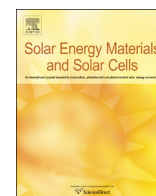




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A comprehensive study on sunlight driven photocatalytic hydrogen generation using low cost nanocrystalline Cu-Ti oxides



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ABSTRACT

A series of Cu doped titania, Cu_xTi_{1-x}O_{2-δ} (x=0.0, 0.02, 0.06) and copper oxide-titanium oxide nanocomposites, xCuO-yTiO₂ (x:y=1:9, 2:8, 5:5) were synthesized by sol-gel method and characterized by relevant techniques. The role of Cu ions in enhancement of photocatalytic evolution of H₂ from H₂O-methanol/glycerol mixtures in both sunlight and UV-visible irradiation over Cu/Ti oxides was investigated. X-ray absorption fine structure (XAFS), supported by X-ray diffraction and Raman studies, revealed that Cu substitution in TiO₂ stabilized anatase lattice, lengthened Ti-O bonds, decreased the coordination number around Cu ions, and induced oxygen ion vacancies and distortion (σ) in lattice. Distorted structures are more open and flexible with improved charge carrier dynamics and favourable photocatalytic properties. Nanosized Cu-Ti-O powders with enhanced N₂-BET surface area and microporosity exhibited improved photocatalytic properties. Reduction of CuO to photocatalytically more active Cu₂O by photo-generated e⁻ on the surface of composites was evident by the absence of Cu²⁺ peak in the XPS spectra of the composite sample after exposure to light. The most active formulations for sunlight assisted photocatalytic H₂ generation were Cu_{0.02}Ti_{0.98}O₂ for the doped samples, referred to as CuTi(2), and xCuO-yTiO₂(x:y=2:8) for the composite samples. Performance of the most active, CuTi(2), was monitored in a up-scaled photoreactor in order to investigate the influence of illumination area, catalyst concentration, form of catalyst (powder/films) and different sacrificial agents on H₂ yield. With an aim to identify practical materials for pilot plants, 6 mg of CuTi(2) was dispersed on (30 cm × 0.7 cm) ITO/PET films that exhibited enhanced efficiency (3.06%) as compared to same amount of CuTi(2) powder (1.41%). The results showed that the utilization of the CuTi(2) photocatalyst (without costly cocatalysts) with the proper selection of optimum operational conditions under sunlight in a up-scaled photoreactor, generated H₂ yield of 1.167 L/h/m² with apparent quantum efficiency, AQE, of 7.5% and solar to fuel efficiency, SFE, of 3.9% for the photocatalytic hydrogen evolution reaction (HER). Our results suggest that with this efficiency, H₂ at 1 L/h would be evolved photocatalytically over 0.9 m² of CuTi(2) photocatalyst, exposed to sunlight. Inputs obtained from the present study will be useful for further scale up of sunlight driven photocatalytic hydrogen production over low cost and efficient Cu modified TiO₂.

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1. Introduction

In the scenario of depleting fossil fuels and the emerging energy crisis, the search for alternate fuels has become a major research goal. Considering production, storage and combustion, hydrogen fuel with a gross calorific value of 141.8 MJ/Kg (~3 times of gasoline), has potential to meet the world's increasing energy

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demand. The revolutionary results of Honda and Fujishima [1] in 1972 about the photosensitized decomposition of water into H₂ and O₂ using an electrochemical cell, led to extensive investigations by researchers worldwide on photoelectrochemical, electrocatalytic or photocatalytic processes to split water. Photocatalytic water splitting is governed by efficiencies of photocatalysts which are generally powdered semiconductors; to convert the solar energy into useful chemical energy with the help of renewable sources [2,3]. The remarkable progress of the past decade in photocatalysis has been limited to the ultraviolet (UV) region instead of the more useful visible-light region. Traditional visible-light photocatalysts, such as CdS, CdSe, are either unstable

