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Highly Stabilized and Finely Dispersed Cu_2O/TiO_2: A Promising Visible Sensitive Photocatalyst for Continuous Production of Hydrogen from Glycerol:Water Mixtures

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Cu-doped TiO_2 with varying amounts of Cu (0.2, 0.3, 0.5, 1, 2, and 5) are prepared by impregnation method and calcined at 350 and 450 °C for 5 h. These catalysts are characterized by X-ray diffraction, diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy energy-dispersive X-ray spectroscopy (EDAX), and transmission electron microscopy (TEM). The DRS studies are clearly showing the expanded photo response of TiO_2 into the visible region on impregnation of copper ions. TEM images are depicting the fine dispersion of Cu particles on TiO_2 surface. XPS studies are showing change in the binding energy values of Ti 2p, O 1s, and Cu 2p, indicating that copper ions are in interaction with TiO_2. XPS results are also confirming that the oxidation state of copper is +2 in samples calcined at 350 °C and +1 in samples calcined at 450 °C. EDAX analysis supports the presence of copper species on the surface layers of TiO_2. Photocatalytic hydrogen production activity studies are conducted over CuO/TiO_2 and Cu_2O/TiO_2 catalysts in pure water and glycerol:water mixtures under solar irradiation. Maximum hydrogen production of 265 and 290 μmol h^{-1} is observed over 2 wt % CuO/TiO_2 and Cu_2O/TiO_2 catalysts in pure water. A significant improvement in hydrogen production is observed in glycerol:water mixtures and maximum hydrogen production of 16,500 and 20,060 μmol h^{-1} is obtained over 0.5 wt % CuO/TiO_2 and Cu_2O/TiO_2 catalysts in 5% glycerol aqueous solutions. No hydrogen production activity is observed on reduced catalysts under solar irradiation. Furthermore, when these catalysts are studied under UV irradiation, 2−3 fold increase in activity is observed on calcined catalysts, and the same level of activity is observed on reduced catalysts, but under these conditions the activity is limited by the dissolution of Cu ions into the solution. However, under solar irradiation a continuous and stable activity is observed over Cu_2O/TiO_2 catalyst. On the basis of the characterization and hydrogen production activity results, finely dispersed Cu in +1 oxidation state that is in interaction with TiO_2 is proposed as a promising visible sensitive photocatalyst for the continuous production of hydrogen from glycerol:water mixtures.

1. Introduction

For the past few decades, fossil fuels like coal, petroleum, and natural gas are playing a dominating role as energy resources. These energy resources are nonrenewable, limited in quantity, and causing serious impact on the environment. Therefore, the production of renewable and nonpolluting fuels by the direct conversion of solar energy into chemical energy is one of the priorities of the scientific community. The production of hydrogen has received much attention because of its potential application as a clean source of energy. Hydrogen production by steam reforming of fossil fuels emits CO_2. Photocatalytic hydrogen production from water splitting using solar energy may be seen as an alternative approach for this issue.

Photocatalytic water splitting in recent years is extended to use the organic pollutants and alcohols as sacrificial agents for hydrogen production.[1,2] Using biomass-derived glycerol as feedstock for hydrogen production is gaining importance as it is produced in large amounts and is rapidly becoming a waste with an additional disposal cost.

TiO_2 has been considered as one of the most promising photocatalysts for various reactions. But its band gap limits its usage in the visible light region. Usually, addition of nonmetals, metal ions, and dye sensitization methods are employed to extend the absorption edge of TiO_2 into visible region.[3−5] Noble metal deposited TiO_2 catalysts are well studied for reforming reactions.[6−10] Daskalaki et al. have reported hydrogen production by photoinduced glycerol reforming over Pt/TiO_2 catalyst. They studied the effect of temperature, pH, catalyst weight in solution, and glycerol concentration on the rate of the reaction.[11] Kondarides reported hydrogen production by photoreforming of biomass-derived components and derivatives over Pt/TiO_2 catalyst at ambient conditions.[12] Bowker et al. have compared the photocatalytic reforming of glycerol and methanol over Au- and Pd-modified TiO_2 catalyst and found that the rate of hydrogen production is more over Pd-modified catalyst.[13] Luo et al. studied the hydrogen production over heteroatom doped titania from glycerol, sucrose, and fructose solutions and they found that Pt-loaded B- and N-codoped TiO_2 is showing maximum hydrogen production.[14]

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Use of noble metals like Pt, Au, and Pd is very expensive compared to transition metal ions, and the use of transition metals makes the material visible sensitive. Among the transition metal ions, Cu-loaded TiO_2 has been studied for hydrogen production under UV as well as solar light irradiation.[15−22]

Earlier in our lab, we were worked on developing the new materials and sensitizing the UV active semiconductor into visible light by noble metal deposition for water splitting reaction.[23−25]

In the present investigation Cu-loaded TiO_2 catalysts are evaluated for hydrogen production from water and glycerol: water mixture under solar irradiation and these results are compared with UV activity to elucidate the structure−activity correlation under solar irradiation.

2. Experimental Section

2.1. Chemicals. TiO_2 P-25 (anatase-80%, rutile-20%, surface area 50 m^2 g^{-1} and particle size 27 nm) from Deggussa Corporation, Germany, $Cu(NO_3)_2$ from LOBA CHEMIE Pvt., Ltd., India, glycerol from Qualigens Fine Chemicals India, Ltd., are procured and used without any further purification.

2.2. Catalyst Preparation. Cu (0.2, 0.3, 0.5, 1, 2, and 5 wt %) was loaded on TiO_2 by impregnation method. For each Cu-modified sample required amount of TiO_2 was dispersed in Cu $(NO_3)_2$ solution in distilled water. Excess water was evaporated to dryness with slow heating and constant stirring. The sample was dried at 110 °C and calcined at 350 °C (catalyst CT-1) and 450 °C (catalyst CT-2) for 5 h.

