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Optimization of semiconductor ns-TiO_2-CuO admixed photoelectrode for photoelectrochemical solar cell in regard to hydrogen production

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ABSTRACT

This paper deals with the investigation on the optimization of ns TiO_2–CuO admixed/Ti with respect to optimum photoelectrode area for semiconductor septum photo electrochemical solar cell. The motivation of the present work was to prepare an electrode having high effective surface area and hence better quantum yield and improved PEC activity. The photoelectrochemical response of ns TiO_2-CuO photo electrodes for four different electrode area has been measured to explore the effect of electrode area on the output power in a chemical fuel (i.e. H_2) produced by SC SEP PEC cell. This was done for determining the electrode area for optimum electrical output and hydrogen production. The photo electrochemical cell having ns TiO_2-CuO admixed/Ti photoanode of several geometric areas like 0.5, 1.0, 1.5, 2.0 and 2.5 cm^2 were fabricated and characterized. It has been found that the photoanode area corresponding to optimum electrical output and hydrogen production rate corresponds to 1.5 cm^2.

Introduction

It is clear from the increasing energy demand that access to renewable energy sources is essential for the development and sustainability of the world. Therefore to meet the energy demand the main efforts of researchers nowadays are to produce hydrogen energy from various ways like biofuels, biohydrogen production, thermochemical, photoelectrochemical etc. [1–6]. In this direction use of solar energy for the production of clean hydrogen fuels by a photoelectrochemical (PEC) cell is gaining importance. Photoelectrochemical (PEC) splitting of water into hydrogen and oxygen is a promising way to directly convert solar energy in to fuel. It represents a very attractive but challenging alternative because of convenience in fabrication and in situ storage facilities [7]. Till date the solar energy conversion efficiency obtained by single photoanode PEC cell is not desirable to meet the energy demand hence improvement in the PEC cell is very much required to fill in the gap between the energy demand and conversion efficiency obtained by the PEC cell.

PEC cell is a very complex system, with many factors governing the device performance. For the photoanode part various types of semiconductor material with energy band positions that favor water oxidation and reduction are employed, among all the semiconductor material titanium dioxide (TiO_2) has been considered the most suitable material due to its low cost, chemical stability and comparatively high photocatalytic efficiency [8,9]. Though TiO_2 is found to be a suitable semiconductor electrode for PEC cells but it suffers from the major drawback of high band gap of 3 eV (410 nm) and because of this high band gap it absorbs only the UV

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region of the solar energy. Therefore several attempts have been made to bring the spectral response of TiO_2 into visible and near visible region. It is known that the spectral response of the TiO_2 films can be improved through admixing with appropriate oxides or by deposition of noble metal nanoparticles on TiO_2 [10–12]. In the earlier studies we have improved TiO_2 photoelectrode by admixing CuO with the nanostructured prepared TiO_2photoelectrode, the surface morphology, structural and PEC characterization of the TiO_2 overland with CuO admixtures have been investigated in relation to hydrogen production through semiconductor septum photo-electro-chemical (SC-SEP PEC) solar cell. CuO is an interesting candidate because it has wide range of applications such as gas sensor, photochromic and electrochromic [13,14].

In the present work we have considered another aspect that is to determine the effective photoelectrode area that will lead to high electrical and hydrogen production. This would help in making modular PEC cell configuration for hydrogen productions. For the investigation of photoelectrochemical solar cells with modular configuration leading to "Hydrogen Production Reactor" estimates of optimum photoelectrode geometric areas form an essential ingredient.

Materials and methods

Titanium isopropoxide (Ti $[OCH(CH_3)_2]_4$) and Copper oxide (An analytical grade from Sigma – Aldrich). Analytical grade Isopropanol, liquid ammonia, sodium hydroxide, sulphuric acid (Merck Pvt. Ltd), was used without any pretreatment. All solution was prepared from deionized water.

