Nanostructured copper oxide photocathodes for photoelectrochemical hydrogen production by water splitting

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Introduction

In 21st century sustainable and clean energy resource is one of the paramount issues for addressing uninterrupted development of modern human society. Hydrogen a future energy carrier due to its high energy density and zero carbon foot print is most promising replacement for extinguishing fossil fuels and associated energy crises.

Among various hydrogen generation techniques, photoelectrochemical (PEC) solar water splitting is considered as sustainable and ecofriendly approach [1]. In PEC cell, semiconductor based photoelectrode absorbs solar energy to generate electron-hole pair which performs water splitting reaction. A wide variety of semiconductor materials based on metal oxides have been reported for photoelectrochemical water splitting. Wide band gap semiconductor material like TiO_2 (3.2eV) only absorbs 10 % light of solar spectrum, which limits its efficiency. Contrary to that small band semiconductor material can absorbs more light and fundamentally leads to higher efficiency.

Copper is an intrinsic p-type semiconductor [2,3] of choice due to its favorable band gap and location of band edges, efficient light absorption, earth abundance etc. are and has proved as an efficient photocathode in PEC cell for water splitting. In the present study attempts have been made to prepare a nanostructured copper oxide based photoelectrode and evaluate its properties for PES water splitting.

Materials and Methods

Facile electrodeposition method was employed in stepwise manner to synthesize copper based photoelectrode due to its ease and reproducibility. Copper nitrate (Merck) and NaOH were used as precursor for copper and as oxidizing agent respectively. Indium tin oxide was used as substrate for electrodeposition. In step 1, a thin metallic copper film was deposited on ITO by reducing precursor solution (0.1M Copper nitrate) at a potential of -1 V for 10 min. Further in step 2, metallic copper is electroxidized in aqueous alkali (NaOH) at specific potential. Finally moderate temperature thermal treatment at 400°C for 1 h was carried out to convert cupper into copper oxides. The electrodes were characterized using XRD, UV-Vis Spectroscopy and photoelectrochemical techniques.

Results and Discussion

The XRD pattern of copper based photoelectrode presented in **Figure 1A** confirms the co-existence of two phases of copper oxides. The intense peaks present at 2θ value 37.4°, along with 30.1, 44.3, 62.5 and 74.2 corresponding to (111) (110) (200) (220) and (311) planes matches with cuprous oxide (Cu_2O, JCPDS card No.34-1354), whereas the peaks present at 2θ value 35.7, 39.1, 49.3, 61.8, 66.2, 68.2 corresponding to (111), (200), (202), (113), (311), (220) confirms presence of cupric oxide (CuO, JCPDS card No.48-1548) phase. The UV-DRS spectra of copper based photoelectrode (**Figure 1B**) also shows co-existence of two phases resulting in dual band gap (1.27 eV and 2.57 eV) with two absorption peaks in range 350-400 nm and 500-650 nm. Photoelectrochemical evaluations presented in **Figure 3** shows high cathodic photocurrent of -1.49 mA/cm^2 at an applied bias of -0.7 V vs Ag/AgCl. Incident to photon conversion efficiency (IPCE%) shows 1.6% efficiency at 0.0 V bias at 400nm. Further evaluations were carried out to determine positions of band edges and flat band potential using Mott-Schottky plots (Flat band potential, V_{FB}= 0.6 V) and conductivity using Nyquist plot. These evaluations also confirm high photoactivity for copper based photoelectrode for PEC hydrogen production..

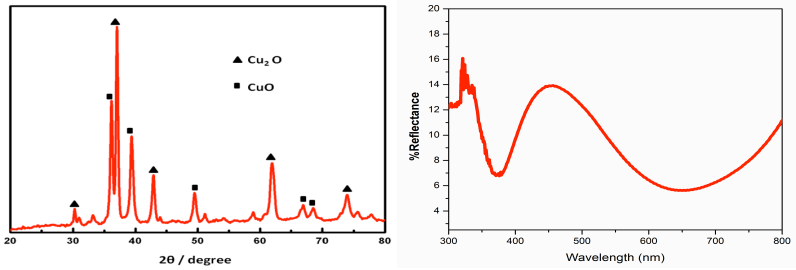

Fig. 1 XRD Pattern (A) and UV-DRS (B) spectra of copper-based photoelectrode

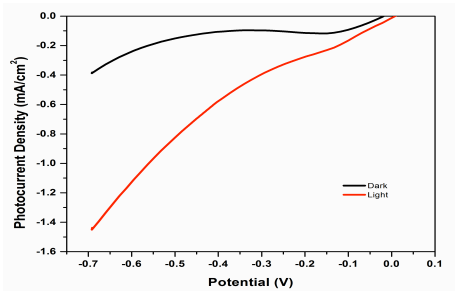

Figure 1: Current-Potential (I-V) characteristics of Cu-based photoelectrode in dark and under illumination in 1M $NaSO_4$ electrolyte.

Significance

A copper based photoelectrode was synthesized via a facile and cost effective electrodeposition route which shows high cathodic photocurrent of -1.49mA/cm^2 at moderate applied bias. Co-existence of dual band gap in UV-Visible region shows better light absorption. Better light absorption due to dual band gap of 1.27eV and 2.57eV leads to high cathodic photocurrent and makes it a promising photocathodic material candidate for PEC water splitting.

References

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