2.3. Characterization. The X-ray diffraction (XRD) patterns of Cu-modified TiO_2 catalysts were recorded with Siemens D-5000 X-ray diffractometer using Cu Kα radiation. The UV−vis diffuse reflectance spectra were recorded on a GBC UV−visible Cintra 10_e spectrometer, in the wavelength range 200−800 nm. The scanning electron microscopy (SEM) analysis of the catalysts was performed on Hitachi S-520 SEM unit. Elemental analysis was carried out using Link, ISIS-300, Oxford, energy-dispersive X-ray spectroscopy (EDAX) detector. A Philips Technai G2 FEI F12 transmission electron microscope operating at 80−100 kV was used to record the transmission electron microscopy (TEM) patterns. X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIC 165 equipped with Mg Kα radiation.

2.4. Catalytic Activity. Photocatalytic reactions were carried out under solar light and UV (400 W Hg vapor lamp) light irradiation. The intensity of solar light was measured using a LT Lutron LX-101A digital light meter. The solar light intensity was measured for every hour between 10:00 and 15:00. The average light intensity value observed was around 1,30,000 lx during the experiments.

The reaction was performed in a 150-mL quartz reactor by taking 50 mL of distilled water containing 100 mg of catalyst. Reactions were also carried out in 5% glycerol:water mixtures. Prior to the irradiation, the reaction mixture was evacuated for 30 min and also purged with nitrogen gas for 30 min to remove the dissolved oxygen. After irradiation, the evolved gaseous products were analyzed at every 1 h by a gas chromatography (Shimadzu GC-2014) with molecular sieve 5A column using thermal conductivity detector and N_2 as a carrier gas. CO_2 was analyzed by using corbaxen-1000 column. For comparison and to identify the active sites the catalyst is also studied after reducing in 30% H_2 and balance N_2 at 350 °C for 3 h.

3. Results

3.1. XRD. On impregnation of copper over TiO_2, no characteristic peaks of Cu are observed in the calcined samples, and only the characteristic 101,200 planes of TiO_2 anatase and 110 of rutile are identified from the XRD results. The absence of copper peak in the calcined samples indicates the fine dispersion of copper species on the surface of TiO_2 as the copper content used in this preparation is 0.5−5 wt %. As the XRD patterns of both CT-1 and CT-2 are identical, the XRD patterns of CT-2 are shown in Figure 1 to represent both the series.

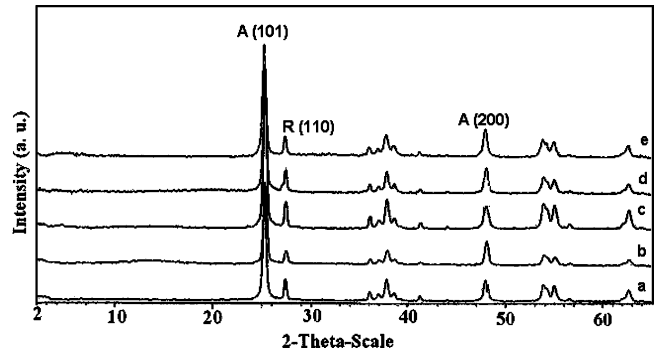


Figure 1. XRD patterns of CT-2 catalysts. Cu wt % (a) 0.2, (b) 0.5, (c) 1, (d) 2, and (e) 5.

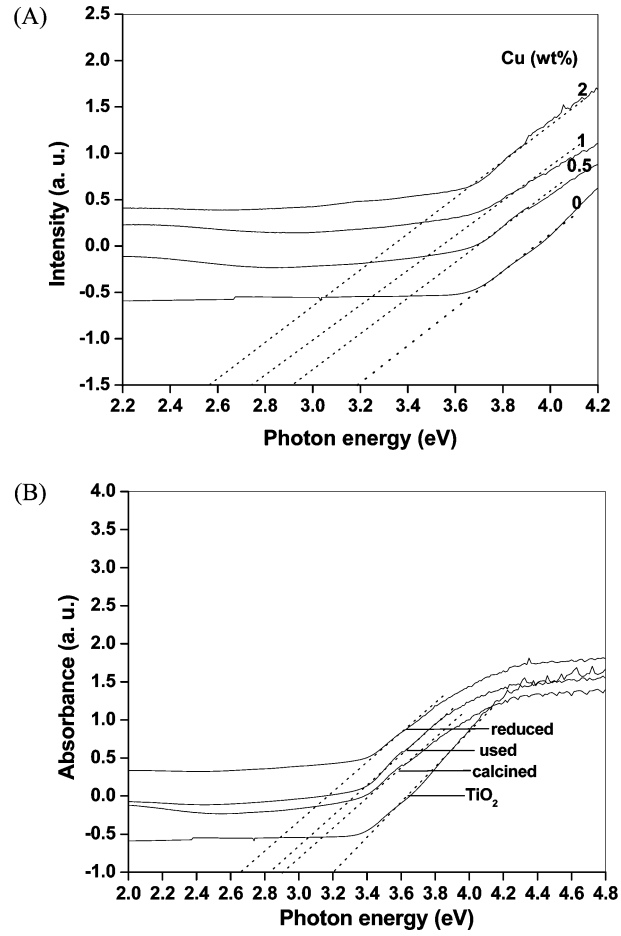


Figure 2. UV−vis DRS of (A) CT-2 catalysts with copper (wt %) loading. (B) Comparison of 0.5 wt % CT-2 calcined, used, and reduced catalysts.