The ns- TiO_2-CuO admixed photoelectrode was prepared by following method firstly TiO_2 was prepared by sol-gel method [7]. Then the thick solution of TiO_2 gel was coated as film on the titanium sheets (~0.33 mm thickness) by spin on technique. In this, we used a clean titanium sheet (rubbed by 1000 griet emery paper and ultrasonically washed in acetone for 30 min at 40 kHz frequency), placed at the center of the rotating substrate holder of the photo-resist spinner.

One drop of TiO_2 viscous solution was placed on titanium sheet and spin coated at 3000 rpm for30 s. In order to obtain TiO_2-CuO photoanode, copper oxide was deposited on the above mentioned ns-TiO_2 coated photoanode by chemical vapor deposition technique. This electrode was annealed in oxygen at 500 °C.

For optimization study titanium sheets (~0.33 mm thickness) with ns-TiO_2–CuO of different areas like 0.25, 0.5, 1.0, 1.5, 2.0 cm^2 were taken and mechanically polished with emery papers of various grades. These were ultrasonically cleaned in acetone for 15 min. The nearly uniform films were deposited by placing ultrasonically cleaned substrate over vacuum interlocked spinner holder. One drop of sol was spread over the substrate rotating at 3000 rpm. The films so obtained were dried in an air oven for 15 min at 80 °C and then fired at 450 °C for 30 min. This process was repeated for about four to five times to increase film thickness. Finally, samples were annealed in an argon atmosphere at 550 °C for 4 h. Electrode thus obtained were then subjected to photoelectrochemical characterization.

Rectangular SC-SEP PEC Cell made of Lucite had a quartz window for illumination. The cells were divided in to two compartments by a Lucite separator which had a hole at its centre over on which the ns-TiO_2-CuO admixed/Ti septum electrode of different areas was glued with araldite. The configuration of present SC-SEP PEC cell consisting of two chambers connected through ns-TiO_2-CuO/Ti septum electrode is:

SCE/1M NaOH/ns-TiO_2–CuO admixed/Ti/H_2SO_4 + K_2SO_4/ $Pt_{CE}Pt_{WE}$

CE = counter electrode, SCE = saturated calomel electrode and WE = working electrode

All electrochemical measurements of electrodes of different areas were carried out by using a Princeton Applied Research (PAR) model 173 Potentiostat/Galvanostat PAR 175 universal programmer coupled with a Houston 2000 x–y/t recorder. A 1000 W Xenon-mercury lamp was used as the illumination source for ns_TiO_2–CuO photoelectrodes. The intensity of incident radiation was adjusted and fixed at 450 mW/cm^2. The hydrogen production kinetics of the SC–SEP, PEC cell has been monitored by collecting hydrogen in the dark compartment over Pt electrode using inverted burette under illumination.

Result and discussion

Fig. 1 shows XRD patterns of the TiO_2 – CuO over the titanium sheet. Analysis of XRD patterns revealed that on alloying ns-TiO_2 with CuO did not lead to the formation of any new composite material. The XRD confirmed the presence of TiO_2 – CuO nanopowder.

With the help of scanning electron microscope, the micro structural characteristics of the synthesized mixed oxide TiO_2 – CuO nanopowder was carried out (Fig. 2). The observed nanostructured characteristics showed a very fine grained structure suggestive of a nanocrystalline like matrix. By employing the Scherer's equation for the powder diffraction peaks andSEM, the average grain size of the TiO_2 – CuO photo electrodes was found to be 50–100 nm respectively.

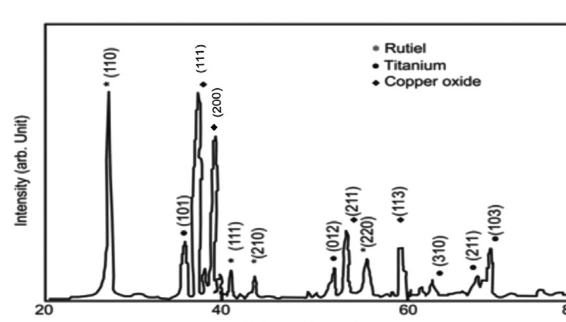

Fig. 1 – X- Ray Diffraction pattern of ns-TiO_2–CuO over the titanium sheet.