

**METAL OXIDE AND CHALCOGENIDES-BASED
MATERIALS FOR ENHANCED
PHOTOELECTROCHEMICAL WATER
SPLITTING RESPONSE**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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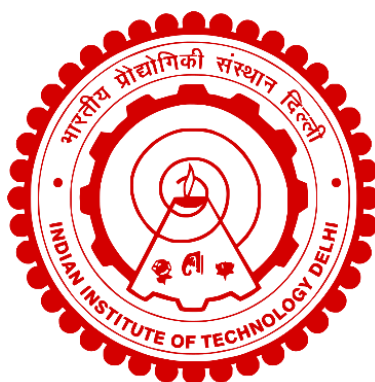
by

JYOTI YADAV

Department of Physics

Submitted

*in fulfillment of the requirements of the degree of Doctor of Philosophy
to the*



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***DEDICATED TO
MY FAMILY FOR THEIR
ENDLESS LOVE AND
SUPPORT***

CERTIFICATE

This is to certify that the thesis entitled “**Metal oxide and chalcogenides-based materials for enhanced Photoelectrochemical water splitting response**” submitted by **Ms. Jyoti Yadav** to the Indian Institute of Technology Delhi is worthy of consideration for the award of the degree of Doctor of Philosophy and is a bonafide record of the research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Place: Delhi

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(Jyoti Yadav)

Abstract

The worldwide supply of energy is one of the most significant challenges that scientists and technologists have faced in the twenty-first century. The energy consumption rate in 2008 reached 15 TW, and due to the expanding world population and production, it has been estimated that this rate will nearly double by 2050. The need for sustainable energy is becoming more critical as environmental degradation and energy demand rise. The total energy resources available worldwide are generally classified into nuclear, fossil, and renewable ones. Fossil fuels are one of the primary causes of greenhouse gas emissions, but over time, the gap between supply and demand has grown. The generation of renewable and sustainable energy sources is one of the major challenges in today's world and to meet the global energy requirements, there has been a huge surge towards developing clean energy sources. In this scenario, solar energy usage remains the most viable way to give a sustainable solution to the energy issue. The solar energy provided to the earth (173000 TW) is approximately 9600 times larger than the daily global energy consumption (17.91 TW in 2017). Converting solar energy into hydrogen appears to be an excellent solution because hydrogen combustion emits no greenhouse gases. Nowadays, the production of hydrogen is attributed to fossil fuels as a feedstock in 96% of cases, with direct water electrolysis accounting for 4% of hydrogen production. Therefore, to reduce dependence on fossil fuels, current efforts are focused on improving hydrogen production from water. Among numerous strategies, Photoelectrochemical (PEC) water-splitting is an edge-cutting technology for solar hydrogen production to build a sustainable, renewable, and clean energy economy. The principle behind PEC water splitting is the conversion of photons incident on the surface of the semiconductor, with energy higher than the bandgap of the semiconductor into electrochemical energy that can split water directly into molecules of H_2 and O_2 . To split water into its components the reaction must carry with a large Gibbs free energy change of $\Delta G^\circ = +237 \text{ kJ/mol}$ and 1.23V is the thermodynamic voltage for overall water splitting. The PEC cell efficiency is mainly affected by the performance of semiconducting electrodes which includes absorption of light, charge separation, and charge transfer at the interface. The conduction band and valence band edges of the semiconducting material should be placed at a