3.2. Diffuse Reflectance Spectroscopy (DRS). Figure 2A shows the diffuse reflectance spectra of TiO_2 and copper-loaded TiO_2 CT-2 catalysts. The band gap energy values are calculated from the plot of absorbance versus photon energy in electron-volts (calculated from the formula $\lambda = 1239.8/E_{bg}$). Absorbance is extrapolated to get the band gap energy, and the values for CT-1 and CT-2 catalysts are given in Table 1. TiO_2 exhibits a

TABLE 1: Physical Characteristics of Cu-Loaded TiO_2 Catalysts

catalyst	band gap energy (eV)		Cu (wt %) by EDAX	
(Cu (wt %)/TiO_2)	CT-1	CT-2	CT-1	CT-2
0	3.2	3.2	–	–
0.2	2.93	3.13	0.17	0.18
0.3	2.86	3.05	0.29	0.285
0.5	2.81	2.91	0.49	0.48
1	2.74	2.75	0.985	0.98
2	2.52	2.56	1.89	1.92
0.5[a]	–	2.65	–	–
0.5[b]	2.79	2.83	0.41	0.42
0.5[c]	2.51	2.62	0.25	0.23

[a] Reduced. [b] Used under solar light. [c] Used under UV light.

strong absorption band around 384 nm corresponding to band gap energy of 3.2 eV. On loading copper, the band edge of TiO_2 is slightly expanded into the visible region, and this may be due to the additional energy levels created by the Cu ions in the band gap of TiO_2.[25] With increasing copper loading over TiO_2, the band gap energy values are decreased from 3.2 eV to a minimum value of 2.56 eV on CT-2 catalysts as shown in Figure 2A. In CT-1 catalysts also the band gap values are decreased with increasing Cu loading over TiO_2 as shown in Table 1. DRS and band gap energy values of 0.5 wt % CT-2 used (under solar and UV) and thermally reduced catalysts are compared with calcined catalyst as shown in Figure 2B and Table 1. The band gap energy of the catalyst used under solar irradiation is slightly decreased (from 2.91 to 2.83 eV), and this value is much less compared to the decrease observed in the band gap of thermally reduced catalyst (2.91 to 2.65 eV) and in the catalyst used under UV irradiation (2.91 to 2.62 eV). The catalysts used under UV irradiation and thermally reduced are showing almost similar band gap (2.62 and 2.65 eV) suggesting that in these two conditions Cu_2O is reduced to the same extent as shown in Table 1. As the difference in the conduction and valence bands is less in the reduced form (Cu^0) compared to the oxide form, the band gaps are decreased in reduced catalysts. However under solar irradiation, even after using the catalyst for 40 h, the decrease in the band gap is very less (0.08 eV) indicating that the catalyst is stable under solar irradiation. This is also in confirmation with the XPS results of used catalyst under solar irradiation wherein Cu^0 is not seen. However the small decrease observed in the band gap of 0.5 wt % CT-2 used catalyst under solar irradiation may be seen as due to the presence of Cu species with oxidation state < 1. From the DRS results it is clear that copper loading can shift the absorption edge of TiO_2 into the visible region, which in turn decreases the band gap for improving the photo absorption and photocatalytic performance of TiO_2 in visible region.

3.3. SEM-EDAX. The morphology of TiO_2 and CT-2 catalysts is investigated by SEM and shown in Figure 3. The surface morphology of TiO_2 seems to be changed after Cu loading and appears slightly dark. EDAX analysis of samples was carried out to determine the copper content on the surface of TiO_2, and the data obtained is shown in Table 1. The results clearly indicate the presence of copper ions on the surface of TiO_2 in the calcined catalysts. In the used catalysts loss of Cu is much less under solar irradiation (for 0.5 wt % CT-1 catalyst, 0.49 to 0.41; for 0.5 wt % CT-2 catalyst, 0.48 to 0.42), and about 50% loss is observed on CT-1 as well as CT-2 catalysts under UV irradiation. The observed loss is seen as due to the dissolution of Cu ions into the solution by the acidic conditions formed during the reaction.

3.4. TEM. The TEM photographs of 0.5 wt % CT-2 calcined and used catalysts are shown in parts A and B of Figure 4. In calcined catalysts, the TiO_2 particles with copper deposition appeared dark against the surface of TiO_2. Used catalyst is also showing the same type of morphology indicating that the catalyst is intact after several hours of reaction.

3.5. XPS. XPS studies are conducted over CT-1 and CT-2 catalysts in order to understand the chemical environment of copper ions on TiO_2. XPS spectra of Ti 2p, Cu 2p, and O1s core level profiles of different wt % Cu-loaded CT-2 catalysts

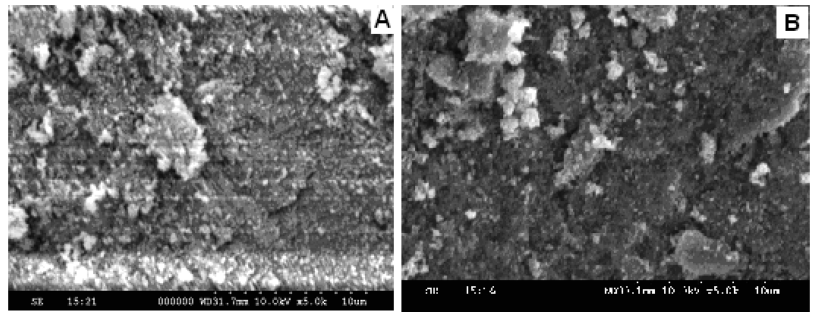
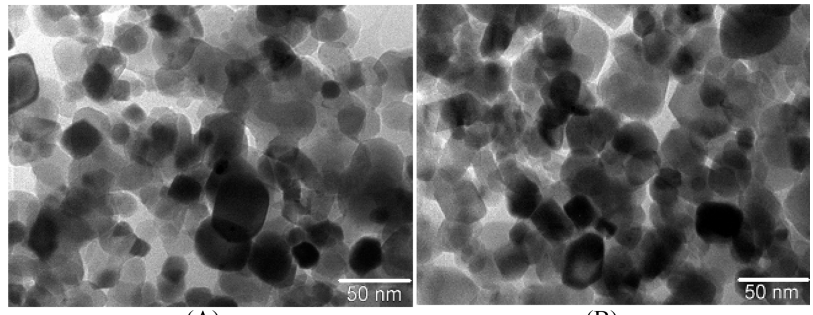


Figure 3. SEM images of CT-2 catalysts, Cu wt % (A) 0 and (B) 1.



