PERFORMANCE OF HEMATITE AND BISMUTH VANADATE BASED PHOTOCATALYSTS IN PHOTOELECTROCHEMICAL REACTOR FOR HYDROGEN PRODUCTION

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Certificate

This is to certify that the thesis entitled "**Performance of Hematite and Bismuth Vanadate based Photocatalysts in Photoelectrochemical Reactor for Hydrogen Production**" submitted by **Mr. Aditya Singh** to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

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Abstract

The development in renewable energy sources is growing rapidly to compensate for the ever-increasing energy consumption demands. Storing solar energy in the form of green fuel like hydrogen (H_2) has been given much importance. The photoelectrochemical (PEC) water splitting is an efficient way of producing H_2 and oxygen (O_2) simultaneously in a single cell using sunlight. The hematite and bismuth vanadate ($BiVO_4$) based-photoanodes stand out due to their narrow optical bandgap, long-term stability, nontoxicity, and earth abundance. The present work focuses on the fabrication of nanostructured materials by different methods such as electrodeposition, chemical route, and sputtering for application in PEC water splitting. The hematite nanorods decorated with $NiMnO_3$ co-catalyst photoanode was prepared by a simple two-step hydrothermal method. $NiMnO_3$ suppressed the charge-carrier recombination on the hematite and significantly decreased the photoanode-electrolyte interface charge-transfer resistance.

The performance of $BiVO_4$ was limited by the surface states electron-hole recombination. This was addressed by devising an integrated photocatalytic (PC) and PEC system to achieve enhanced water oxidation performance of a $BiVO_4$ photoanode. The reduced gC_3N_4 (R-gC_3N_4) photocatalyst was suspended in the anode compartment electrolyte of the PEC reactor to integrate the PC-PEC systems. The R-gC_3N_4 produced hydroxyl radicals and hydrogen peroxide in the electrolyte, which reduced the onset potential for oxygen evolution reaction (OER) at the $BiVO_4$ photoanode.

The performance of $BiVO_4$ was further enhanced by preparing a heterojunction with WO_3. The WO_3/$BiVO_4$ heterojunction was synthesized by sputtering WO_3, followed by spin-coating of $BiVO_4$. The sputtered WO_3 enhanced electron-hole separation in the heterojunction. The incorporation of Cr into NiFe-layered double hydroxide (LDH) co-catalyst increased the

electrical conductivity of LDH. This resulted in an enhanced charge-carrier transfer with significant promotion of the OER kinetics. The heterojunction with sputtered WO_3 underlayer and NiFeCr-LDH co-catalyst provided photocurrent density of 4.9 mA cm^{-2} at 1.23 V vs. RHE with an incident photon to current conversion efficiency (IPCE) greater than 56% in the 350-470 nm range, with H_2, and O_2 evolution of 98 and 47 μmol cm^{-2} h^{-1}, respectively.

Furthermore, the patterned metal grid was sputtered under the WO_3/$BiVO_4$ heterojunction to reduce resistive losses and improve the homogeneity of distributed potential in large-area substrates (5 cm × 5 cm), and thus increased the PEC performance of the heterojunction. A PEC reactor was designed to enable electrolyte flow which exhibited prolonged stability of 80 h owing to fast bubble detachment from the photoanode surface and reduced the crossover of gas products. The electrolyte flow replenished the H^+/OH^- species near the electrode surface, which resulted to suppression of pH gradient across the electrode. Overall, the study was focused on the development of electrochemical engineering strategies to achieve enhanced PEC performance of large area photoanode.

सार

बढ़ती ऊर्जा खपत की मांगों की भरपाई करने के लिए नवीकरणीय ऊर्जा स्रोतों के विकास में तेजी से वृद्धि हो रही है। सौर ऊर्जा के भंडारण के लिए हाइड्रोजन (H_2) जैसे रासायनिक बंधों के रूप को बहुत महत्व दिया गया है। प्रकाशिक विद्युत् रसायनिकी (प्र.वि.र.) द्वारा सूर्य के प्रकाश की मदद से एक ही सेल में पानी का विभाजन करके एक साथ हाइड्रोजन और ऑक्सीजन (O_2) का उत्पादन करना एक प्रभावी तरीका है। हेमेटाइट और बिस्मथ वैनाडेट ($BiVO_4$) आधारित प्रकाशिक धनाग्र अपने छोटे प्रकाशीय उर्जा अंतराल, दीर्घकालिक स्थिरता, निराविराशुता और पृथ्वी में प्रचुरता के कारण सबसे श्रेष्ठ हैं। वर्तमान कार्य प्र.वि.र. जल विभाजन में उपयोग के लिए नैनोसंरचित पदार्थ के निर्माण के विभिन्न तरीकों जैसे इलेक्ट्रोडीपोजिशन, रासायनिक मार्ग, और स्पटरिंग पर केंद्रित है। $NiMnO_3$ सह-उत्प्रेरक से लेपित हेमेटाइट नैनोरोड्स प्रकाशिक धनाग्र को एक सरल और दो-चरणीय जलतापीय विधि द्वारा तैयार किया गया है। $NiMnO_3$ ने हेमटाइट पर आवेश-वाहक पुनर्संयोजन को दबा दिया और प्रकाशिक धनाग्र-विद्युतअपघट्य अंतराप्रस्ठ में आवेश-स्थानांतरण के प्रतिरोध को काफी कम कर दिया।