position more negative than the reduction potential of H_2O (0 V vs SHE) and more positive than the oxidation potential of H_2O (1.23 V vs SHE). To get the profitable PEC splitting response, the semiconducting electrode must have a tuned bandgap for good visible light absorption, favorable band edge alignment with water redox potential, and photo-stability against photo corrosion. Achieving all the aforementioned requirements in a single photoelectrode is still one of the major challenges for the fabrication of PEC electrodes. The above background forms the basis of the objective of the present work. The central objective of the thesis is to explore the metal oxide and chalcogenides-based materials for enhanced PEC water splitting response. In this regard, various methodologies have been adopted for improving PEC performance such as geometry modification, heterojunction, doping, plasmonic effect, and effect of magnetic field. To serve that purpose Ag_2S , MoS_2 , WO_3 , and CO_3O_4 nanostructures were fabricated by glancing angle deposition (GLAD), electron-beam evaporation, chemical vapor deposition, and solution method. In the present research work, the GLAD technique was used for the fabrication of Ag_2S nanorods because it provides different columnar films with controlled porosity due to geometric shadowing effects. The geometry and length of the nanorods as well as the inter-nanorods separation can be adjusted by varying the deposition conditions.

In the initial section of the work, we fabricated the zig-zag nanorods of Ag_2S utilizing the GLAD technique followed by sulfurization. The PEC performance was studied by varying the number of zig-zag arms of Ag_2S . The zig-zag nanorods of Ag_2S offer better optical absorption than perpendicular nanorod arrays. This might be attributed to the significant photon loss by reflection from the substrate in perpendicular nanorods. However, the wavy nature of zig-zag nanostructures provides enhanced scattering and increased rod-to-rod plasmonic coupling due to a fixed gap between nanorods, leading to superior light absorption. The optical absorption was also theoretically investigated using rigorous coupled wave analysis (RCWA) simulations. The as-prepared four-arm Ag_2S zig-zag electrodes exhibited the highest photocurrent density of 3.04 mA/cm^2 (at 1 V vs Ag/AgCl), compared to one-arm Ag_2S nanorods with minimum charge transfer resistance at the semiconducting electrode/electrolyte interface. The improved photocurrent density of the four-arm Ag_2S zig-zag nanorods electrode was attributed to increased optical trapping

and hence, effective absorption of light due to its wavy structure. Thus, this work provides a simple and effective approach to the development of an efficient PEC electrode by tuning the morphology of nanostructured materials.

Another approach is the fabrication of a heterojunction-based system. This is one of the most viable ways as it prolongs the light absorption by tuning the band gap of base material with effective separation of charge carriers at the semiconductor interface. Among all semiconducting materials, WO_3 has gained enormous attention, as it shows excellent electron-transport properties, good visible light absorption, and longer hole diffusion length. To prepare the working electrodes of $\text{WO}_3/\text{Ag}_2\text{S}$ -based heterojunction, a two-step method was adopted which includes, a thin film of WO_3 deposited using DC sputtering and well-separated Ag_2S nanorods fabricated by glancing angle deposition. The PEC response was studied for bare WO_3 , Ag_2S , and $\text{WO}_3/\text{Ag}_2\text{S}$ heterojunction. The as-prepared $\text{WO}_3/\text{Ag}_2\text{S}$ heterojunction samples revealed higher absorption as well as a higher photocurrent density of 2.40 mA/cm^2 (at 1 V Ag/AgCl) as compared to bare WO_3 thin film (0.34 mA/cm^2). The enhancement in the photocurrent density of $\text{WO}_3/\text{Ag}_2\text{S}$ electrodes could be ascribed to the formation of the type-II heterojunction between WO_3 and Ag_2S which effectively separates and transfers the charge carriers at the interface. In addition, increased trapping of light due to vertically tilted Ag_2S nanorod structures results in effective absorption of light. Furthermore, electrochemical impedance spectra measurements showed that $\text{WO}_3/\text{Ag}_2\text{S}$ samples have lower charge transfer resistance at the semiconductor electrolyte interface with high flat band potential. This work offers not only an effective way to tune the PEC electrode's performance but also provides a deeper insight into the mechanism behind nanostructured $\text{WO}_3/\text{Ag}_2\text{S}$ heterojunction. Furthermore, the functionalization of semiconducting materials with plasmonic nanoparticles (NPs) has been widely used in PEC water splitting due to their enormous light-confining capability in the vicinity of the semiconducting material's surface. The localized surface plasmonic resonance of the noble metal nanoparticle is sensitive to incident light which enhances the local electromagnetic field, expands the solar light absorption range, and internally excites the electron-hole pairs. Therefore, to study the role of plasmonics in PEC, we have fabricated the $\text{Ag}_2\text{S}/\text{Au}/\text{Al}_2\text{O}_3$ photoelectrode using the GLAD method followed by RF sputtering

