INVESTIGATIONS TO ENHANCE THE STABILITY & PERFORMANCE OF NANOSTRUCTURED MATERIALS FOR PHOTO-ELECTROCHEMICAL WATER SPLITTING APPLICATIONS

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by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

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Dedicated
To
My Parents

CERTIFICATE

This is to certify that the thesis entitled, "**Investigations to enhance the stability & performance of nanostructured materials for photo-electrochemical water splitting applications**", is being submitted by **Ms. Shalini**, to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Ms. Shalini has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this dissertation 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

Global energy demands require the development of clean or alternative fuels to mitigate the substantial environmental damage caused by the use of fossil fuels. In today's world, rising energy demand and maintaining a pollution-free environment is a major challenge. Solar to hydrogen conversion by electrochemical or photoelectrochemical (PEC) process through photocatalysts is one of the most promising techniques for getting a pollution-free and sustainable fuel. The photoelectrode is a fundamental component of PEC water splitting, and it should be made of low-cost materials with adequate bandgaps, band edge positions, high absorption coefficients, effective charge separation efficiency, and high electrical conductivity. PEC cells consist of two half-reactions: the Hydrogen Evolution Reaction (HER) on the photocathode and the Oxygen Evolution Reaction (OER) on the photoanode. The photocathode, which reduces water, is an important part of the PEC water-splitting mechanism. Most photocatalysts suffer from charge recombination and photocorrosion, which limits their catalytic performances. Photocorrosion refers to the participation of photogenerated charge carriers in the self-oxidation and/or self-reduction process, instead of water splitting. The photocorrosion phenomenon can be minimized by forming a passivation layer on the photocatalyst's surface, which can be accomplished by mixing the photocatalyst with other appropriate semiconductors via a core/shell heterojunction or composite formation. As a result, improving PEC water-splitting technology requires the creation of effective photocathodes for water reduction.

In this thesis, the surface of a Cu_2O photocathode is modified using a MoS_2/rGO co-catalyst and a $NaNbO_3/SnS_2$ core/shell heterostructure to improve the photogenerated charge carrier separation, reduce Cu_2O photocorrosion, and enhance the PEC activity of the Cu_2O photocatalyst. Photocatalyst VS_4 and CuS are less explored as photocathodic materials in PEC application, we have modified the surface of VS_4 and CuS to prevent the photocatalyst from

photocorrosion by making a heterostructure of VS_4 with MoS_2-rGO and CuS with $BaTiO_3$. The modified heterostructure is shown the improved photocurrent density due to lower photogenerated electron-hole pairs recombination or effective charge carriers separation efficiency. The goal is to develop a stable photocatalyst that prevents photocorrosion and improved photoelectrochemical water splitting application.

