STUDIES ON THE PHOTOELECTROCHEMICAL SPLITTING OF WATER FOR HYDROGEN GENERATION WITH Cu_2O AND $BiVO_4$ BASED PHOTOELECTRODES

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by

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Submitted

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Dedicated to Faizan &my family …

CERTIFICATE

This is to certify that the dissertation entitled "**Studies on the photoelectrochemical splitting of water for hydrogen generation with Cu_2O and $BiVO_4$ based photoelectrodes**" being submitted by **Ms. Iqra Reyaz Hamdani** to the Department of Chemical Engineering, Indian Institute of Technology Delhi, for fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis. The research reports 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.

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ABSTRACT

Solar energy is the largest reservoir of energy that can be utilized to address the current energy crisis and rising energy demands. One of the most attractive ways to harness solar energy is to directly convert it into a storable, renewable, and sustainable fuel, such as hydrogen. One promising approach is to use a photoelectrochemical (PEC) monolithic device where the light-absorption and electrolysis of water both occur at the same place.

In this thesis, modified Cu_2O (Cu_2O nanowires based p-n homojunction/$KTaO_3$/MoS_2) and $BiVO_4$ (Mo-W doped $BiVO_4$/Co-Pi/$NiFeO_x$) based photoelectrodes are being suggested as the promising photoelectrode materials for the photoelectrochemical water-splitting for H_2 production. Detailed investigations were carried out on both Cu_2O and $BiVO_4$ to determine the factors responsible for limiting their water-splitting capabilities. Certain plausible solutions were suggested and efforts were made to address the critical issues, such as overpotential losses due to the rapid recombination of photogenerated charge carriers. Various modifications to the Cu_2O photocathode were carried out, such as the formation of 1-D Cu_2O structures in the form of nanowires, development of a buried Cu_2O p-n homojunction, overlayering with $KTaO_3$, and co-catalyzing with MoS_2. Improvements to $BiVO_4$ were also done to enhance its photocatalytic performances, such as doping with Mo and W, improving OER kinetics by co-catalyzing with Co-Pi and $NiFeO_x$. A conventional dye-sensitized solar cell (DSSC) was developed based on the TiO_2 working electrode and Pt counter electrode.

The planar unmodified Cu_2O photocathode was capable of generating only -2.82 mA/cm^2 of photocurrent density at 0 V vs. RHE, resulting in only 62% of Faradaic efficiency. The performance was enhanced when the size-scale was changed to 1-D where the current density obtained the value of -3.97 mA/cm^2 at 0 V vs. RHE, and raising the Faradaic efficiency to 82%. Formation of Cu_2O nanowires based p-n homojunction resulted in the generation of photovoltage of +0.9 V vs. RHE, and improved the photocurrent density to -7.42 mA/cm^2 at 0

V vs. RHE. A surface protective layer of $KTaO_3$ was applied on to the best performing photocathode sample, and a layer of 199 nm of $KTaO_3$ improved the photostability of Cu_2O to 84 hours under illumination. Co-catalyzing the protected Cu_2O with MoS_2 caused the photocurrent density to increase drastically to -11.1 mA/cm^2 at 0 V vs. RHE in an electrolyte of pH 4, in the presence of ethanol as a sacrificial agent. The Faradaic efficiency of the modified Cu_2O was 95%, producing around 186 mmol/cm^2 of $H_2$for 84 hours under illumination.

Photocatalytic properties of $BiVO_4$were observed to increase by doping with Mo and co-doping with Win the weight ratio of 1:1, where the photocurrent density achieved was 4.27 mA/cm^2 at 1.23 V vs. RHE. Co-catalyzing the doped $BiVO_4$ with Co-Pi raised the value of current density to 5.6 mA/cm^2 at 1.23 V vs. RHE while maintaining the stability for 12 hours under illumination. Coating of the modified $BiVO_4$ with an excellent OER photocatalyst $NiFeO_x$ was observed to increase the current density to 6.21 mA/cm^2 at 1.23 V vs. RHE. The developed photoanode was stable for 32 hours in an electrolyte of pH of 9 and 18 hours at a pH of 4. The applied bias-to-photon efficiency (ABPE) of the developed photoanode was 2.48% which is the highest ABPE achieved for $BiVO_4$. The in-house built DSSC exhibited the conversion efficiency of 6.7% with 0.8 V as the open-circuit voltage.

A stand-alone PEC device employing the developed Cu_2O photocathode and $BiVO_4$ photoanode, and driven by an in-house built dye-sensitized solar cell (DSSC) was fabricated and tested towards the hydrogen generation. The current density produced by the constructed PEC device was around -5.8 mA/cm^2 at 0 V vs. RHE in the pH of 4 with the stability for 15.2 hours under illumination. The un-assisted solar-to-hydrogen (STH) conversion efficiency of 3.3% was achieved, thereby setting a benchmark for a PEC device based on Cu_2O and $BiVO_4$ photoelectrodes.