(A) (B)

Figure 4. TEM images of 0.5 wt % CT-2 catalysts (A) calcined and (B) used.

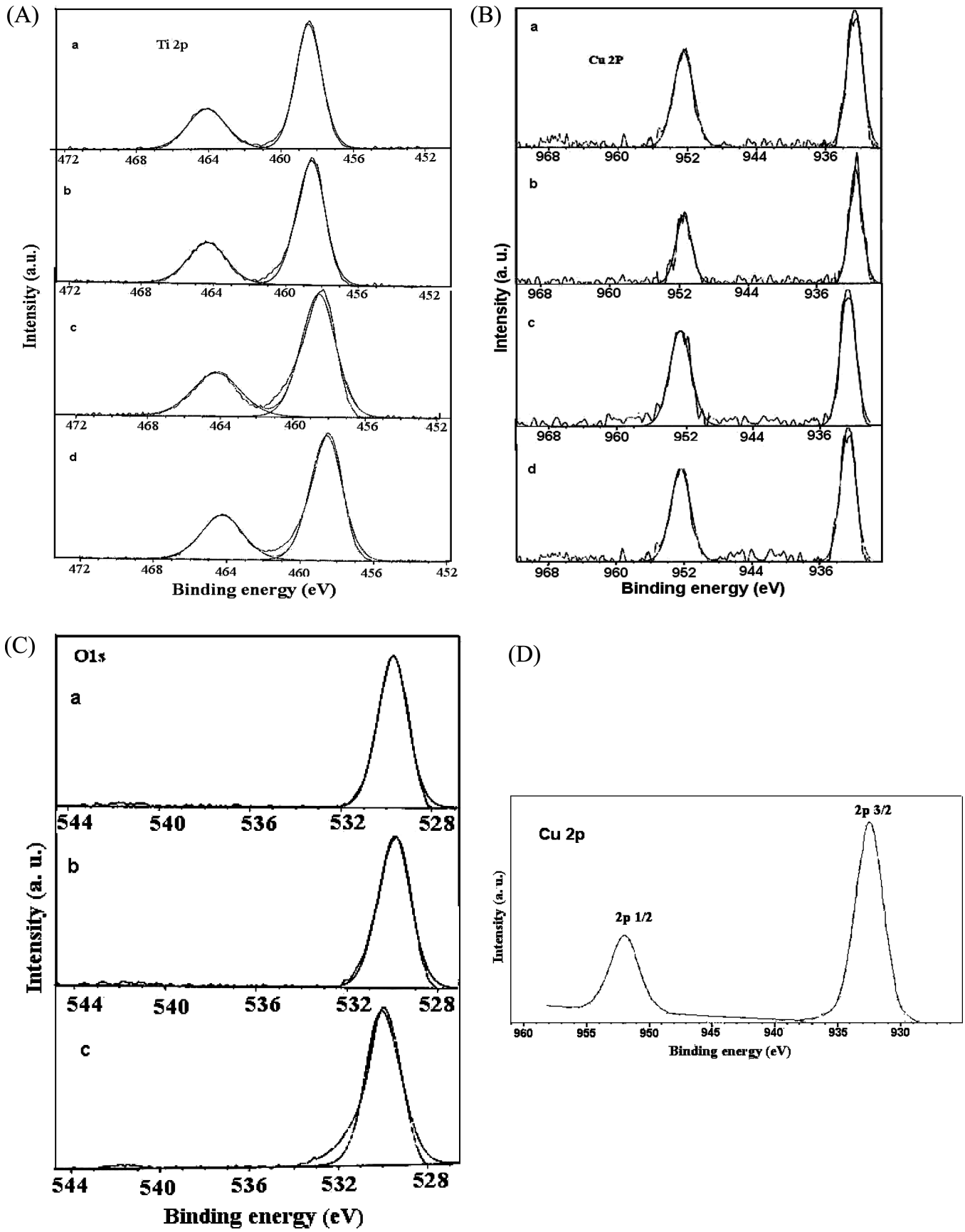


Figure 5. XPS of CT-2 catalysts. (A) Ti 2p at Cu wt % (a) 0.5, (b) 1, (c) 2, (d) 5. (B) Cu 2p at Cu wt % (a) 0.5, (b) 1, (c) 2, (d) 5. (C) O 1s at Cu wt %(a) 0.5, (b) 1, (c) 2. (D) Cu 2p spectra of 0.5 wt % CT-2 used catalysts.

are shown in parts A−C of Figure 5. The characteristic peaks of Ti $2p_{3/2}$ and $2p_{1/2}$ in TiO_2 (P-25) appear at binding energy values of 458.2 and 464.2 eV, respectively.[26] In CT-2 catalysts the Ti $2p_{3/2}$ and $2p_{1/2}$ binding energy values are slightly shifted to higher binding energy regions and appear at 458.6 and 464.2 eV (Figure 5A). Cu $2p_{3/2}$ characteristic peaks for Cu^0, Cu_2O,