संक्षेप

वैश्विक ऊर्जा मांगों के लिए जीवाश्म ईंधन के उपयोग से होने वाली पर्याप्त पर्यावरणीय क्षति को कम करने के लिए स्वच्छ या वैकल्पिक ईंधन के विकास की आवश्यकता है। आज की दुनिया में ऊर्जा की बढ़ती मांग और प्रदूषण मुक्त वातावरण बनाए रखना एक बड़ी चुनौती है। फोटोकैटलिस्ट्स के माध्यम से इलेक्ट्रोकेमिकल या फोटोइलेक्ट्रोकेमिकल (PEC) प्रक्रिया द्वारा सौर से हाइड्रोजन रूपांतरण प्रदूषण मुक्त और टिकाऊ ईंधन प्राप्त करने के लिए सबसे आशाजनक तकनीकों में से एक है। फोटोइलेक्ट्रोड पीईसी जल विभाजन का एक मूलभूत घटक है, और इसे पर्याप्त बैंडगैप, बैंड किनारे की स्थिति, उच्च अवशोषण गुणांक, प्रभावी चार्ज पृथक्करण दक्षता और उच्च विद्युत चालकता के साथ कम लागत वाली सामग्री से बना होना चाहिए। पीईसी कोशिकाओं में दो अर्ध-प्रतिक्रियाएं होती हैं: फोटोकैथोड पर हाइड्रोजन इवोल्यूशन रिएक्शन (HER) और फोटानोड पर ऑक्सीजन इवोल्यूशन रिएक्शन (OER)। फोटोकैथोड, जो पानी को कम करता है, पीईसी जल-विभाजन तंत्र का एक महत्वपूर्ण हिस्सा है। अधिकांश फोटोकैटलिस्ट चार्ज पुनर्संयोजन और फोटोकॉर्शन से पीड़ित हैं, जो उनके उत्प्रेरक प्रदर्शन को सीमित करता है। फोटोकॉर्शन पानी के बंटवारे के बजाय सेल्फ-ऑक्सीडेशन और/या सेल्फ-रिडक्शन प्रक्रिया में फोटोजेनरेटेड चार्ज कैरियर्स की भागीदारी को संदर्भित करता है। फोटोकैलेटिस्ट की सतह पर एक निष्क्रियता परत बनाकर फोटोकोर्सियन घटना को कम किया जा सकता है, जिसे कोर / शेल हेटेरोजंक्शन या समग्र गठन के माध्यम से अन्य उपयुक्त अर्धचालकों के साथ फोटोकैटलिस्ट को मिलाकर पूरा किया जा सकता है। नतीजतन, पीईसी जल-विभाजन प्रौद्योगिकी में सुधार के लिए पानी की कमी के लिए प्रभावी फोटोकैथोड के निर्माण की आवश्यकता होती है।

इस थीसिस में, एक Cu_2O फोटोकैथोड की सतह को MoS_2/rGO सह-उत्प्रेरक और एक $NaNbO_3/SnS_2$ कोर/शेल हेटरोस्ट्रक्चर का उपयोग करके संशोधित किया गया है ताकि फोटोजेनरेटेड चार्ज कैरियर पृथक्करण में सुधार हो, Cu_2O फोटोकॉर्शन को कम किया जा सके, और Cu_2O फोटोकैटलिस्ट की पीईसी

गतिविधि को बढ़ाया जा सके। फोटोइलेक्ट्रोकेमिकल अनुप्रयोग में फोटोकैटलिस्ट VS_4 और CuS को फोटोकैथोडिक सामग्री के रूप में कम खोजा जाता है, हमने MoS_2-rGO के साथ VS_4 की हेटरोस्ट्रक्चर और $BaTiO_3$ के साथ CuS बनाकर फोटोकैटलिस्ट को फोटोकैलेटिस्ट से रोकने के लिए VS_4 और CuS की सतह को संशोधित किया है। संशोधित हेटरोस्ट्रक्चर को कम फोटोजेनरेटेड इलेक्ट्रॉन-होल जोड़े पुनर्संयोजन या प्रभावी चार्ज वाहक पृथक्करण दक्षता के कारण बेहतर फोटोक्रेक्ट घनत्व दिखाया गया है। लक्ष्य एक स्थिर फोटोकैटलिस्ट विकसित करना है जो फोटोकोर्सोशन को रोकता है और फोटोइलेक्ट्रोकेमिकल वॉटर स्प्लिटिंग एप्लिकेशन में सुधार करता है।

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Abbreviations and Symbols

Å	Angstroms
˚C	Centigrade
μm	Micrometer
nm	Nanometer
sec	Second
min	Minutes
h	Hours
mL	milliliter
M	molar
XRD	X-ray Diffraction
PXRD	Powder X-Ray Diffraction
TEM	Transmission Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray Spectroscopy
AFM	Atomic Force Microscopy
PL	Photoluminescence
VB	Valence band
CB	Conduction band
NHE	Normal Hydrogen Electrode
RHE	Reversible Hydrogen Electrode
eV	Electron – Volt
K	Kelvin

°	Degree (angle)
Eg	Bandgap
λ	Wavelength
CB	Conduction Band
VB	Valence Band
UV	Ultraviolet - Visible
PEC	Photoelectrochemical
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction
STH	Solar-to-hydrogen efficiency
LSV	Linear sweep voltammetry
M-S	Mott-Schottky
EIS	Electrochemical Impedance spectroscopy
TPR	Transient Photocurrent Response