सार

सौर ऊर्जा ऊर्जा का सबसे बड़ा भंडार है जिसका उपयोग वर्तमान ऊर्जा संकट और बढ़ती ऊर्जा मांगों को संबोधित करने के लिए किया जा सकता है। सौर ऊर्जा का दोहन करने के सबसे आकर्षक तरीकों में से एक इसे सीधे तौर पर एक हवादार, नवीकsरणीय और टिकाऊ ईंधन में बदलना है, जैसे हाइड्रोजन। एक आशाजनक दृष्टिकोण एक फोटोइलेक्ट्रॉनिक (PEC) अखंड डिवाइस का उपयोग करना है जहां प्रकाश-अवशोषण और पानी के इलेक्ट्रोलिसिस दोनों एक ही स्थान पर होते हैं।

इस थीसिस में, संशोधित Cu_2O (Cu_2O nanowires pn homojunction पर $KTaO_3$ / MoS_2) और $BiVO_4$ (Mo-W doped $BiVO_4$ / Co-Pi / NiFeOx) पर आधारित फोटोइलेक्ट्रोड को फोटोइलेक्ट्रॉनिक वाटर-स्प्लिटिंग के लिए आशाजनक फोटोइलेक्ट्रोड सामग्री के रूप में सुझाया जा रहा है। उनकी पानी-बंटवारे की क्षमताओं को सीमित करने के लिए जिम्मेदार कारकों का निर्धारण करने के लिए Cu_2O और $BiVO_4$ दोनों पर विस्तृत जांच की गई। कुछ प्रशंसनीय समाधान सुझाए गए थे और महत्वपूर्ण मुद्दों को संबोधित करने के प्रयास किए गए थे, जैसे कि फोटोजेनरेटेड चार्ज वाहकों के तेजी से पुनर्संयोजन के कारण अत्यधिक नुकसान। Cu_2O फोटोकैथोड के लिए कई संशोधन किए गए, जैसे कि nanowires के रूप में १-D Cu_2O संरचनाओं का निर्माण, एक बरीड Cu_2O p-n होमोजिशन का विकास, $KTaO_3$ के साथ ओवरलेयरिंग, और MoS_2 के साथ सह-उत्प्रेरित होना। $BiVO_4$ में सुधार इसके फोटोकैटलिटिक प्रदर्शन को बढ़ाने के लिए भी किया गया था, जैसे कि Mo और W के साथ डोपिंग, Co-Pi और NiFeOx के साथ सह-उत्प्रेरक द्वारा OER कैनेटीक्स में सुधार करना। एक पारंपरिक डाई-सेंसिटाइज़्ड सोलर सेल (DSSC) को TiO_2 वर्किंग इलेक्ट्रोड और Pt काउंटर इलेक्ट्रोड के आधार पर विकसित किया गया था।

प्लेनर अनमोडिफाइड Cu_2O फोटोकैथोड 0 V vs RHE में केवल -२.८२ mA / cm^2 photocurrent घनत्व उत्पन्न करने में सक्षम था, जिसके परिणामस्वरूप केवल ६२% फैराडिक दक्षता थी। प्रदर्शन को बढ़ाया गया था जब आकार-स्केल को १-डी में बदल दिया गया था, जहां वर्तमान घनत्व ने 0 V बनाम आरएचएच पर -३.९७ mA /cm^2 का मूल्य प्राप्त किया था, और फरैडिक दक्षता को ८२% तक बढ़ा दिया था। Cu_2O nanowires आधारित पी-एन होमोजिशन के गठन के परिणामस्वरूप, फोटोकॉल वोल्टेज +0.९ V बनाम RHE की उत्पत्ति हुई, और फोटोकल घनत्व में -७.४२ mA / cm^2 में 0 V

बनाम RHE में सुधार हुआ। $KTaO_3$ की एक सतह सुरक्षात्मक परत को सबसे अच्छा प्रदर्शन करने वाले फोटोकैथोड नमूने पर लागू किया गया था, और $KTaO_3$ के १९९ nm की परत ने रोशनी के तहत Cu_2O की फोटोस्टेबिलिटी को ८४ घंटे तक सुधार दिया। MoS_2 के साथ संरक्षित Cu_2O को सह-उत्प्रेरित करने से photocurrent घनत्व में पीएच ४ के एक इलेक्ट्रोलाइट में 0 V बनाम RHE पर एक एजेंट के रूप में इथेनॉल की उपस्थिति में -११.१ mA / cm^2 में अत्यधिक वृद्धि हुई। संशोधित Cu_2O की फैराडिक दक्षता ९५% थी, जो रोशनी के तहत 84 घंटों के लिए H_2 के १८६ mmol / cm^2 का उत्पादन करती है।