$BiVO_4$ का प्रदर्शन सतही अवास्थाओं में इलेक्ट्रॉन-होल के पुनर्संयोजन द्वारा सीमित था। इसका संबोधन प्रकाशिक उत्प्रेरकीय (प्र.उ.) और प्र.वि.र. प्रणाली को एकीकृत करके किया गया, जिसके परिणामस्वरूप $BiVO_4$ प्रकाशिक धनाग्र पर पानी ऑक्सीकरण के प्रदर्शन में वृद्धि हुई। प्र.उ. और प्र.वि.र. प्रणाली को एकीकृत करने के लिए अपचयित gC_3N_4 (R-gC_3N_4) प्रकाशिक उत्प्रेरक को प्र.वि.र. रिएक्टर के धनाग्र विभाग वाले विद्युतअपघट्य में परिक्षेपित कर दिया गया। R-gC_3N_4 ने विद्युतअपघट्य में हाइड्रॉक्सिल रेडिकल्स और हाइड्रोजन पराक्साइड का उत्पादन किया, जिसने $BiVO_4$ प्रकाशिक धनाग्र में ऑक्सीजन उद्भव अभिक्रिया (ऑ. उ. अ.) के शुरुआत के लिए आवश्यक वोल्टेज को कम कर दिया।

$BiVO_4$ के प्रदर्शन को और अधिक बढ़ाने के लिए , $BiVO_4$ का WO_3 के साथ एक विषमसंधि बनाया गया। WO_3/$BiVO_4$ विषमसंधि को तैयार करने के लिए पहले WO_3 को स्पटरिंग द्वारा बनाया गया, इसके बाद $BiVO_4$ की स्पिन-कोटिंग की गयी। स्पटर्द WO_3 ने विषमसंधि में इलेक्ट्रॉन-होल के प्रथक्करण को बढ़ाया। NiFe-लेयर्ड डबल हाइड्रॉक्साइड (LDH) सह-उत्प्रेरक में Cr को संयुक्त करने से LDH की विद्युत चालकता में वृद्धि हुई। इसके परिणामस्वरूप आवेश-वाहक के स्थानांतरण में वृद्धि के साथ-साथ ऑ. उ. अ. गतिकी में सार्थक बढ़ावा हुआ। स्पटर्द WO_3 निचलीसतह और NiFeCr-LDH सह-उत्प्रेरक के साथ तैयार किये गए विषमसंधि ने 4.9 mA cm^{-2} (1.23 V बनाम RHE) का प्रकाशिक धारा घनत्व, 350-470 nm सीमा में 56% से अधिक IPCE तथा H_2, और O_2 का क्रमशः 98 और 47 $\mu mol\ cm^{-2}\ h^{-1}$ उत्पादन दिया।

इसके अतिरिक्त, सांचा धातु ग्रिड को $WO_3/BiVO_4$ के नीचे स्पटर्द किया गया, ताकि प्रतिरोधी नुकसान को कम किया जा सके और बड़े क्षेत्रफल (5 cm × 5 cm) के अध:स्तर में वोल्टेज के वितरण की समरूपता में सुधार किया जा सके, और इसके परिणामस्वरूप विषमसंधि के प्र.वि.र. प्रदर्शन में वृद्धि हुई। विद्युतअपघट्य के प्रवाह के लिए एक प्र.वि.र. रिएक्टर की रचना की गयी, जिसके फलस्वरूप 12 घंटे की लम्बी स्थिरिता मिली, तथा गैस के बुलबुलों को बड़े क्षेत्रफल वाले प्रकाशिक धनाग्र की सतह से तेजी से प्रथक करने का प्रावधान किया और गैस उत्पादों के आर-पार को कम कर दिया। विद्युतअपघट्य के प्रवाह ने इलेक्ट्रोड सतह के पास H^+/OH^- आयन को पुन: भर दिया, जिसके परिणामस्वरूप इलेक्ट्रोड में पीएच प्रवणता की कमी हुयी। कुल मिलाकर, यह अध्ययन बड़े क्षेत्रफल वाले प्रकाशिक धनाग्र में अधिकतम प्र.वि.र. प्रदर्शन को प्राप्त करने के लिए विद्युत् रसायनिक अभियांत्रिकीय उपायों के विकास पर केंद्रित था।

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ABPE	Applied Bias to Photon conversion Efficiency
AFM	Atomic Force Microscopy
CA	Chronoamperometry
CB	Conduction Band
CE	Counter Electrode
DC	Direct Current
EDX	Energy Dispersive X-ray (spectroscopy)
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transformed Infra-red (spectroscopy)
GC	Gas Chromatography
FTO	Fluorine Doped Tin Oxide
gC_3N_4	Graphitic Carbon Nitride
HER	Hydrogen Evolution Reaction
HPLC	High Performance Liquid Chromatography
HRTEM	High-Resolution Transmission Electron Microscopy
IMPS	Intensity-Modulated Photocurrent Spectroscopy
IPCE	Incident Photon-to-Current Conversion Efficiency
LSV	Linear Sweep Voltammetry

MUMPS	Multifrontal Massively Parallel Sparse Direct Solver
NF	Non-Flow
NHE	Normal Hydrogen Electrode
NP	Non-Patterned
OCV	Open Circuit Voltage
OER	Oxygen Evolution Reaction
PBS	Phosphate Buffer Solution
PC	Photocatalytic
PEC	Photoelectrochemical
PL	Photo Luminescence
PVD	Physical Vapor Deposition
RE	Reference Electrode
RF	Radio Frequency
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
VB	Valence Band
WE	Working Electrode
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction