Preparation and characterization of stable nano-crystalline p-type Cu_2O semiconductors modified with different metal doping for their applications in photoelectrochemical water splitting for Hydrogen generation.

Funding Agency	BRNS-DAE
Sanctioned Amount	Rs. 24.51 Lakhs-
Project Duration	3 Years
Project Status	Continuing since March 2014

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Collaborative Institute(s) (if any): BARC, Mumbai

Brief Description of the Project

1. Synthesis of nanocrystalline p-type Cu_2O semiconductors and their characterization for photoelectrochemical water splitting applications.
2. Modifications of the materials with various metal ions to enhance their activity.
3. Further modification using hydrogen evolution co-catalyst.
4. Physical characterizations of the semiconductor.
5. Electrochemical characterizations of the semiconductor through linear sweep voltammetry, chronoampeometry and electrochemical impedance spectroscopy.

Keywords: Doped p-type Cu2O nano crystals, Photoelectrochemical water splitting application. Scanning electrochemical microscopy (SECM), Controlled Intensity Modulated Photo-Spectroscopy (CIMPS), Absorbed photon to current conversion efficiency (APCE), Incident photon to current conversion efficiency (IPCE)

Methodologies/Approaches Adopted (Simple description):

1. Synthesis of Cu_2O semiconductor through electrodeposition techniques.
2. Preparation and Characterization of Cu_2O semiconductors nanoparticles through hydrothermal techniques.
3. Development of suitable metal doped Cu_2O semiconductor thin film through chemical bath deposition techniques.

Project Highlights

1. Cu_2O is the potential photoactive material should be abundant and cheap to make PEC technology competitive with chemical production of hydrogen from coal or natural gas.
2. Synthesis of nano crystalline p-type Cu_2O is a cost effective and easy technique and it is a non toxic material.
3. Identification of suitable dopants for improved performance of p-type Cu_2O for photoelectrochemical water splitting application.
4. Modification of semiconductor surface by applying coating of other compounds as well as cocatalysts for better stability and enhanced activity.
5. The optimized material will generate hydrogen photoelectrochemically directly from water.

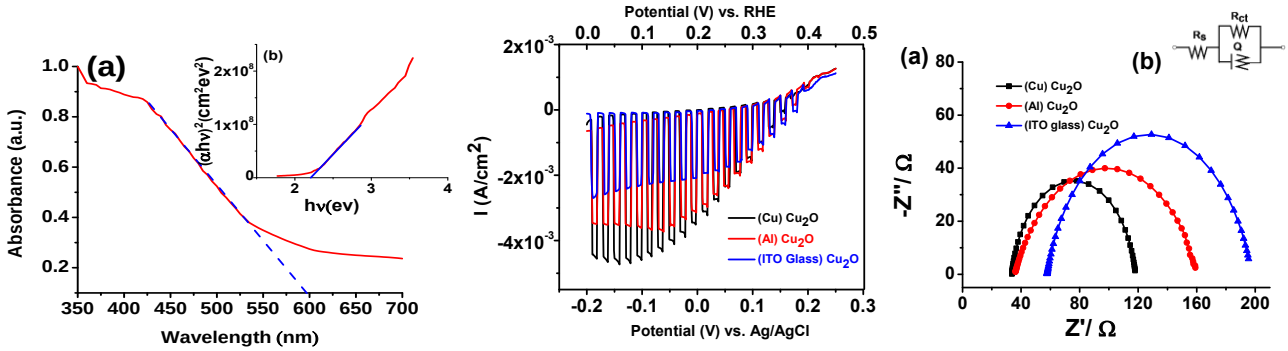
Project Achievements

Substrate Variation

We developed of p-Cu_2O thin films through cathodic electrodeposition technique at constant current of 0.1mA/cm² on Cu, Al and ITO substrates from basic $CuSO_4$ solution containing Triton X-100 as the surfactant at 30-35°C. The photoelectrochemical reduction of water ($H_2O \rightarrow H_2$) in pH 4.9 aqueous solutions over the different substrates are found to be of the order of Cu > Al > ITO and the highest current of 4.6mA/cm² has been recorded over the Cu substrate even at a low illumination of 35mW/cm², which is significantly higher than the value (2.4mA/cm² on Au coated FTO or 4.06mA/cm² on Cu foil substrate at an illumination of 100mW/cm²) reported in literature.

