Synthesis and characterization of vertically aligned 1-D nanostructured CuO/Cu_2O heterojunction on passivated Cu template for solar water splitting

Iqra Reyaz Hamdani[1], Ashok N. Bhaskarwar[*]

[1]Chemical Engineering Department, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India.

[*]Corresponding Author. Tel: (+91) 11 26591028, E-mail: ashoknbhaskarwar@yahoo.co.in

Abstract: Nanostructures, particularly 1-D nanostructures of copper compounds, have gained increased research interest recently due to their better electrical and optical properties, and hence potential applications in renewable energy harvesting. 1-D nanostructures, such as nanowires, nanoneedles, nanotubes etc. independently decouples the light absorption length and minority charge carrier diffusion length of a semiconductor photo-electrode in a solar water splitting system, by allowing the length of nanostructure to absorb light while diameter to carry the charge transfer across the electrolyte/electrode interface, besides having larger surface area to absorb photons to a more better capacity. We fabricated 1-D nanoneedles of CuO/Cu_2O heterojunction by self-organized electrochemical oxidation of Cu in a highly alkaline medium, in an aqueous KOH, with pH maintained at 13 at room temperature. Prior to the anodization of Cu susbtrate, it was electropolished in a 15 M H_3PO_4 solution and run for cyclic voltammetry in 1 M KOH to analyse its redox potentials in a three-electrode system, with Pt spiral as the counter electrode ,and Ag/AgCl as the reference electrode, at a scan rate of 10 mV/s. According to the obtained voltammetric results, we noticed three peaks corresponding to the oxidation of Cu, and as per the literature (Ambrose et al., 1973), oxidation of cu at – 0.1 V occurs to Cu_2O, and at 0.15 V, it oxidizes to CuO or $Cu(OH)_2$, depending upon the temperature. Different samples were prepared by oxidizing Cu at different potentials from -0.2 V to +0.3 V vs Ag/AgCl, all in a chemically inert atmosphere of N_2. All the oxidezed samples were dried by a purge of N_2 flow and then investigated for composition and morphology. X-Ray diffraction showed the peaks were corresponding to CuO/Cu_2O mixed heterojunction in samples which were oxidized at potentials between 0.1 V to 0.2 V. Morphology study using scanning electron microscopy showed the highly vertically aligned nanoneedles structures for the samples oxidized at 0.1 V with the nanoneedles density decreasing towards 0.2 V. There were no nanostructures for samples oxidized at lower than 0.1 V potentials. Thus, the CuO/Cu_2O nanoneedles heterojunction samples prepared at +0.1 V were analysed for the photo-electrochemical performance for solar water splitting, and compared to the planar CuO/Cu_2O heterojunction samples. It was observed that the photocurrent density was highly increased from -3 µA/cm^2 for planar samples to -0.15 mA/cm^2, under the same light intensity of 100 W/m^2 of visible light. This resulted into a significant increase in the photo-efficiency of the semiconductor from 0.02 % to 0.24 %. Thus, it could be concluded that the nanostructured CuO/Cu_2O having the larger surface area, and higher capability of absorbing light and charge transfer resulted into a better photocurrent density of the vertically aligned nanostructured samples, and hence, causing better efficiency for solar water splitting.

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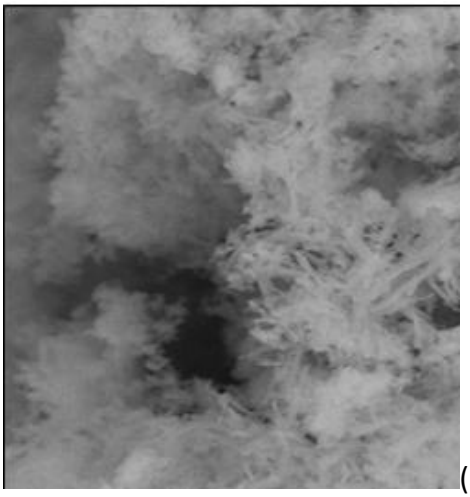
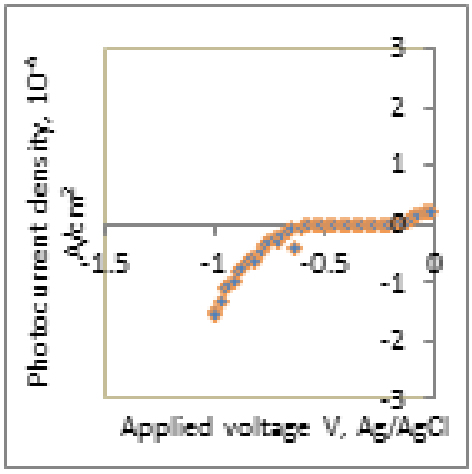

(a)



(b)

Figure 1: (a) Nanoneedle structure of CuO/Cu_2O heterojunction, (b) Photo-current density of nano CuO/Cu_2O.

Reference: Ambrose, J., Barradas, R.G., Shoesmith, D.W., 1973. INVESTIGATIONS OF COPPER IN AQUEOUS ALKALINE SOLUTIONS. Ectroanalytical Chem. Interfacial Electrochem. 47, 47–64.

Biography: Iqra Reyaz Hamdani received her B. Tech. in Chemical Engineering from National Institute of Technology Srinagar (2012). She worked in the capacity of Assistant Manager (Technical) in one of the Maharatna PSUs of India, Coal India Limited (2012-2015). She is currently pursuing her PhD from the Department of Chemical Engineering, Indian Institute of Technology Delhi under the supervision of Prof. Ashok N. Bhaskarwar (2015- present).

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