Cu-S Coped TiO₂ NanoPhotocatalyst for the Degradation of Environmental and Industrial Pollutants

S.T. Hussain*,1, M. Mazhar2, Asima Siddiqa1, Hina Javid2 and M. Siddiq2

1National Centre for Physics, Quaid-i-Azam University, Islamabad 43520, Pakistan
2Chemistry Dept. Quaid-i-AZam University, Islamabad 43520, Pakistan

Abstract: Sulfur doped titanium dioxide anatase nano-photocatalyst with different copper loadings (5, 10, 15, and 20 w/w %) was synthesized by hydrothermal method. The fabricated nanocatalysts were found to have high surface area, high aspect ratio, good surface morphology and high metals dispersion. The synthesized nanocatalysts were characterized by X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), Diffuse reflectance spectroscopy (DRS), Fourier transform infrared spectroscopy (FTIR), Energy dispersive X-ray (EDX), Brunauer Emmett teller method (BET). The results revealed that photocatalyst possesses anatase phase having particle size in the range of 9 to 12 nm. The band gap of the photocatalyst was determined using transformed diffuse reflectance spectroscopy according to the Kubelka-Munk theory, showed prominent band gap decrease with increase in the Cu loadings.

The photocatalytic activity of S-TiO₂ and copper loaded S-TiO₂ nanocatalyst were determined for degradation of phenol into hydrocarbons (methane, ethene, and propene) and photo reduction of CO₂ into ethanol. The activity results revealed that degradation of phenol and photoreduction of CO₂ increased with increasing copper loadings, due to creation of electronically modified active sites and change in the electron accepting properties of TiO₂ with Cu addition and creation of electron hole pair.

Keywords: K doped TiO₂, nano-photocatalyst, CO₂ conversion, phenol degradation, UV, sun radiation.

1. INTRODUCTION

Titanium Dioxide (TiO₂) based nonmaterials have been broadly studied as the most promising photocatalyst due to its nontoxicity, low cost, photo stability, non toxicity and high catalytic reactivity. Much attention has been paid in photocatalysis of titanium dioxide since photoinduced electrochemical decomposition of water into oxygen and hydrogen under ultraviolet light irradiation by Fujishima [1]. Nanophased TiO₂ which has a large surface area that can facilitate a fast rate of surface reactions, is a widely used wide–band-gap semiconductor which has attained considerable attention due to its distinctive applications as photocatalysts, gas sensors, solar cells and electrochemical devices [2,3]. Current research on TiO₂ is intended at understanding its strong photocatalytic activity because it has been proven to be an exceedingly efficient catalyst for energy conversion purposes and environmental remediation such as air purification, water disinfection, hazardous waste remediation [3-5].

The presence of pollutants such as CO₂, NOₓ, SOₓ in air, organic dyes and many other organic hydrocarbons such as phenol, formaldehyde methylene blue, reactive blue, methyl red and gasoline generated as a result of many industrial reactions have caused the sever environmental problems since couple of decades [6,7]. Titanium dioxide has sufficient band gap energies for promoting or catalyzing a wide range of chemical reactions of environmental interest [7]. In particular it has been used to oxidize industrial pollutants and to convert them into harmless products of H₂O, alcohols and other useful hydrocarbons. Though, its practical application was limited by several factors, including the most restrictive one: it is only responsive to light radiation in the UV and near-UV range (λ<387 nm) as it is a wide band-gap semiconductor (3.2 eV for anatase, 3.0 eV for rutile phase) [7,8]. Less than 5% of the whole radiant solar energy can be captured by pure titania [9].