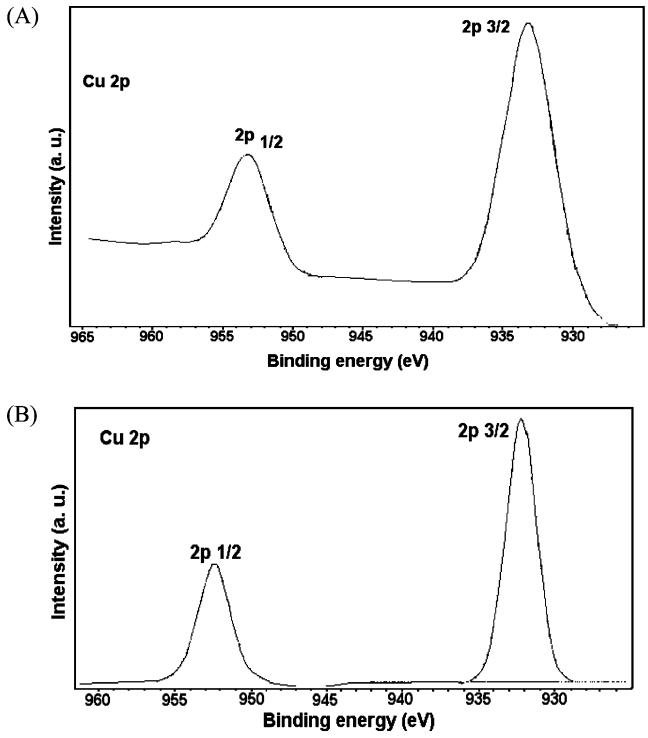


Figure 6. Cu 2p XP spectra of 0.5 wt % CT-1 catalysts (A) calcined and (B) used.

and CuO appear at 932, 932.7, and 933.6 eV.[26] The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ binding energy values of CT-2 catalysts appeared at 932.4 and 952.0 eV, confirming the presence of Cu^{1+} in CT-2 catalysts (Figure 5B). These results are in confirmation with earlier reports, where lower oxidation state of Cu is observed at higher calcintion temperatures.[16] O1s spectra of TiO_2 show the characteristic peaks of Ti−O linkages at a binding energy value of 529.9 eV. In CT-2 catalysts the binding energy values for O1s (Figure 5C) are shifted slightly toward higher binding energy values and appear at 530.6 eV. Figure 5D shows the Cu 2p XPS spectra of 0.5 wt % CT-2 used catalyst. On this catalyst the binding energy values appeared at 932.4 and 952.2 eV for Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, indicating that the oxidation state of Cu is the same (+1) even after using the catalyst for several hours under solar irradiation.

Cu 2p XPS spectrum of 0.5 wt % CT-1 catalyst is shown in Figure 6A. In CT-1 catalyst, the binding energy values appeared at 933.2 and 953.1 eV for Cu $2p_{3/2}$ and Cu $2p_{1/2}$ indicating that copper is in +2 oxidation state.[26,27] In CT-1 used, the BE values appeared at 932.8 and 952.2 eV (Figure 6B) indicating that CuO is converted into Cu_2O under solar irradiation.

3.6. Photocatalytic Activity. Photocatalytic hydrogen evolution studies are conducted over TiO_2 and Cu-loaded TiO_2 catalysts from pure water as well as glycerol:water mixtures under solar irradiation. Figure 7A shows the effect of Cu loading on photocatalytic hydrogen evolution from pure water on CT-1 and CT-2 catalysts. Hydrogen production is not observed on