[4,5] or have low activity in the case of Fe_2O_3 , WO_3 and others [6]. Efficient H_2 generation over several photocatalysts, CoO [7], Pt-PdS/CDS [8], $\text{Cr}_x\text{Rh}_{2-x}\text{O}_3/\text{GaN}:\text{ZnO}$ [9] and $\text{Ru}/\text{SrTiO}_3:\text{Rh}-\text{BiVO}_4$ [10] are reported, but have associated limitations. Hence, the development of new and superior visible light photocatalysts is a major issue. A detailed account of the fundamental limitations for photocatalytic water splitting and the methods by which it could be addressed is provided in our chapter in a book edited by Banerjee and Tyagi [11].

Various methodologies are adopted to modify the electronic band structure of titania by introducing structural defects such as Ti^{3+} and oxygen vacancies or by incorporation of non-metals such as N, C, and S or transition metal and rare earth ions in its lattice so as to design an efficient visible light photocatalyst [12–16]. The cationic dopants add impurity levels in the conduction band of TiO_2 modifying its electronic structure. These defects and dopants create sub-band states in the band gap of TiO_2 and shift the absorption edge of TiO_2 towards the visible region, thus enhancing the visible light photoactivity. The advantages of transition metal ions is attributed to their behaviour as electron scavengers via $\text{M}^{n+} + e_{\text{cb}}^- \rightarrow \text{M}^{(n-1)+}$ where $\text{M}^{n+} = \text{Cu}^{2+}$, Mn^{3+} , Fe^{3+} . Cu has been considered to be important owing to the narrow band gap energies of its oxides (cupric oxide, CuO possesses 1.4 eV and cuprous oxide, Cu_2O possesses 2.2 eV) and their high light absorption coefficients [17–22]. As a p-type semiconductor with narrow band gap, cupric oxide has found use in a wide range of applications. Nanocrystalline CuO exhibits improved optical, electronic and catalytic properties that differ from those of bulk CuO [22,23]. Hara et al. [24] introduced Cu_2O powder as a p-type visible light photocatalyst that unlike electrodes does not photodegrade for overall water splitting. Since then, copper oxide has been considered as a potential photocatalyst and has been extensively studied. The absorption of visible light by Cu_2O or CuO greatly extends the wavelength range of TiO_2 when coupled; therefore further enhancing the efficiency of solar energy usage. Cu doping can also effectively reduce the wide band gap of TiO_2 by creating defects and d-band states of Cu in TiO_2 and can also act as active trap centers of electrons to reduce carrier re-combination [25]. Cu-doped TiO_2 or CuO/TiO_2 composites serve as an efficient photocatalytic material in the degradation of phenol [26], 4-nitrophenol [27], gas phase alcohols, acid red [28], methylene blue, sucrose, low concentration of mercury [29], SO_2 and NO removal etc. [30]. Wang et al. [31] have reported that the Cu-doped TiO_2 thin films exhibited enhanced photocatalytic activity compared to the reference TiO_2 thin film, for the degradation of methylene blue (MB) solution under simulated solar-driven irradiation. Cu-doped TiO_2 /graphene composites can also effectively photodegrade methyl orange (MO), and show an excellent photocatalytic enhancement over pure TiO_2 [32]. The role of surface/interfacial Cu^{2+} sites in the photocatalytic activity of coupled $\text{CuO}-\text{TiO}_2$ nanocomposites is emphasized by Li et al. [33].