There are however, a number of attempts physical and chemical processes which were devoted to design and develop a second generation of visible-light sensitive photocatalysts of titanium dioxide [10]. Until now, several strategies involving noble metal deposition, transition-metal ions doping, coupled semiconductor systems [11,12] has been reported. Recently an innovative technique involves the doping of TiO₂ with anions such as carbon, nitrogen, phosphorous, sulfur and fluorine reported as a good tool in a desired band gap narrowing and an enhancement in the photodegradation efficiency under visible light [9,11]. Doping with anions not only modifies the conductivity and optical properties but also introduce new surface states that may lie close to the conduction or valence band of TiO₂. Extending the TiO₂ spectral response and of improving its photoreactivity is doped with transition metals such as Cr, V and Fe [12,13] have also been explored recently. It was believed that transition metals could act as shallow traps in the lattice of TiO₂, which benefit to suppress the recombination of photoinduced electron-hole pairs when migrating from inside of the photocatalyst to the surface.
Doping with metals and non metals were the most feasible methods for improving the photocatalytic activity of titania [9]. Khan et al. [14] reported that the photocatalytic degradation of toluene by using Boron and Carbon co-doped titania nanoparticles. Zhao et al. [15] reported that photocatalytic response of titania could be enhanced by using B–Ni co-doped photocatalyst by the modified sol–gel method. They proposed that Boron incorporated into TiO₂ extends the spectral response to the visible region while Ni doping could greatly enhance the photocatalytic activity. Balek et al. [16] reported N and F co-doped titania photocatalyst for acetaldehyde decomposition. They investigated the effects of N-F co-doping on photocatalytic activity in detail and elucidated the reasons for exhibiting the photocatalytic activity under visible light. Yin et al. [17] synthesized F and Zn co-doped TiO₂ nanopowders for improving the photocatalytic performance. Wei et al. [18] reported the preparation boron and cerium co-doped TiO₂ for extending spectral response to the visible light region and pointed out that the photocatalytic activity of Boron-Ce codoped titania was much higher than that of P25. These reports clearly indicated that modification of titania by co-doping proved to be an effective tool for enhancing its photocatalytic activity. The primary event taking place on the illuminated TiO₂ is the generation of electron-hole pairs. These photoionized electrons and holes are powerful reducing and oxidizing agents, which migrate to TiO₂ surface and ultimately become available for direct or indirect consecutive reduction and oxidation reactions [13,15,16].

In this study, we report the single step, size controlled fabrication of S doped and Cu-S co-doped TiO₂, and its application towards the carbon dioxide conversion to alcohol and degradation of organic waste like phenol under UV radiations. The effect of sulfur and particle size on the optical properties, degradation of phenol, conversion of carbon dioxide to alcohols were also studied for comparison. The variation in band gap was compared with the photocatalytic degradation and CO₂ conversion.

2. MATERIAL AND METHODS

2.1. Chemicals

Titanium tetrachloride purum (98.0%), Sodium hydroxide and Sulphuric acid (96%), Copper (II) chloride dihydrate (99%), Ammonium hydroxide (33%), of analytical grade were obtained from Fluka. Argon, hydrogen gas cylinders were used for preparation of sulfur and copper doped TiO₂ photocatalyst.

2.2. Preparation of S Doped TiO₂

TiO₂ nano particles were synthesized by precipitation method from TiCl₄. Fluka TiCl₄ (98% purity, Analra grade) was diluted up to 15% (1.33 M) in 15% H₂SO₄ in distilled water. The solution was stirred for two hours at room temperature. During the stirring 3M NaOH solution was added drop wise (the flow of NaOH solution was controlled through HPLC (High Performance Liquid Chromatography) during the reaction with continuous monitoring of pH. The drop wise addition of NaOH was continued until the pH of the resulting solution reached to 4, at this pH white precipitates were formed. The precipitates were then washed with distilled water many times. Dried overnight at 100 °C. The TiO₂ powder thus obtained was calcined at 500 °C for 6 hours.

2.3. Preparation of Copper Doped TiO₂

Copper sulfur doped TiO₂ material was produced by reducing Cu⁺ ions hydrothermally using CuCl₂.2H₂O along with NH₄OH. Suspensions of sulfur doped TiO₂ was extended by using B–Ni co-doped photocatalyst by the modified sol–gel method. Finally autoclave was cooled to room temperature. The resulting grey powder was washed twice to remove ammonia solution and dried in the air at 110 °C, followed by calcination in air stream at 500°C for 6h. The experimental arrangement is presented in the Fig. (1).