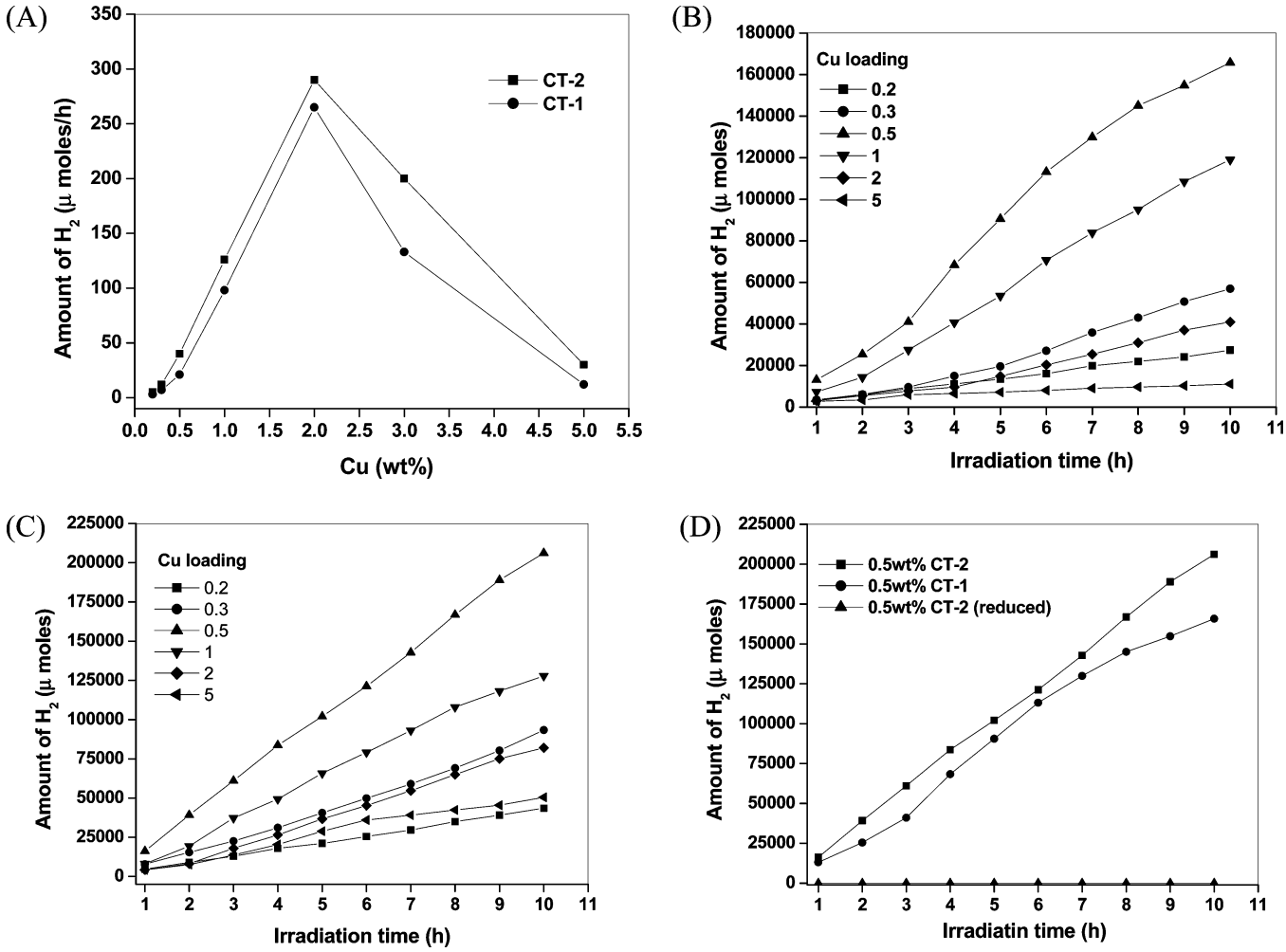


Figure 7. Cu loading vs hydrogen production activity over (A) CT-1 and CT-2 from pure water, (B) CT-1, (C) CT-2, and (D) 0.5 wt % CT-1, CT-2, and CT-2 reduced catalyst from glycerol:water mixtures under solar irradiation.

TABLE 2: H_2, O_2, and CO_2 Production over CT-1 and CT-2 Catalysts under Solar Irradiation

	H_2 production (μmol/h)		O_2 production (μmol/h)		CO_2 production (μmol/h)	
catalyst	water	glycerol + water	water	glycerol + water	water	glycerol + water
TiO_2	nil	600	nil	nil	nil	220
0.2 CT-1	3	2800	2	nil	nil	−
0.2 CT-2	5	4200	8	nil	nil	−
0.3 CT-1	7	5600	5	nil	nil	−
0.3 CT-2	12	9300	10	nil	nil	−
0.5 CT-1	21	16500	17	nil	nil	6050
0.5 CT-2	40	20060	30	nil	nil	7500
1 CT-1	98	11900	51	nil	nil	−
1 CT-2	126	12700	85	nil	nil	−
2 CT-1	265	4100	189	nil	nil	−
2 CT-2	290	8200	155	nil	nil	−
5 CT-1	12	1100	8	nil	nil	−
5 CT-2	30	4900	21	nil	nil	−

bare TiO_2 catalyst, whereas hydrogen and oxygen production is observed on copper-loaded TiO_2 catalysts as shown in Table 2.

TiO_2 and Cu-loaded TiO_2 catalysts are also evaluated for hydrogen production from glycerol:water mixtures under solar irradiation. Figure 7B shows the hydrogen production as a function of irradiation time over different CT-1 catalysts. Hydrogen production increased with increasing copper loading up to 0.5 wt % (16,485 μ mol/h), and above this loading the activity is seen decreasing. Figure 7C shows the hydrogen production over different CT-2catalysts from glycerol:water mixtures. Over these catalysts also the optimum amount of copper loading is found to be same. The hydrogen production over 0.5 wt % CT-2 catalyst is about 20,060 μmol/h. Of all the CT-1 and CT-2 catalysts studied, maximum hydrogen production activity is observed on 0.5 wt % CT-2 catalyst. When the reaction on CT-1 catalyst is compared with CT-2 catalyst, it is observed that the initial activity on CT-1 catalyst is only 50% that of CT-2 and after a period of 2−4 h, the activity is seen increasing to 80% of CT-2 catalysts. This may be seen as due to the reduction of Cu^{2+} on CT-1 to Cu^{+} during the course of reaction, which is confirmed by the XPS study of CT-1 used catalyst (Figure 6B). Thus hydrogen production activity can be studied on both CT-1 and CT-2 catalysts. As the CT-2 catalyst is showing high activity this system is further investigated to confirm Cu species in the +1 oxidation state is active for hydrogen production under solar irradiation. Thus thermally reduced CT-2 catalyst is also studied, and the results show that Cu in reduced state is not active for hydrogen production activity under solar irradiation. A comparative hydrogen production activity of 0.5 wt % CT-1, CT-2, and CT-2-reduced catalysts is shown in Figure 7D.

Activity studies are also conducted over 0.5 wt % CT-1, CT-2, and CT-2-reduced catalysts in glycerol:water mixtures under UV irradiation and shown in Figure 8.

About a 2−3-fold increase in the activity is observed under these conditions on CT-1 as well as CT-2 catalysts. Reduced catalyst is also showing almost equal activity as that of the calcined catalysts under UV irradiation. Under UV irradiation TiO_2 is the light-harvesting source and the loaded metal whether in the form of metal or metal oxide minimizes the electron−hole recombination and thus enhances the photocatalytic activity. These observations are in agreement with our earlier studies.[25]

The effect of glycerol concentration on hydrogen production activity over 0.5 wt % CT-2 catalyst was also studied under solar irradiation and is shown in Figure 9. With increasing glycerol concentration the hydrogen production activity increased and reached optimum at 5 vol %, and with further increase in glycerol concentration, the hydrogen production activity is seen decreasing. Earlier researchers found that after reaching the optimum concentration further increase in alcohol concentration decreases the activity, and they illustrated that this behavior results from the saturation of active sites.[7]

As 0.5 wt % CT-2 catalyst is showing optimum hydrogen production it is further subjected to time on stream activity.