and atomic layer deposition. However, to improve the photostability and reduce the surface charge recombination, a passivating layer of Al_2O_3 was deposited. The as-prepared $\text{Ag}_2\text{S}/\text{Au}/\text{Al}_2\text{O}_3$ samples revealed a higher photocurrent density of $2.50 \text{ mA}/\text{cm}^2$ (at $0.95 \text{ V Ag}/\text{AgCl}$) as compared to bare Ag_2S ($1.70 \text{ mA}/\text{cm}^2$) with a corresponding less charge transfer resistance at the semiconducting interface. The superior PEC response may be ascribed to the synergic effect of plasmonic Au NPs and the tilted Ag_2S nanorods. The plasmonic effect of Au NPs increases the visible-light response of Ag_2S as well as provides the hot electrons to enhance the photocurrent density. In addition, the increased trapping of light due to the tilted architecture of Ag_2S nanorods resulted in an effective absorption of light. The theoretical simulations based on finite difference time domain were also performed to explore the distribution of the electric-field intensity and optical trapping of light between the nanorods of Ag_2S and $\text{Ag}_2\text{S}/\text{Au}$. The experimental and theoretical results not only show a deeper insight into the role of plasmonic nanostructures decorated Ag_2S nanorods but also shed light on designing semiconductor nanostructures for the next generation photoelectrodes.

In addition to harnessing the visible light, it is crucial to alter the electronic band structure of the solids. Doping could be a way to tune the position of energy levels and electronic band structure for better PEC response. Here, the influence of Ti and Co-doping on the PEC response of WO_3 nanocomposite with MoS_2 photoanode is being investigated using experimental and theoretical studies. A simple hydrothermal and sol-gel method was adopted for the growth of working electrodes. Among all samples, the Ti-doped WO_3 - MoS_2 sample showed the maximum optical absorption with a photocurrent density of $1.15 \text{ mA}/\text{cm}^2$ at $1.6 \text{ V vs Ag}/\text{AgCl}$. The improvement in photocurrent density may be due to the presence of a large number of active sites in MoS_2 as well as the upward shifting of the conduction band edge towards the H^+/H_2 redox potential which results in better transfer and separation of charge carriers. Mott-Schottky results also confirmed the highest values of flat band potential in Ti-doped WO_3 - MoS_2 with the lowest charge transfer resistance at the semiconducting electrode/electrolyte interface. Furthermore, density functional theory calculations indicate that on doping WO_3 with Ti and Co, there is a slight upward shift in the conduction band minimum, without any significant change in the valance band maximum, with respect to the Fermi level. As a result, the conduction

band minimum of WO_3 shifts upward closer to H^+/H_2 redox potential. Therefore, by modifying the morphology as well as doping of the nanostructured materials, this study represents a straightforward and practical technique for developing an efficient PEC electrode.