Deposition Bath | Deposition Setup | Deposited Cu_2O thin film

Fig. 1: Electro-deposition of Cu_2O



Absorbance Plot | LSV | Nyquist Plot

Fig. 2: Characterization of Cu_2O Thin Film

Modification of Cu2O

For the first time we found out that, photoelectrochemical performance of the cathodically electrodeposited Cu_2O thin film improves dramatically by ~2 fold when BiNPs are added in the form of suspension or acts as a matrix coated over ITO glass. Further addition of an optimized amount (10 nM) of Bi^{3+} also facilitate the hydrogen evolution reaction of Cu_2O. Maximum photocurrent for Cu_2O film developed form three different condition are as: (i) -5.2 mA/cm² for ITO/$BiNP_{film}$/Cu_2O, (ii) -4.9 mA/cm² for ITO/$BiNP_{sus}$/Cu_2O, (iii) -3.7 mA/cm2 for ITO/$Bi^{3+}{}_{ion}$-Cu_2O whereas that for pure Cu_2O on ITO appears as -2.6 mA/cm2. This is the highest reported photocurrent of Cu_2O on any conducting glass substrates without hydrogen evolution catalyst.

Thin Film

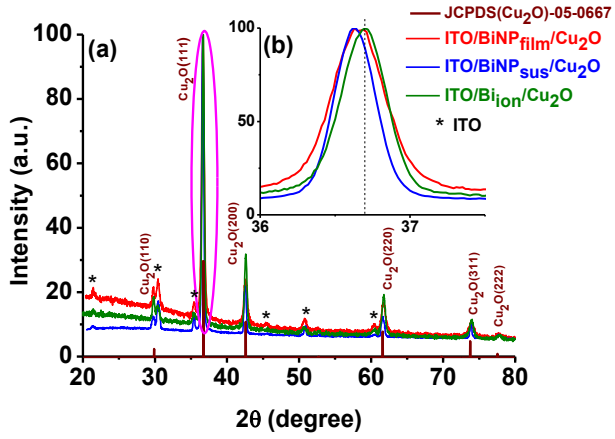


Fig. 3: XRD pattern of Cu_2O with BiNP

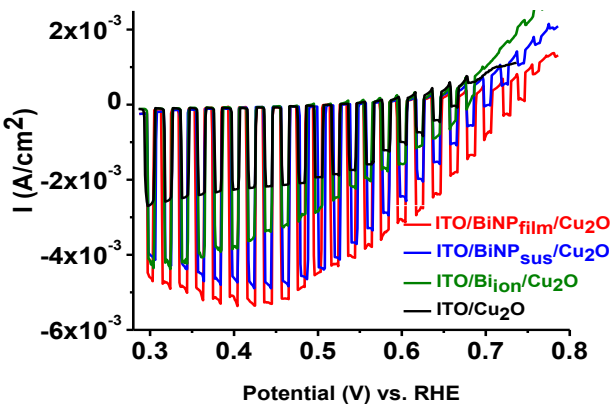


Fig. 4: LSV Plot for H_2 production

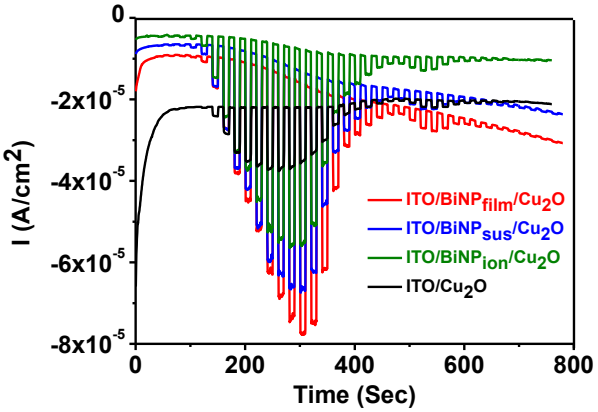


Fig. 5: Action Spectrum

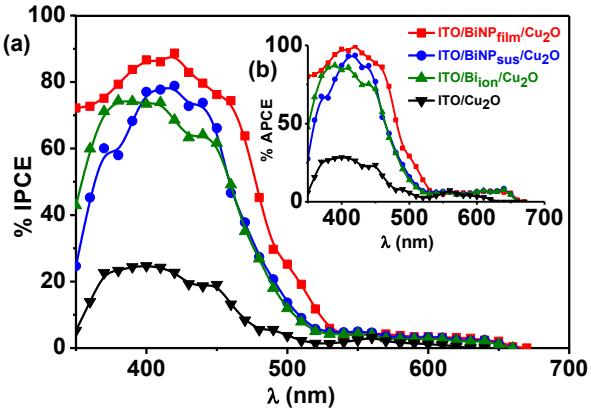


Fig. 6: IPCE & APCE plot

Publications (Please follow any one specific bibliographic style)

1. Sanjib Shyamal, Paramita Hajra, Harahari Mandal, Jitendra Kumar Singh, Ashis Kumar Satpati, Surojit Pande, and Chinmoy Bhattacharya, Effect of Substrates on the Photoelectrochemical Reduction of Water over Cathodically Electrodeposited p-Type Cu2O Thin Films, ACS Appl. Mater. Interfaces 2015, 7, 18344–18352.
2. Technical paper entitled "Catalytic role of Bi on electrodeposited p-type Cu2O thin films for photoelectrochemical production of H2 from water" presented at "Current Trends in Analytical Chemistry" organized by BARC-AEACI, Mumbai on May 26-29, 2015.