2.4. Photocatalytic Reactions

Batch photoreactor of cylindrical shape with a capacity of 1000 ml as shown in Fig. (2) was used for the degradation of Phenol and conversion of Carbon dioxide reactions. 0.3 gms of TiO₂ nanoparticles were suspended in water with pure oxygen bubbling in case of degradation of phenol (the initial concentration of phenol was 0.1 M) while for CO₂ conversion 0.2 gm of catalyst were suspended into 0.2 N NaOH solution with pure CO₂ bubbling at the rate of 100 mls/min. In both systems a mercury lamp (Ultra-Violet Products Inc., USA; LF-204,LS), UVC (254 nm) was placed on the top of reactor to irradiate the reactor. The whole system was tightly sealed off during the irradiation, with continuous stirring using magnetic stirrer to prevent the sedimentation of the catalyst. The liquid sample was withdrawn after every two hours from reactor and analyzed using GC/MS after the chloroform extraction method.

3. CHARACTERIZATION

The crystallinity, structure and phase of samples were determined by XRD (Phillips PW 3040/60 X Pert Pro) powder diffractometer with Cu Kα radiation of wavelength of 1.5406 Å. The XRD profiles were collected between 15° to 75° (2θ) with a step size of 0.05° and step time of 3s. The crystallite sizes of the samples were estimated from FWHM (full-width at half maximum) of XRD by Scherrer equation. Transmission Electron Microscope S-3500 N with Absorbed Electron Detector S-6542 (Hitachi Science System, Ltd), EDX (Inca Energy, Oxford Instruments Microanalysis, Ltd) under specific conditions of 20 keV, 25 nm working distance and magnification varying from x 300-1000 were used to examine the surface comparison of the samples. The Brunauer–Emmett–Teller (BET) specific surface area was determined by Nitrogen adsorption-desorption isotherms (Quantachrome Instrument, NOVA 1000 series). IR spectra were recorded on a Nicolet NEXUS 670 FTIR instrument to identify adsorbed species and / or adsorbed reaction intermediates and their structures on well dispersed catalysts and surfaces.
Cu-S Coped TiO\textsubscript{2} NanoPhotocatalyst

A (Lambda -950 Perkin-Elmer) UV-Vis spectrophotometer equipped with an integrated sphere was used to record the diffuse reflectance spectra (DRS) of the samples. The reflectance spectra of the samples were analyzed under ambient condition in the wavelength range of 200-1000 nm. The high performance liquid chromatograph pump (Shirama, Model LC-6A) was used for the drop wise addition of solution into the reaction mixture. The pH of reaction mixture was determined by pH meter (Inolab, Model pH 720). The chemical states and shift of the catalyst binding energies due to doping were analyzed by X-ray photoelectron spectroscopy (XPS) using a VG Microtech MT500 spectrometer, operated with a constant pass energy of 50 eV and with Mg K\textalpha radiation as the excitation source ($h\nu = 1253.6$ eV). The catalyst was pressed into a pellet, and then adhered on sample holder by carbon tape. The products of photocatalytic reactions were analyzed by using gas chromatograph (GC) (Shimadzu, Model GC-17) equipped with 30 m molecular sieve 5A plot column and a TCD detector.

4. RESULTS AND DISCUSSIONS.

4.1. XRD Studies

Fig. (3) showed the XRD patterns of prepared TiO\textsubscript{2} nano particles. The diffractogram of S/TiO\textsubscript{2} and Cu loaded S-TiO\textsubscript{2} showed Bragg reflection at about 25, 38, 48, 54, 63 and 75 degrees corresponding to 101, 004, 200, 211, 204, 204 tetragonal crystal planes of anatase phase of TiO\textsubscript{2} [19]. The presence of the anatase phase was confirmed by comparing JCPDS standard files #21-1272. Using Scherrer’s formula at $\lambda = 1.5418$, $\beta = 0.774^\circ$, $2\theta = 24.882$, the crystallite size of all the samples were calculated and presented in Table 1. A closer look at Fig. (3) reveals that the broadening of FWHM is observed with the increase in Cu-loadings with consequent decrease in particle size and no change was observed in the crystalline form of TiO\textsubscript{2}.