$BiVO_4$ के Photocatalytic गुणों को १: १ के वजन अनुपात में Mo के साथ डोपिंग और W के साथ सह-डोपिंग द्वारा देखा गया , जहां प्राप्त फोटोकरेंट घनत्व १.२३ V बनाम RHE पर, ४.२७ mA / cm^2 था । Co- Pi के साथ डोप किए गए $BiVO_4$ को सह-उत्प्रेरित करते हुए रोशनी के तहत १२ घंटे तक स्थिरता बनाए रखते हुए वर्तमान घनत्व का मान १.२३ V बनाम RHE पर ५.६ mA / cm^2 कर दिया गया। एक उत्कृष्ट OER फोटोकैटलिस्ट NiFeOx के साथ संशोधित $BiVO_4$ की कोटिंग के वर्तमान घनत्व को बढ़ाकर १.२३ V बनाम RHE पर ६.२१ mA / cm^2 किया गया। विकसित फोटोएनोड ९ के पीएच और ४ पीएच पर इलेक्ट्रोलाइट में ३२ घंटे के लिए स्थिर था। विकसित फोटोनोड की लागू पूर्वाग्रह-से-फोटॉन दक्षता (ABPE) २.४ is% थी जो $BiVO_4$ के लिए प्राप्त उच्चतम ABPE है । इन-हाउस में निर्मित DSSC ने ओपन-वोल्टेज वोल्टेज के रूप में 0.8 V के साथ ६.७% की रूपांतरण दक्षता का प्रदर्शन किया।

एक एकल-अकेले PEC यंत्र ने विकसित Cu_2O फोटोकैथोड और $BiVO_4$ फोटोएनोड को नियोजित किया है, और एक इन-हाउस निर्मित डाई-सेंसिटाइज़्ड सोलर सेल (DSSC) द्वारा संचालित किया गया है और इसे हाइड्रोजन जेनरेशन की ओर टेस्ट किया गया है। निर्मित PEC यंत्र द्वारा निर्मित वर्तमान घनत्व रोशनी के तहत 15.2 घंटे की स्थिरता के साथ ४ के पीएच में 0 V बनाम RHE पर -५.८ mA / cm^2 था। ३.३% की गैर असिस्टेड सोलर-टू-हाइड्रोजन (STH) रूपांतरण दक्षता हासिल की गई, जिससे Cu_2O और $BiVO_4$ फोटोइलेक्ट्रोड पर आधारित PEC यंत्र के लिए एक तल चिह्न स्थापित किया गया।

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ABPE	Applied bias-to-photon efficiency
A.M.	Air Mass
CB	Conduction band
CE	Counter electrode
CPE	Constant phase element
CV	Cyclic voltammetry
DSSC	Dye-sensitized solar cell

EIS	Electrochemical impedance spectroscopy
FF	Fill factor
FTO	Fluorine-doped tin oxide coated glass
HEC	Hydrogen-evolution catalyst
HER	Hydrogen-evolution reaction
HOMO	Highest occupied molecular orbital
IPCE	Incident photon-to-current conversion efficiency
LSV	Linear sweep voltammetry
LUMO	Lowest unoccupied molecular orbital
NHE	Normal hydrogen electrode
OCP	Open-circuit potential
OER	Oxygen evolution reaction
PEC	Photoelectrochemical
PV	Photovoltaic
RE	Reference electrode
RHE	Reversible hydrogen electrode
STH	Solar-to-hydrogen
UV	Ultraviolet
VB	Valence band
WE	Working electrode
WOC	Water-oxidation catalyst

LIST OF ACRONYMS

A	Optical absorbance

α	Absorptivity
β_{hkl}	Full width half maximum (FWHM)
C_{sc}	Space-charge capacitance
d	Mean diameter of nanowires
E_F	Fermi-level energy
E_g	Bandgap energy
$\Delta E°$	Standard cell potential
e^-	Electrons
ε	Relative permittivity
$\varepsilon_\circ$	Permittivity of free space
h^+	Holes
hν	Energy of incident light
I_a	Anodic peak of CV plot
I_c	Cathodic peak of CV plot
j_p	Photocurrent density
j_{sc}	Short-circuit current
l	Mean length of nanowires
m*	Effective mass of holes
N_A	Acceptor density
N_D	Dopant density
N_V	Effective density of states in the valence band
N_d	De-magnetization factor
η_F	Faradaic efficiency
P	Rate of power of incident light
P_{mono}	Rate of power of monochromatic incident light

Q	Constant phase element
R_{ct}	Charge transfer resistance
R_s	Solution or series resistance
V_{app}	Applied potential
V_{fb}, V_f	Flatband potential
V_{bi}	Built-in potential
$V_{Ag/AgCl}$	Potential at Ag/AgCl scale
$V^0{}_{Ag/AgCl}$	Standard potential of Ag/AgCl
V_{RHE}	Potential at RHE scale
W	Warburg's impedance
Z	Impedance
Z'	Real part of the impedance
Z''	Imaginary part of the impedance