocatalytic degradation of Co-Cu-codoped TiO$_2$ nanoparticles is discussed on the basis of energy band diagram as shown in Figure 3(b). The impurity levels of dopants Co 3d and Cu 3d generates below the conduction band of TiO$_2$, which results in decrease of band gap energy. When the TiO$_2$ surface is illuminated by photon of energy equal or greater than the band gap energy of TiO$_2$, then electron-hole pairs will form. The transfer of electron takes place from valence band to Cu 3d state leaving behind holes in valence band. This effective charge transfer may decrease the electron-hole pair recombination rate. The Cu$^{2+}$ trapped the electrons and reduces in unstable form (Cu$^-$) which further react with dissolved O$_2$ to reduce it to superoxide radical anion ($\cdot$O$_2^-$). These superoxide radical anions can form hydrogen peroxide and on reduction with electron produces hydroxyl radical (OH$^-$). The photo generated holes in valence band due to their high oxidation potential can oxidize water molecules adsorbed by TiO$_2$ surface to form hydroxyl radical (OH$^-$). The azo dye pollutant was attacked by the hydroxyl radicals formed both by trapped electrons and hole in the valence band to generate organic intermediates which further undergo reaction with hydroxyl radicals to produce final product [22-23]. The degradation efficiency was calculated using Lambert-Beer Law and the Langmuir-Hinshelwood model [24] 

$$\eta = \frac{c_0-c}{c_0} \times 100$$  

(3)

Where c$_0$ & c are the concentration of dye solution at initial time and at any time t respectively.

The time-dependent photo degradation performance of all the prepared samples are shown in Figure 4 (a &b). Where the irradiation time plays important role in the decoloration of the dyes as it was observed that dye removal percentage increased with increase of irradiation time.

The degradation efficiency increases with increase in dopant concentration and reaches to 79% and 72% respectively for congo red and methyl orange in the presence of 0.12 mol % Co-Cu-codoped TiO$_2$ nanoparticles after 120 min of irradiation time.

On the basis of these observations, it is concluded that the photocatalytic activity against both dye increases with increase in cobalt concentration (x) and is due to decrease in charge carrier recombination rate attributed to decrease in energy band gap and increase in surface area arises from decrease in particle size of the synthesized nanoparticles.
**Table 1** - Average Particle size, Optical band gap energy and Percentage degradation efficiency of prepared samples against both organic dyes after exposure to visible radiation.

<table>
<thead>
<tr>
<th>Sample matrix Co, Cu_x Ti_{1-x}O_2</th>
<th>Average Particle size (nm) from XRD</th>
<th>Band gap (E_g) eV</th>
<th>Percentage degradation efficiency of two different dyes after 120 minutes of visible light exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Methyl orange</td>
</tr>
<tr>
<td>x=0.04 mol %</td>
<td>16.4</td>
<td>2.87</td>
<td>29</td>
</tr>
<tr>
<td>x=0.08 mol %</td>
<td>14.9</td>
<td>2.61</td>
<td>46</td>
</tr>
<tr>
<td>x=0.12 mol %</td>
<td>13.1</td>
<td>1.90</td>
<td>72</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Cobalt & Copper doped Co_x Ti_{1-x} Cu_{0.05}O_2; x = 0.04, 0.08 & 0.12 mol % nanoparticles have been successfully prepared by sol-gel technique. The X-ray diffraction and EDXS measurements confirm the formation of anatase phase of TiO_2 nanoparticles. The average particle size and energy band gap found to decrease with increase in dopant concentration. The absorption edges of the prepared samples shifted to higher wave length indicate the reduction in band gap energy. The FTIR spectra analysis confirms the formation of stable anatase phase of TiO_2. The photocatalytic degradation efficiency of prepared samples for degradation of both organic dyes increases with increase in cobalt concentration. These observations suggest that prepared nanoparticles are suitable for photocatalytic application in removal of congo red and methyl orange dye from organic dissolved contaminated water.

**REFERENCES**

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