4.2. BET Measurements

Measurements of specific surface area of all copper loaded S-TiO\textsubscript{2} samples are presented in Table 1, the surface area of the commercial TiO\textsubscript{2} is also included for comparison. It is known that BET surface area has no effect on the phase of the TiO\textsubscript{2} nano particles [18] but they do have an effect on the photocatalytic reaction. Larger surface area has increased adsorption/desorption capacity, consequently good photocatalytic activity [19]. As it could be seen in Table 1, copper loading significantly resulted in the increase in surface area of S/TiO\textsubscript{2}.

4.3. SEM/EDX Studies

The surface morphology of all copper loaded S-TiO\textsubscript{2} samples was studied using scanning electron microscopy. Morphologies of S-doped TiO\textsubscript{2} and S-doped TiO\textsubscript{2} with various copper loadings were determined by SEM micrographs as shown in Fig. (4a-e). As seen from the SEM images, the nanoparticles are nearly round in shape and porous in nature.
EDX analysis was accomplished to assay the existence of dopant on TiO$_2$. Table 1 presents the EDX study of the S-doped TiO$_2$ and S doped TiO$_2$ with various copper loadings, showing the percentage of S, O, Cu and Ti confirming the formation of doped TiO$_2$ nano particles.

Based on the results obtained from XRD patterns, scanning electron microscopy and EDX studies, we concluded that a homogeneous surface dispersion of Cu was achieved for all doped samples.

### 4.4. Band Gap Measurements

UV-Vis diffuse reflectance spectroscopy was used to probe the band structure and energy levels in the crystal. The absorbance spectra of all samples were taken in the range of 200-800nm at room temperature and shown in Fig. (5). Fig. (5) represents the DRS absorbance spectra of S-TiO$_2$, 5% Cu loaded S-TiO$_2$, 10% loaded Cu loaded S-TiO$_2$, 15% Cu loaded S-TiO$_2$ and 20% Cu loaded S-TiO$_2$. It is evident from the above Fig. (5) that increase in the Cu loadings resulted in bathochromic shift of the absorption edge toward the visible region and decrease in the band gap of S/TiO$_2$ nanoparticles.

The change in the band gap with copper loadings were determined by Kubelka-Munk function $F(R)$ which is related to the diffuse reflectance, $R$, of the sample and given by the following relation [19,20].

$$F(R) = \frac{(1-R)^2}{2R}$$

where $R$ is the absolute value of reflectance. The energy bandgap of the samples were determined from their diffuse-reflectance spectra by plotting the square of the Kubelka-Munk function $F(R)^2$ vs Energy in electron volts. The direct energy bandgap was obtained by linear part of the curve by extrapolating to $F(R)^2 = 0$. The optical band gap energies of all samples were estimated by using the above method.

Figs. (5, 6a-c) shows the bandgap calculation of all samples determined from K-Munk function. As it is clear from Fig. (6) that energy bandgap decreases with increases Cu loadings, which are less than the S-doped sample. The band gap energies determined from the intercept of the tangents to the plots are 3.2eV for S-TiO$_2$, 2.9eV for 5% loaded S-TiO$_2$, 2.6eV 10% loaded S-TiO$_2$, 2.4eV for 15% loaded S-TiO$_2$ and 1.9eV for 20% loaded S-TiO$_2$. The narrowing of the band gap with increase in Cu percentage can be ascribed to Cu atom that would be incorporated into the lattice of titania, thus resulting in the change in crystalline and electronic structures [2,6,21]. In addition, this change in energy bandgap is directly reflected in the