3. Technical paper entitled "Galvanostatic Electrodeposition of p-type Cu2O thin Films: Effect of Cu / Al / Conducting Glass Substrates for Photoelectrochemical Hydrogen Production" " presented at "Young Scientist's colloquium" organized by MRSI, Kolkata chapter, Kolkata on September 11, 2015.
4. Technical paper entitled "Modification of Cu2O semiconductor using Bismuth (Nanoparticles or Ions) for Photoelectrochemical Hydrogen Production" presented at "International Conference on Materials for the Millennium, MATCON-2016" organized by Department of Applied Chemistry, CUSAT, Kochi on January 14-16, 2016, ISBN 978-93-80095-738.
5. Sanjib Shyamal, Paramita Hajra, Harahari Mandal, Aparajita Bera, Debasis Sariket, Ashis Kumar Satpati, Sukumar Kundu and Chinmoy Bhattacharya, Benign role of Bi on an electrodeposited Cu2O semiconductor towards photo-assisted H_2 generation from water, J. Mater. Chem. A, 2016, 4, 9244-9252.

Facilities Developed

1. Photoelectrochemical instrument set up with Controlled Intensity Modulated Photo-Spectroscopy (CIMPS) consisting of software & hardware of electrometer and computer controlled high power Xenon arc lamp source and monochromatic beam intensity.
2. Computer controlled high power Xenon arc lamp source (white light) with monochromatic beam intensity for dynamic measurements on photo-active systems.

Project Staff

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Plan of Future Project Proposal based on the Current Project:

1. Production of H_2 and O_2 through visible-light driven photocatalytic water splitting process using dual semiconductors-graphene mediator composite materials in Z-scheme device.
2. Improved design for the Z-scheme device for production of H_2 from water splitting process, as measured through Membrane Electrode Assemble (MEA) using in the Fuel cell Technology.