Electrochemical Fabrication of Cu₂O-Nanowires-based Photo-cathodes for Enhanced Solar Water Splitting

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Abstract

Solar-power driven photoelectrochemical (PEC) water splitting using semiconductor photoelectrodes is one of the most promising approaches for energy conversion, in terms of production of renewable hydrogen with a minimum carbon footprint. There are, however, enormous challenges to be overcome to obtain sufficient solar water-splitting efficiency, such as over-potential losses due to fast recombination rates of charge carriers, electrode photo-degradation, limited light-harvesting capacities, to name a few. In this work, we report an extensive study on Cu₂O based photocathode for hydrogen evolution reaction (HER) in terms of enhancing its solar-to-hydrogen (STH) conversion efficiency, while using low-cost fabrication methods. We have addressed the inefficiency of Cu₂O which mainly arises due to incompatible light absorption and charge carrier diffusion lengths, by fabricating highly reproducible Cu₂O-nanowire arrays on Cu substrate. The reported optimal thickness of Cu₂O for efficient absorption of sunlight is around 2-4 μm , while the minority charge carrier diffusion length is limited to 200-250 nm only. The nanostructured Cu₂O, especially in the form of nanowire arrays, improves its performance through morphology control, by improving the light-harvesting capacity along the full length of wire and providing a shorter diffusion path length corresponding to the radial distance in the wire, towards the electrolyte. We prepared the photocathode by anodizing Cu foil to Cu(OH)₂ nanowires at 10 mA/cm², followed by oxidation to Cu₂O nanowires in an inert atmosphere. Experimental measurements showed that the process was highly reproducible and resulted in an increased current density from -0.5 mA/cm² for planar Cu₂O to -82.3 mA/cm² for Cu₂O nanowires, both at 0.9 V cathodic bias. The photocurrent density was enhanced from -0.15 mA/cm² for planar Cu₂O to -5.54 mA/cm² for the nanowire morphology, while using visible light source in all cases. All the photoelectrodes were reproducible in the regime of 4 μm thicknesses of Cu₂O nanowires, oxidized over Cu-foil substrates. The STH efficiency calculated for all the fabricated photoelectrodes was as high as 3.54% $\pm$ 0.21%, in comparison to 0.24% for the planar Cu₂O photoelectrodes.

Keywords: Cu₂O, nanowires, photocathode, solar water splitting, photoelectrochemistry, STH efficiency, PEC.

1. Introduction

The current rate of world's energy consumption is predicted to be doubled by 2050, and a majority of this energy today comes from the fossil fuels, such as coal, petroleum, and natural gas, whose combustion results also into the emission of greenhouse gases (Bak et al., 2002). As the demand for energy is increasing and the accessible resources of fossil fuels are limited, an attractive alternative to the current energy sources would be to harness the solar energy. But the diurnal and regional variations in the solar energy incident on earth require materials which are capable of absorbing and storing it in a useful and retrievable form of energy. One of the most promising options is to store solar energy in a chemical form, hydrogen, produced by splitting water (Dodds and Mcdowall, 2012) (figure1). Semiconductors are, by far, the best candidates for absorbing the sunlight and converting it

into the electrical energy, which in turn can be used to split water into hydrogen and oxygen (Tamirat et al., 2015). Thermodynamically, the standard electrode potential required to split water is 1.23V ($\Delta G = 475$ kJ/mol) (Stern et al., 2017). However, practically, due to the over-potential losses and series resistances at the electrode/electrolyte junction and in the solution, the potential requirement for splitting water is increased approximately by 0.8V (Li et al., 2016). Semiconductor materials having bandgaps favourable for the visible-light absorption ($1.5 \leq E_g \leq 2.5$), with proper valence and conduction band alignments for water oxidation and reduction potentials, and with stability with respect to photo-oxidation, are considered to be the suitable materials for photo-electrochemical water splitting (Yang et al., 2016). Metal-oxide semiconductors (MOS), as such, could be the best replacement for the expensive noble metals which are normally used for the photo electro-catalysis of water. The MOS are known to be earth-abundant, non-toxic, environment-friendly, and cost-effective materials. The versatility of the metal-oxide, copper(I)oxide, also known as cuprous oxide has received an increased attention in recent years for its potential as a solar-cell material (Choi et al., 2017; Pavan et al., 2015). It is one of the few metal oxides which, intrinsically shows the p-type conductivity, has a direct band gap of 2.0-2.1 eV, and has its conduction and valence band edges at the positions of -0.75V and 1.3V, respectively, and thereby straddles the whole redox potential of water (figure 2). Cu_2O has a theoretical maximum photo-current density of -14.7 mA/cm² under A.M. 1.5 illumination, and STH of 18% (Tilley et al., 2014), which is one the highest theoretical STH efficiencies known for metal oxides. Cu_2O suffers from the challenges of photo-corrosion in an aqueous medium, over-potential losses due to high charge-recombination rates, and a limited light harvesting capacity. The minority charge-carrier diffusion length for Cu_2O is approximately 200-250 nm (Jiang et al., 2017), while the light absorption-length is in the micron range of the scale (figure 3). This incompatibility of the light-harvesting lengths of Cu_2O results into a faster recombination of photo-excited electrons and holes in the bulk of material, while a high percentage of the absorbed photons go un-utilized.