### Table 1. Particle Size, BET Surface Area, EDX Analysis of S-TiO$_2$ and S-TiO$_2$ Loaded with Various Copper Concentrations

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle Size (nm)</th>
<th>BET Surface Area (m$^2$g$^{-1}$)</th>
<th>EDX Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>O (%)</td>
</tr>
<tr>
<td>S-TiO$_2$</td>
<td>11.8</td>
<td>142</td>
<td>20.31</td>
</tr>
<tr>
<td>5% Cu loaded S-TiO$_2$</td>
<td>11.6</td>
<td>178</td>
<td>20.28</td>
</tr>
<tr>
<td>10% Cu loaded S-TiO$_2$</td>
<td>10.8</td>
<td>189</td>
<td>20.22</td>
</tr>
<tr>
<td>15% Cu loaded S-TiO$_2$</td>
<td>10.5</td>
<td>215</td>
<td>20.27</td>
</tr>
<tr>
<td>20% Cu loaded S-TiO$_2$</td>
<td>10</td>
<td>230</td>
<td>20.26</td>
</tr>
</tbody>
</table>

Fig. (3). XRD of (a) S-TiO$_2$ (b) 5% Cu loaded S-TiO$_2$ (c) 10% Cu loaded S-TiO$_2$ (d) 15% Cu loaded S-TiO$_2$ (e) 20% Cu loaded S-TiO$_2$. 
photocatalytic activity studies, where appreciable change is detected due to Cu addition.

**Fig. (4). (a-e):** SEM micrograph of (a) S-TiO$_2$ (b) 5% Cu loaded S-TiO$_2$ (c) 10% Cu loaded S-TiO$_2$ (d) 15% Cu loaded S-TiO$_2$ (e) 20% Cu loaded S-TiO$_2$.

**Fig. (5).** Diffuse Reflectance spectra of all samples at room temperature.

### 4.5. FTIR Analysis

The FTIR experiments were conducted to evaluate the reaction mechanism of the catalyst and the nature of organics present in the final products. The FTIR results of fresh and spent catalysts after phenol degradation and photo reduction of carbon dioxide are presented in Table 2. The bands appearing at 520-590 cm$^{-1}$ are due to stretching vibrations of M-O (Ti-O & Cu-O) and band at 1040-1060 cm$^{-1}$ is due to bending vibrations of Ti-S bonds in both samples [22]. The broad band peak appearing at 3200-3600 cm$^{-1}$ was assigned to fundamental stretching vibration of O-H hydroxyl groups (free or bonded), which are further confirmed by a weak band at about 1570-1620 cm$^{-1}$ which may be due to bending vibration of coordinated H$_2$O as well from the Ti-OH [23]. After photocatalytic activity the products were identified by growing up of absorption peaks in FTIR spectra on the surface of catalyst. The ethanol product formed after phenol degradation was identified by the appearance of vibration bands at 1340-1390 cm$^{-1}$, 3200-3600 cm$^{-1}$, 1710-1780 cm$^{-1}$ and 1263-1280 cm$^{-1}$, which are assigned to asymmetric bending vibrations of C-H and symmetric stretching vibration of O-H, C-O and C-C bonds, respectively [24], on the surface of spent catalyst. In FTIR of spent catalyst after carbon dioxide reduction absorption band in the range of 1637-1650 cm$^{-1}$, 1265-1280 cm$^{-1}$ and 1340-1390 cm$^{-1}$ indicates the presence of C≡C, C-C and C-H group indicating the formation of some hydrocarbons intermediates.
on the surface of catalyst [21]. This indicates that whole catalytic process take different interaction routes on different types of active sites due to different oxidation states and phases of copper as confirmed by XPS studies. The FTIR data of fresh (F) and spent (S) catalyst before and after catalytic reaction is presented in Table 2, which supports our findings.

