STUDY OF PHOTO-ASSISTED ELECTROLYSIS OF WATER

SANGEETA

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

SANGEETA

Department of Chemical Engineering

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CERTIFICATE

This is to certify that the thesis entitled "**Study of Photo-assisted Electrolysis of Water**" being submitted by **Sangeeta** to the Department of Chemical Engineering, Indian Institute of Technology, New Delhi, in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Chemical Engineering, is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

Ashok N. Bhaskarwar

Professor

Department of Chemical Engineering

Indian Institute of Technology, Delhi

New Delhi 110016, India

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ABSTRACT

The interest in extracting hydrogen from water is fueled by the need to find a renewable, sustainable, and environmentally safe alternative energy source. **P**hoto-**E**lectrochemical **C**ells (*PECs*) convert solar energy into chemical energy (hydrogen) using a light-absorbing and semiconducting material to generate the necessary photovoltage to split water into hydrogen and oxygen. However, the acceptance of this technology will depend on the development of stable and cheap semiconductor electrodes with high efficiencies. The objective of this thesis is to develop a photoelectrochemical system for hydrogen generation using solar energy. Films of different semiconducting oxides have been prepared and analyzed by standard photochemical and photoelectrochemical methods. The physical characterizations of semiconducting materials have been done by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray spectroscopy (EDX).

Cuprous oxide on copper has been tested as a photocathode in a *PEC* with brine as an electrolyte. Effects of different parameters, namely, nature of substrate, thickness of nickel layer, nature of electrolyte, and deposition potential have been studied. The deposition of a 5μm-thick nickel layer on the photocathode, i.e. cuprous oxide, increased its photoefficiency 3.5 times.

Films of two materials, viz. copper titante and strontium titanate have been tested as a photoanode. Unlike with a photocathode, the performance of both of these photoanodes decreases on deposition of a nickel layer. Deposition potential affects the crystallinity of the films, and the maximum photoefficiency for copper titanates has been obtained for the films which have a high crystallnity in a single plane and a wide range of absorption spectrum.

To provide the remaining bias voltage required for splitting of water, dye-sensitized solar (DSSCs) cells have been looked at as an alternative, thereby making the whole process completely solar dependent and hence sustainable. Performance of nine new ruthenium sensitizers and two redox shuttles, i.e. iodine and cobalt have been analyzed in DSSCs by IV characteristics, transient photo-voltage measurements, electron-recombination, dye-adsorption, and IPCE studies. Bulky substitutions in a cyclopenta(2,1-b;3,4-bA)dithiophene (CDT) ruthenium(II) bipyridyl metal complex, coded TT-230, have been found to give a high open-circuit potential in the dye-sensitized solar cell with cobalt redox couple. DSSC with TT230 as sensitizer and Y960 as electrolyte gave an efficiency of 6.06 %.

The recombination studies have shown that the devices with TT-230 as a sensitizer exhibit a lower recombination rate. This opens up an avenue to engineer a new generation of highly efficient sensitizers.

DSSC, with TT230 dye as a sensitizer and Y960 as an electrolyte has finally been connected with the *PEC* having nickel/cuprous oxide/copper as a photocathode, strontium titanate/copper as a photoanode and 0.5 M brine as an electrolyte. For the coupled system, hydrogen is generated with an overall efficiency of 44 %, which is comparable to the commercially available silicon solar cells.

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LIST OF ABBREVIATIONS AND SYMBOLS

c = velocity of light, (ms^{-1}).

E_g = band gap, (eV).

ε_o = molar extinction coefficient, ($mole^{-1}dm^3cm^{-1}$).

h= Planck's constant, (6.6×10^{-34} Js).

I_p = photocurrent density, (Am^{-2}).

IPCE = incident photon to current conversion efficiency, (dimensionless).

J = current density, (Am^{-2}).

J_{max} = photocurrent density from the cell at the maximum power conversion, (Am^{-2}).

J_{sc}= short circuit current, (Am^{-2}).

$\boldsymbol{\eta}$ = overall efficiency, (dimensionless).

$\boldsymbol{\eta}_P$ = photoefficiency, (dimensionless)

$P_{illumination}$ = power density of source of illumination, (Wm^{-2}).

P_{total} = total power density input, (Wm^{-2}).

V = potential, (V).

V_b = bias potential, (V).

V^0_{rev} = standard-state reversible potential for the water-splitting reaction, (1.229 V).

V_{oc} = open circuit potential, (V).

V_{max} = photovoltge derived from the cell at the maximum power conversion, (V).

ν = frequency of radiation, (s^{-1}).

λ_{max} = absorption maximum, (nm).

e^- = electrons.

h^+ = holes.

DSSC = Dye-Sensitized Solar Cell.

EDX = Energy Dispersive X-ray Spectroscopy Analysis.

PEC = photoelectrochemical cell.

SEM = Scanning electron microscopy.

XRD = X- Ray diffraction.

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