In recent years, external field-supported techniques have emerged as an effective strategy for improving photoelectrochemical performance. The key stage in the external field-assisted PEC water-splitting process is the recombination of manipulated carriers, which has been a hot issue. The fundamental cause is that the external field supplies more energy to the electrode system and promotes greater electron-hole pair separation, thereby improving PEC water-splitting efficiency. In the present study, we have fabricated the Co_3O_4 nanorods (NRs) and thin film (TF) to achieve enhanced PEC water-splitting performance in the presence of a magnetic field. The working electrodes of Co_3O_4 NRs and TF were deposited using a two-step procedure. The synthesis was carried out using the glancing angle electron beam evaporation method followed by chemical vapor deposition. The PEC performance was studied for Co_3O_4 NRs and TF in a magnetic field. The Co_3O_4 NRs samples exhibit better optical absorption compared to the TF of Co_3O_4 . Among all the samples, Co_3O_4 NRs showed the highest photocurrent density of 0.12 mA/cm^2 in the presence of a magnetic field. The enhancement in photocurrent density of Co_3O_4 NRs in the presence of a magnetic field may be due to the limitation of non-radiative recombination of carriers manipulated by Lorentz force and due to shape anisotropy. Electrochemical impedance spectra of Co_3O_4 NRs in the presence of a magnetic field show the least charge transfer resistance at the semiconductor electrolyte interface. This work offers a straightforward and practical method for modifying the morphology of nanostructured materials using an external magnetic field to create an efficient PEC electrode.