4.6. XPS Studies

To study the surface composition and chemical states of the synthesized catalyst, the S-TiO$_2$ and copper loaded S-TiO$_2$ were also investigated by XPS and shown in Fig. (7a, b). XPS spectra of pure TiO$_2$ were also studied for comparison. The individual peaks of O1s at 529.5 eV and Ti 2p at 458.2 and 463.9 eV [21,22] can be clearly seen in the high-resolution spectra (Fig. 7a, b), which mean that chemical state of the sample is Ti$^{4+}$ bonded with oxygen (Ti$^{4+}$–O), which has been modified after addition of S and copper. The binding energy of the Ti 2p3/2 and 2p1/2 band in case of doped Cu$_2$O /S–TiO$_2$ samples was found to be higher than that of the pure TiO$_2$. Increasing the copper loadings the peaks shifted to high binding energy value as shown in Fig. (7) and Table 3. This shift towards higher side could be attributed to an atomic dispersion of copper on TiO$_2$ and electronically modification of TiO$_2$ surface geometry [20,25].

4.7. Photocatalytic Degradation of Phenol under UV Irradiations

The TiO$_2$ anatase is the main catalyst used in the contaminants photodegradation. However, the photocatalytic activity of TiO$_2$ nanoparticles have been little investigated in the literature [25,26]. In this study the photocatalytic activity of photocatalysts were evaluated in terms of degradation of phenol (1g/L) employing UV–visible spectrometry. The phenol conversion was estimated using the following formula [19,20].

\[
\text{Phenol Conversion (\%)} = \frac{[\text{Phenol}]_0 - [\text{Phenol}]_t}{[\text{Phenol}]_0} \times 100
\]  

(1)

Fig. (8) shows the degradation efficiencies of phenol versus illumination time over the different catalysts under
UV irradiations. It is clear from the Fig. (8) that the phenol degradation on the S-doped TiO$_2$ is less in comparison with S-doped TiO$_2$ photocatalyst loaded with copper, this degradation increases with increasing the copper doping. The order of photocatalytic activity was S-doped TiO$_2$ > 5% Cu loaded S- TiO$_2$ > 10 % Cu loaded S-TiO$_2$ > 15% Cu loaded S-TiO$_2$ > 20% Cu loaded S-TiO$_2$. About 60% phenol is degraded after 6hrs irradiation in the presence of 20% copper loaded sample while without copper S-TiO$_2$ showed 0.8-5% production of hydrocarbons.

We suggest that copper ions influence the photoactivity of TiO$_2$ by electron or hole traps, where the trap causes the formation of some active species that benefit degradation of phenol [15,16]. Cu(II) resides in the substitutional sites into the lattice of TiO$_2$ thus introducing a dopant energy level below the conduction band of TiO$_2$ and prevents the recombination of electron and hole pairs by scavenging the electron. The presence of copper dopant present at interstitial sites could create intra-band-gap states close to the valence band edges, both copper and sulfur co modification leads to a narrower band gap than S-doped TiO$_2$. In copper-doped...
samples, electrons are either directly trapped at Ti(IV) surface sites (form Ti^{3+}) or in deeper copper(II) sites (form Cu^{1+}). In this case, the trapped electron can be easily transferred from Cu^{1+} to a neighboring surface Ti^{4+} because of the proximity of the energy levels [10,23,25]. It could be suggested here that the S species could trap the part of photogenerated holes, thus suppressing the recombination of photogenerated electrons and holes. Moreover, Cu loaded S-TiO_{2} has abundant amount of OH- group than S-TiO_{2} sample, which would be beneficial for the absorption of organic compounds, capturing the photogenerated holes and formation of OH radicals (shown in Fig. 10) [26]. Furthermore the most important reason is that synergistic effects of copper and sulfur on titania may improve the separation efficiency of photogenerated electrons and holes and largely modified the photocatalytic activity under visible light irradiations. The increase in efficiencies in degradation of phenol may be attributed to the increase in copper concentration, which resulted in the increase of e-trapping by Cu^{2+} ions on Ti surface sites [27]. In the absence of Cu, the S-TiO_{2} provides “weak active species” that are not effective to oxidize the organic species into products under UV irradiation [20,26]. The proposed possible mechanism for synergistic effects of copper and sulfur is presented in Fig. (10).