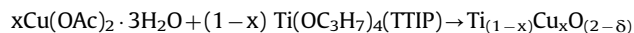
Recently, we have reported the photocatalytic H_2 generation over Cu_2O oxides prepared by various simple one pot synthetic routes using inexpensive precursors [34]. Photocatalytic properties determined by the combined effect of the surface area, porosity and crystallinity of the Cu_2O nanocrystals achieved with different synthetic routes were discussed. We have also reported the photocatalytic properties of solid solutions of TiO_2 with In_2O_3 to yield, novel UV-active In_2TiO_5 oxides and observed enhanced H_2 yield in the visible photoillumination after substitution by Nd^{3+} and Ni^{2+} ions [35–37]. In the present manuscript we report investigations on TiO_2 , a series of doped $\text{Cu}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ ($x=0.0, 0.02, 0.06$) and composites, $x\text{CuO}:\text{yTiO}_2$ ($x:\text{y}=1:9, 2:8, 5:5$) and compared their activities for photocatalytic H_2 generation under sunlight and UV-visible light in identical conditions. The samples have been synthesized by sol-gel and characterized by X-ray diffraction

(XRD), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), N_2 -Brunauer, Emmett and Teller (N_2 -BET) surface area, Raman spectroscopy, inductively coupled plasma-optical emission spectroscopy (ICP-OES), high resolution transmission electron microscopy/ selected area electron spectroscopy (HR-TEM/SAED) and diffuse reflectance UV-visible spectroscopy (DRS). The role of Cu ions as a dopant or as a composite in enhancing the photocatalytic properties of TiO_2 was investigated by *ex-situ* characterization of both fresh and used catalysts. The dependence of H_2 yield on geometrical factors such as illumination area, form of catalyst (powder/films), catalyst concentration and different sacrificial agents were investigated in up-scaled reactors. With an aim to identify practical materials for pilot plants, small amount of photocatalyst was spread over maximum available illumination area. 6 mg of $\text{CuTi}(2)$ was uniformly coated on 30 cm long and 0.7 cm wide ITO/PET films by a doctor blade technique. The performance of such films was compared with same amount of powder photocatalyst under identical conditions. Apparent quantum efficiency (AQE) and solar to fuel efficiency (SFE) of the photocatalysts under different conditions were calculated. Relevant related information including images and a video film are given in supplementary information.

2. Experimental

2.1. Synthesis of catalyst/co-catalyst

Nanoparticles of TiO_2 and doped $\text{Cu}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ ($x=0.0, 0.02, 0.06$) and composites, $x\text{CuO}:\text{yTiO}_2$ ($x:\text{y}=1:9, 2:8, 5:5$) with nominal compositions were synthesized through sol-gel method by mixing reactants in appropriate stoichiometry as depicted by following equation:



Cupric acetate (> 99%, SDFCL, s d fine-chem Ltd), titanium tetraisopropoxide (TTIP, 97%, Aldrich) and propan-2-ol (AR > 99.5%, SDFCL, s d fine-chem Ltd) were used as received. An appropriate amount of cupric acetate was dissolved in 10 ml distilled water to prepare solution A. Another solution referred as B containing appropriate amounts of propan-2-ol and TTIP was also prepared. Solution B was added drop wise to the solution A under constant stirring till a gel was formed. The gel was left overnight undisturbed for nucleation to take place. After nucleation, the gel was heated at 50 °C, stirred and was vacuum dried for ~1 h to remove the moisture from the sample. The dried samples were heated in oven at 100 °C for ~1 h. Further, all samples were calcined at 500 °C for 5 h at a heating rate of 2 °C min^{-1} in air to ensure the uniformity and the completion of the reaction. Depending on Cu content, white to brownish-black to black coloured photocatalyst powders were obtained.

To further improve the photocatalytic hydrogen production, Pt as cocatalyst (~1% by weight) was loaded on the $\text{Cu}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ ($x=0.02$ and 0.06) samples, by the photo-deposition method. For this purpose, 0.1 g of the catalyst was mixed with 25 ml of water, 5 ml of ethanol and 2.5 ml of chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 0.002 M). The resulting reaction mixture was evacuated in a quartz cell and then irradiated under medium-pressure mercury lamp (Hg, Ace Glass Inc., 450 W) for about 3 h. After irradiation, the solution was washed with ethanol, filtered and the residue was dried in an oven at 100 °C.

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