In this work, we have addressed the challenges of the limited efficiency of Cu_2O , caused by a fast recombination of charge carriers, by reducing the transverse length scale of Cu_2O film to nano-scale diameter wires, thereby reducing the dimensions effectively to 1-D. Fabricating Cu_2O in the form of nanowires increases the surface-to-volume ratio, and hence, the photo-current density, and reduces the recombination rates of the electron-hole pairs across the diameter of wires (Fumagalli et al., 2016). Here, we report an enhanced photo-current density of Cu_2O nanowires, and for the first time, with a better stability than that of the planar Cu_2O in an alkaline medium without using any over-protection layers.

2. Experimental work

2.1 Synthesis of Cu_2O nanowires

KOH, HCl, HNO_3 , ethanol, acetone, and Na_2SO_4 were purchased from Fischer Scientific, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, lactic acid, and de-ionised water were purchased from Merck. Pilkington fluorine doped tin oxide (FTO) substrates of sheet resistance of ≤ 9 ohms/sq, and thicknesses of 1.5 mm were used. All the materials were of analytical grade, and were used directly for experimental work without any further purification. The reference and the counter electrodes, platinum loop and Ag/AgCl, were purchased from Metrohm Pvt. Ltd. The silver conductive ink was purchased from Alfa Aesar, and the non-conductive epoxy paste (Hysol Loctite 3423) was purchased from RS Components Pvt. Ltd. All the PEC measurements were carried out using the PSGS, Autolab (model 302 N – Metrohm). The spectrum of xenon light source was measured by Ocean Optics Spectrometer (figure 6). The optical properties were measured by Perkin – Elmer UV-Visible Spectrometer.

Cu₂O nanowires were prepared by the electrochemical oxidation of Cu foils in a 5 M aqueous KOH solution, keeping pH as high as 13, at a current density of 10 mA/cm² for minutes. This resulted in the formation of blue coloured Cu(OH)₂ nanowires, which were further oxidized in an inert atmosphere of N₂ at 850°C for 4 hours to form the reddish-brown coloured Cu₂O nanowires (figure 4). The diffraction patterns in XRD clearly confirmed the formation of Cu₂O over the Cu substrate, which was also used as a sacrificial anode.

After developing the Cu₂O nanowires through the simple reactions, (1) to (3), these were examined for their structural and optical properties in more detail. The Cu(OH)₂ nanowires of an average diameter of approximately 100-150 nm and an average length of around 10-12 µm were analysed by transmission electron microscopy (TEM) (figure 9 (a)). After annealing, the Cu₂O nanowires produced were approximately 80-90 nm in diameter and 8-9 µm long, resulting in a very good aspect ratio of more than 100 (figure 9 (b)). Scanning electron microscopy (SEM) was done to further confirm the surface morphology of the nanowires, which showed dense, though rough arrays of nanowires over the sacrificial Cu substrate (figure 9 (c)).

The optical response was measured by UV- Visible spectrometer, which showed a good absorption of light in the solar region, ranging from 248–600 nm in wavelengths (figure 10). The electrochemical impedance spectroscopy (EIS) was used to confirm the p-type conductivity of Cu₂O, using the Mott-Schottky equation.

$$\frac{1}{C^2} = \frac{2}{(\epsilon\epsilon_0 A^2 e N_D)} \left(V - V_{FB} - \frac{k_B T}{e} \right) \quad \dots (1)$$

, where C is the space-charge region capacitance, ϵ the relative permittivity of Cu₂O, reported to be equal to 7.5 for Cu₂O, ϵ_0 the permittivity of free space, k_B the Boltzmann constant, T the absolute temperature, e the electronic charge, N_D the doping density, A the active area of the working electrode, V the bias potential, and V_{FB} the flat band potential. After the confirmation of p-type conductivity, Cu₂O was then used as a photo-cathode for the reduction of water in photo-electrochemical (PEC) measurements.

2.2 Electrodeposition of simple planar Cu₂O

To compare the photo-current densities, the planar Cu₂O was also synthesized by the electrodeposition method (Wang et al., 2012). Before carrying out the electrodeposition of Cu₂O, the FTO substrates were cleaned by subjecting them to the ultrasonication in isopropanol, and ethanol, each for 15 minutes, followed by sonication in dilute HCl for 5 minutes. Electrodeposition of Cu₂O was then carried out at -0.65V vs Ag/AgCl for 30 minutes to achieve similar thicknesses for all the samples as for the Cu₂O nanowires samples. The phase and composition were analysed under X-Ray Diffraction, where the diffraction patterns corresponded to FTO and Cu₂O. The electrodeposition was carried out in a three-electrode cell, with the aqueous electrolyte containing 0.5M CuSO₄.5H₂O, and 3.75M lactic acid. Alkaline pH was maintained by the addition of 4M NaOH to the solution (figure 5).