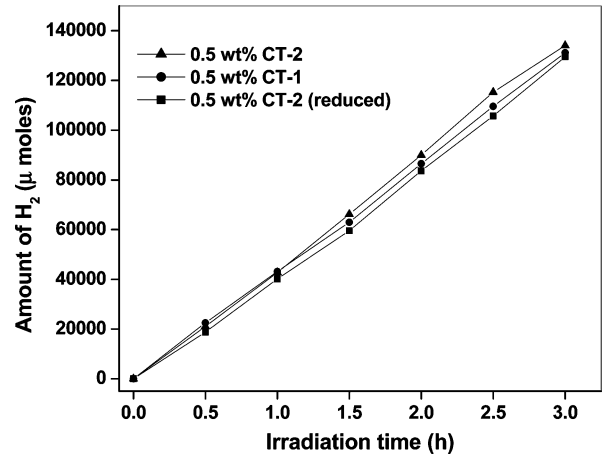


Figure 8. Cu oxidation state vs hydrogen production activity under UV irradiation.

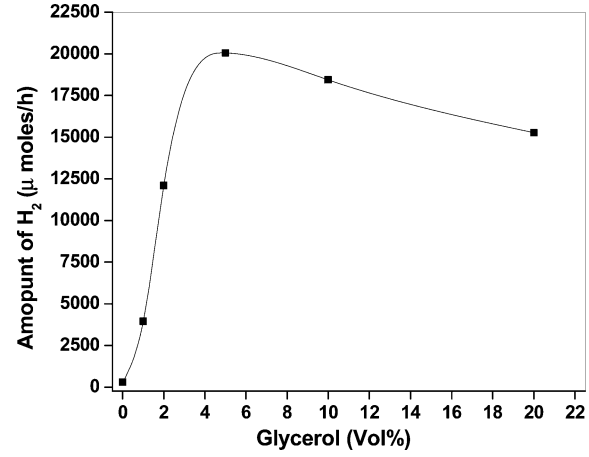


Figure 9. Glycerol concentration vs hydrogen production activity under solar irradiation.

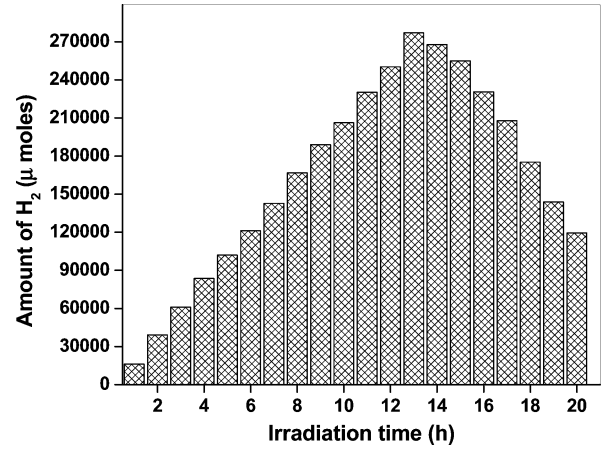


Figure 10. H_2 production activity over 0.5 wt % CT-2 catalyst under solar irradiation.

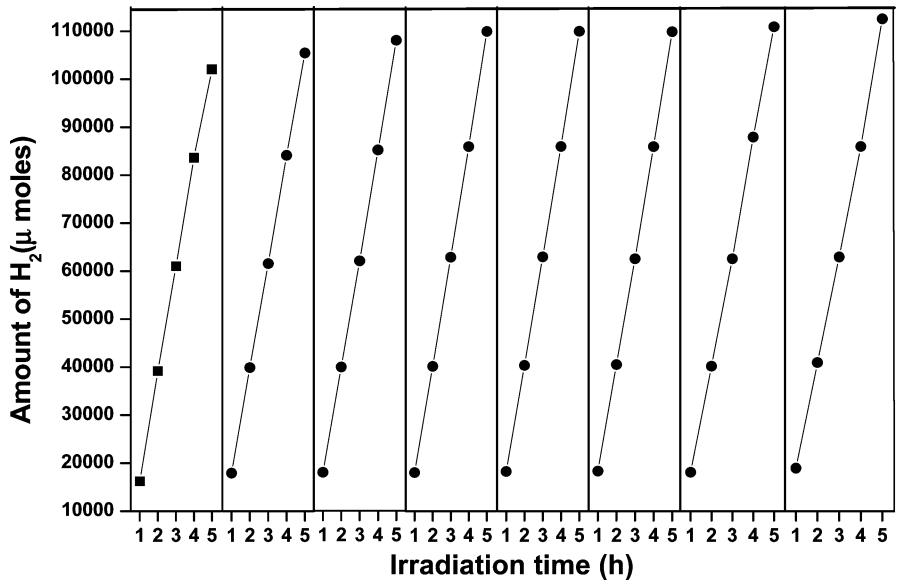
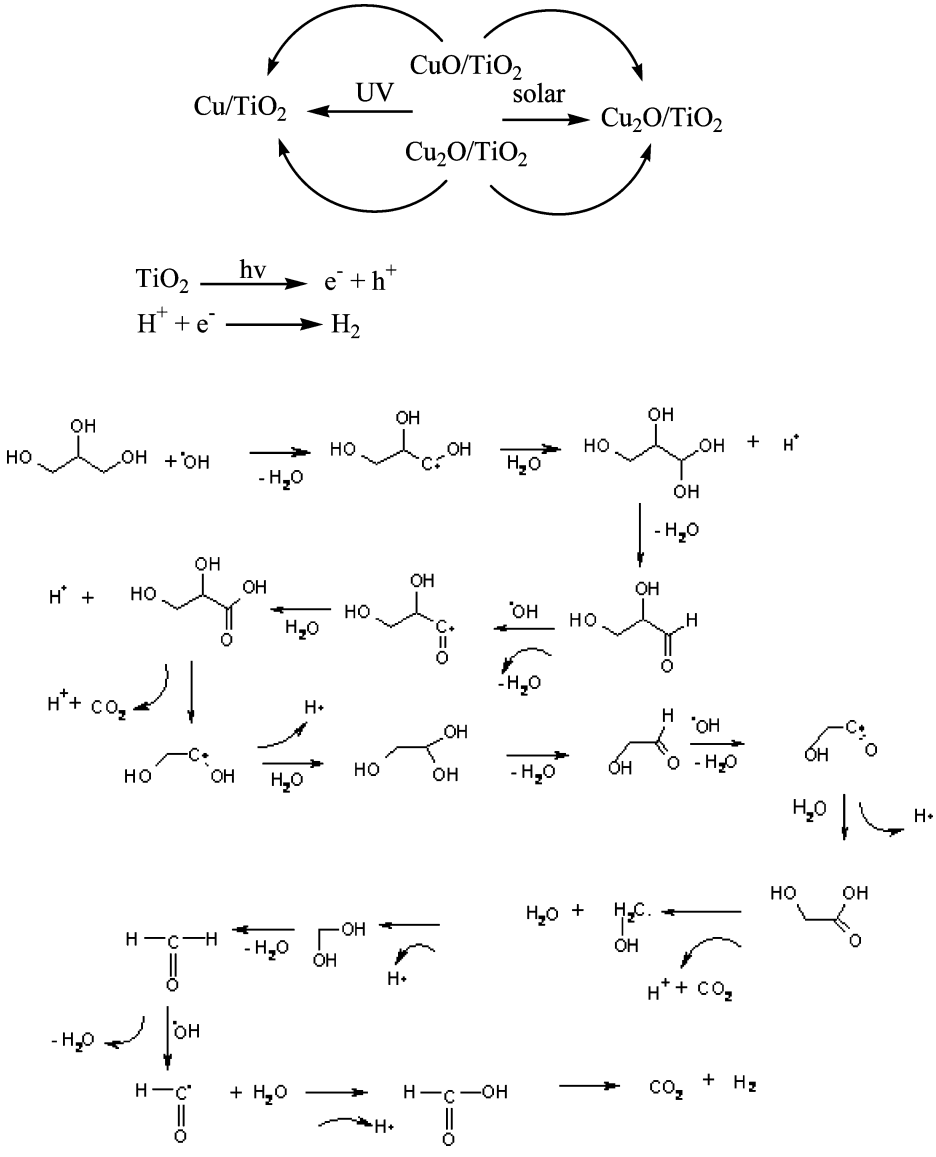