Table 3. Binding Energy Values of S-TiO_{2} with and without Copper Loadings

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding Energy Values (eV)</th>
<th>Ti 2p3/2</th>
<th>Ti 2p1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO_{2}</td>
<td></td>
<td>458.60</td>
<td>464.40</td>
</tr>
<tr>
<td>S-doped TiO_{2}</td>
<td></td>
<td>457.75</td>
<td>464.55</td>
</tr>
<tr>
<td>5% Cu loaded S-TiO_{2}</td>
<td></td>
<td>458.92</td>
<td>464.72</td>
</tr>
<tr>
<td>10% Cu loaded S-TiO_{2}</td>
<td></td>
<td>459.09</td>
<td>464.89</td>
</tr>
<tr>
<td>15% Cu loaded S-TiO_{2}</td>
<td></td>
<td>459.24</td>
<td>465.04</td>
</tr>
<tr>
<td>20% Cu loaded S-TiO_{2}</td>
<td></td>
<td>459.39</td>
<td>465.19</td>
</tr>
</tbody>
</table>

Fig. (8) Photocatalytic degradation of Phenol determined by S-TiO_{2} and S-TiO_{2} with various copper additions at different time rates.

Fig. (9). Percent production (a) ethene (b) propene (c) methene by S-TiO_{2} and S-TiO_{2} with various copper loadings under UV and IR irradiation at room temperature at different time rates.

4.8. Conversion of CO_{2} + H_{2}O by Solar Energy

The photochemical conversion of CO_{2} + H_{2}O into alcohols (ethanol) was computed after 1hr using UV radiation by S-TiO_{2} and copper loaded S-TiO_{2} is shown in Fig. (11). CO_{2} conversion was calculated using the following formula (equation 2) [19,20].

\[ \text{CO}_{2} \text{ conversion (\%)} = \frac{[\text{CO}_{2}]_{i}}{[\text{products}]_{\text{out}}} \times 100 \] (2)
The study of Fig. (11) clearly indicates that the conversion of CO$_2$ + H$_2$O into ethanol increases with increasing Cu loadings on S-TiO$_2$ nano particles and best conversion (85%) was achieved with 20% copper loaded S-TiO$_2$ after illumination of UV irradiations for 6hrs. Photochemical conversion of CO$_2$ + H$_2$O into ethanol follows the similar mechanism as discussed previously in section 5, Fig. (10). The electrons trapped by Cu transferred smoothly to surface where they reduce appropriate electron acceptor molecules i.e., react with oxygen molecules to form super oxide anions making the reaction exothermic while the positive holes can oxidize donor molecules i.e., break apart water molecules to form hydrogen gas and hydroxyl radicals which combines with carbon to form ethanol [25-27]. The effect of copper loadings on the ethanol selectivity is depicted in Fig. (12). The ethanol production increases with increasing copper percentage, reaching a maximum of 52% on 20% copper concentration.

5. CONCLUSIONS

• S-doped titanium dioxide nanoparticles with various copper loadings are synthesized in a single step using hydrothermal method.
• Copper loaded S-TiO$_2$ photocatalyst showed high specific area, small crystallite size, narrow band gap which contribute to their high photocatalytic activity.
• The photocatalytic activity suggests that increasing copper-addition on TiO$_2$ resulted in increase the photocatalytic degradation of phenol and conversion of CO$_2$ + H$_2$O to alcohol.
• The copper loaded S-TiO$_2$ was found to be feasible and attractive to be used for further investigation of industrial and environment management studies.

ACKNOWLEDGEMENT

Declared none.

CONFLICT OF INTEREST

Declared none.

REFERENCES

3.0/) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.

Received: July 6, 2011
Revised: September 20, 2011
Accepted: April 11, 2012