On an average, the film thicknesses of all the samples, measured with an optical profilometer for both planar as well as nanowires samples, were in the vicinity of 4 µm (figure 12).

2.3 Photo-electrochemical (PEC) measurements

All the PEC measurements, for both planar and nanowired Cu₂O samples, were carried out in the same single-compartment three-electrode cell, using a xenon light source, and the counter

and reference electrodes used were the Pt loop and Ag/AgCl, respectively. 0.1M N_2SO_4 solution was used as an electrolyte, buffered at pH of 13.

3. Results and discussion

Figure 7 shows the potential vs. time response of the chronopotentiometry of Cu substrate in aqueous 5M KOH solution. From the V-t response, the nanowires synthesis of Cu_2O by this process is proved to be highly reproducible, besides being very facile. The Cu_2O nanowires were formed next by thermal annealing of the prepared $\text{Cu}(\text{OH})_2$ nanowires in an inert atmosphere of N_2 . XRD analysis showed that the prepared samples were highly crystalline in nature, with cubic crystal structure in both the cases. The diffraction patterns corresponded to Cu and Cu_2O only, while no peak confirmed the presence of any traces of CuO for the nanowires samples (figure 8 (a)) and the patterns expectedly corresponded to FTO and Cu_2O for the planar samples (figure 8 (b)). The morphology of the nanowires was determined by SEM (Zeiss EVO 50 & EVO 18 special) and the confirmation of nanowires' structure done by TEM (JEM – 1400). A very good aspect ratio of approximately 112 could be confirmed from the TEM analysis of the nanowires with the average length in the range of about 8-9 μm and the average diameter of about 80 – 90 nm. SEM micrographs revealed that the nanowires prepared were highly dense, though roughly arranged. The electrodeposited Cu_2O was also analysed under SEM, which showed the planar morphology. The optical properties of the prepared nanowires samples of Cu_2O were measured by UV-Visible spectrophotometer, which showed a good absorbance of light in the UV and visible regions of the solar spectrum. For all the samples of Cu_2O , the film thicknesses measured with the help of an optical profilometer were approximately 4 μm . From PEC measurements (figure 14), it was observed that the photocurrent density measured for the nanowires morphology of Cu_2O was enhanced by a factor of 37 from -0.15 mA/cm^2 for the planar film to -5.54 mA/cm^2 for the nanowires film. The STH efficiency was enhanced fifteen fold to 3.54% for the nanowires morphology from 0.24% for the planar film. Figure 15 showed that under cyclic voltammetry (CV), the nanowires samples of Cu_2O showed a better stability than that of the planar ones upto the 10th cycle, after which the current density started to decrease. The CV of planar samples showed a stability up to the 2nd cycle only of CV only in the same electrolyte. For the reproducibility, we observed the similar results for three different samples. It is, for the first time ever, observed that the nano-structured material has a better stability than its planar counterpart. We hypothesize that any impurities, present in the electrolyte or on the surface of electrode, might adsorb onto the electrode more readily for the nanowires, because of their higher surface energies as compared to that for the planar films. Since the impurities are present in small quantities, they would form a thin coating thick enough to protect the nanowires from photo-corrosion, but yet thin enough to be permeable to the charge carriers. This might have caused the higher photocurrent density in the case of nanostructures.

Conclusions

The nanowires of Cu_2O were successfully synthesized with a high reproducibility and a good aspect ratio of above 100, with uniform diameters of about 80-90 nm and lengths of about 8-9 μm . Their crystalline structure was confirmed by XRD, which showed the presence of (111) crystal plane in all samples. The potentiostatic deposition of Cu_2O was achieved by the cathodic reduction of alkaline copper lactate solution on FTO substrates to obtain the pure planar Cu_2O . It was concluded from the PEC measurements that the inefficiency of Cu_2O , caused due to the incompatibility of minority carrier diffusion length and the photo-absorption length, could be successfully addressed by fabricating Cu_2O in the form of nanowires. The photocurrent density for the electrodeposited Cu_2O was estimated to be -0.15

mA/cm², which was enhanced in the nanowire morphology to -5.54 mA/cm², both at -0.9V bias vs Ag/AgCl reference electrode. The STH efficiency was observed to increase with the nanowire morphology from 0.24% to 3.54%. Our work has for the first time shown an enhanced stability for the nanowire structure as compared to that of planar one, based on the observations of the CV peaks. This finding possibly opens up new vistas for stabilization of nanostructures through the introduction of controlled levels of specific impurities.

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Additional information

A separate file for the figures, equations, and proposed reactions are provided for the supplementary information.

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