Figure 11. H_2 production activity in cycles over 0.5 wt % CT-2 catalyst under solar irradiation.

SCHEME 1



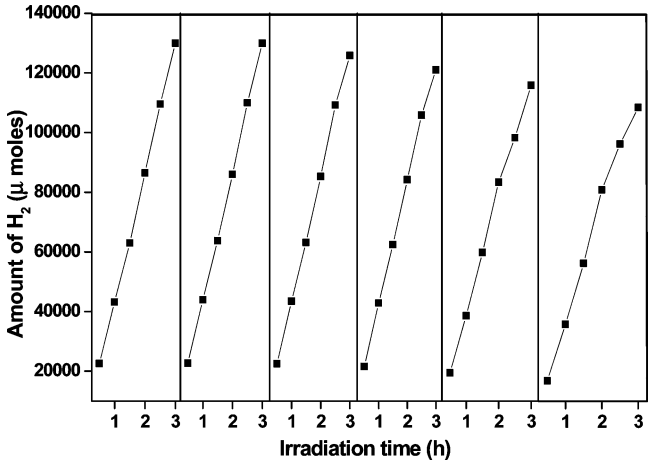


Figure 12. H_2 production activity in cycles over 0.5 wt % CT-2 catalyst under UV irradiation.

When the reaction is carried out continuously without evacuating the gases formed during the reaction, the activity is seen decreasing after 13 h (Figure 10), and this may be seen as due to the saturation of catalyst surface by the evolved gases suppressing the activity. When the activity tests were conducted by evacuating the evolved gases at regular intervals (5 h), a continuous and stable activity is observed under solar irradiation as shown in Figure 11. When this reaction was carried out under UV irradiation, after fourth cycle, the activity is seen decreasing (Figure 12). All the experiments were repeated 2−3 times, and the results are highly reproducible with ±1% variation.

3.7. Structure−Activity Correlation. The XPS results clearly illustrate that the oxidation state of Cu in the catalysts calcined at 350 °C is +2, and it is +1 in samples calcined at 450 °C. When the activity tests were conducted over these catalysts, CT-2 is showing higher and stable activity compared to CT-1 under solar irradiation. The initial activity over CT-1 catalysts is less, and after a period of 2−4 h, the activity increased steadily. This is seen as CuO becoming Cu_2O by consuming the electrons from initial irradiation. Once it is Cu_2O the activity is increased and resembles that of CT-2 catalysts. When these reactions are studied under UV irradiation CT-1 and CT-2 calcined and CT-2 reduced are showing almost same activity. Under UV conditions continuous activity is limited and decreases even after evacuating the evolved gases due to the possible dissolution of Cu ions in to the solution under the reaction conditions. From the characterization results and activity evaluations, a structure−activity correlation is observed, wherein the interacted copper ions with the surface of TiO_2 in the +1 oxidation state are playing an important role in harvesting the solar energy and responsible for continuous hydrogen production activity under solar irradiation as shown in Scheme 1.

4. Conclusions

By impregnating copper ions on TiO_2 surface, the absorption of TiO_2 is expanded into the visible region. EDAX confirms the presence of copper species on the surface of TiO_2. TEM photographs show the fine dispersion of copper species on titania surface. XPS analysis confirms the interaction of copper ions with TiO_2 and in that Cu is in the +2 oxidation state when calcined at 350 °C, and it is in the +1 oxidation state when calcined at 450 °C. Cu_2O/TiO_2 is showing stable and continuous activity under solar irradiation, and no activity is observed on reduced catalyst which is seen due to the decreased band gap. From these results it may be concluded that interacted copper ions in the +1 oxidation state with TiO_2 surface are responsible for continuous and stable hydrogen production activity under solar light irradiation. This study provides an efficient and low cost method for hydrogen production using solar energy.

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