सारांश

दुनिया भर में ऊर्जा की आपूर्ति सबसे महत्वपूर्ण चुनौतियों में से एक है जिसका वैज्ञानिकों और प्रौद्योगिकीविदों ने इक्कीसवीं सदी में सामना किया है। 2008 में ऊर्जा खपत दर 15 TW तक पहुंच गई, और बढ़ती विश्व जनसंख्या और उत्पादन के कारण, यह अनुमान लगाया गया है कि यह दर 2050 तक लगभग दोगुनी हो जाएगी। पर्यावरणीय गिरावट और ऊर्जा की मांग बढ़ने के कारण टिकाऊ ऊर्जा की आवश्यकता अधिक महत्वपूर्ण होती जा रही है। दुनिया भर में उपलब्ध कुल ऊर्जा संसाधनों को आम तौर पर परमाणु, जीवाश्म और नवीकरणीय में वर्गीकृत किया जाता है। जीवाश्म ईंधन ग्रीनहाउस गैस उत्सर्जन के प्राथमिक कारणों में से एक है, लेकिन समय के साथ, आपूर्ति और मांग के बीच अंतर बढ़ गया है। नवीकरणीय और टिकाऊ ऊर्जा स्रोतों का उत्पादन आज की दुनिया में प्रमुख चुनौतियों में से एक है और वैश्विक ऊर्जा आवश्यकताओं को पूरा करने के लिए, स्वच्छ ऊर्जा स्रोतों को विकसित करने की दिशा में भारी उछाल आया है। इस परिदृश्य में, ऊर्जा मुद्दे का स्थायी समाधान देने के लिए सौर ऊर्जा का उपयोग सबसे व्यवहार्य तरीका है। पृथ्वी को प्रदान की जाने वाली सौर ऊर्जा (173000 TW) दैनिक वैश्विक ऊर्जा खपत (2017 में 17.91 TW) से लगभग 9600 गुना अधिक है। सौर ऊर्जा को हाइड्रोजन में परिवर्तित करना एक उत्कृष्ट समाधान प्रतीत होता है क्योंकि हाइड्रोजन दहन से कोई ग्रीनहाउस गैसों उत्सर्जित नहीं होती हैं। आजकल, 96% मामलों में हाइड्रोजन के उत्पादन का श्रेय फीडस्टॉक के रूप में जीवाश्म ईंधन को दिया जाता है, जिसमें प्रत्यक्ष जल इलेक्ट्रोलिसिस 4% हाइड्रोजन उत्पादन के लिए जिम्मेदार होता है। इसलिए, जीवाश्म ईंधन पर निर्भरता कम करने के लिए, वर्तमान प्रयास पानी से हाइड्रोजन उत्पादन में सुधार पर केंद्रित हैं। कई रणनीतियों में से, फोटोइलेक्ट्रोकेमिकल (पीईसी) जल विभाजन एक टिकाऊ, नवीकरणीय और स्वच्छ ऊर्जा अर्थव्यवस्था बनाने के लिए सौर हाइड्रोजन उत्पादन के लिए एक अत्याधुनिक तकनीक है। फोटोइलेक्ट्रोकेमिकल जल विभाजन के पीछे का सिद्धांत अर्धचालक की सतह पर घटना वाले फोटॉन का रूपांतरण है, अर्धचालक के बैंडगैप से अधिक ऊर्जा के साथ विद्युत रासायनिक ऊर्जा में जो पानी को सीधे H_2 और O_2 के अणुओं में विभाजित कर सकता है। पानी को उसके घटकों में विभाजित करने के लिए प्रतिक्रिया में $\Delta G^\circ = +237 \text{ kJ/mol}$ का एक बड़ा गिब्स मुक्त ऊर्जा परिवर्तन होना चाहिए और 1.23V समग्र जल विभाजन के लिए थर्मोडायनामिक वोल्टेज है। पीईसी सेल दक्षता मुख्य रूप से अर्धचालक इलेक्ट्रोड के प्रदर्शन से प्रभावित होती है जिसमें इंटरफ़ेस पर प्रकाश का अवशोषण, चार्ज पृथक्करण और चार्ज स्थानांतरण शामिल है। अर्धचालक सामग्री के चालन बैंड और वैलेंस बैंड किनारों को H_2O (0 V बनाम SHE) की कमी क्षमता से अधिक नकारात्मक और H_2O (1.23 V बनाम SHE) की ऑक्सीकरण क्षमता से अधिक सकारात्मक स्थिति पर रखा जाना चाहिए। लाभदायक पीईसी विभाजन प्रतिक्रिया प्राप्त करने के लिए, अर्धचालक इलेक्ट्रोड में अच्छे दृश्यमान प्रकाश अवशोषण के लिए एक ट्यून्ड बैंड गैप, पानी रेडॉक्स क्षमता के साथ अनुकूल बैंड एज संरेखण और फोटो संक्षारण के खिलाफ फोटो-स्थिरता होनी चाहिए। एक ही फोटोइलेक्ट्रोड में उपरोक्त सभी आवश्यकताओं को प्राप्त करना आवश्यक है पीईसी इलेक्ट्रोड के निर्माण के लिए अभी भी प्रमुख चुनौतियों में से एक है। उपरोक्त पृष्ठभूमि वर्तमान कार्य के उद्देश्य का आधार बनती है। थीसिस का केंद्रीय उद्देश्य उन्नत फोटोइलेक्ट्रोकेमिकल जल विभाजन प्रतिक्रिया के लिए धातु ऑक्साइड और चॉकोजेनाइड्स-आधारित सामग्रियों का पता लगाना है। इस संबंध में, पीईसी प्रदर्शन में सुधार के लिए विभिन्न पद्धतियों को अपनाया गया है जैसे कि ज्यामिति संशोधन, हेटेरोजंक्शन, डोपिंग, प्लास्मोनिक प्रभाव और चुंबकीय क्षेत्र का प्रभाव। उस उद्देश्य को पूरा करने के लिए Ag_2S , MoS_2 , WO_3 , और CO_3O_4 नैनोस्ट्रक्चर को ग्लॉसिंग कोण जमाव, इलेक्ट्रॉन-बीम वाष्पीकरण, रासायनिक

वाष्प जमाव और समाधान विधि द्वारा निर्मित किया गया था। वर्तमान शोध कार्य में, Ag_2S नैनोरोड्स के निर्माण के लिए ग्लैसिंग एंगल डिपोजिशन (GLAD) विधि का उपयोग किया गया था क्योंकि यह ज्यामितीय छाया प्रभाव के कारण नियंत्रित सरंध्रता के साथ विभिन्न स्तंभ फिल्में प्रदान करता है। ज्यामिति, नैनोरोड्स की लंबाई के साथ-साथ अंतर नैनोरोड्स पृथक्करण को जमाव स्थितियों को अलग-अलग करके समायोजित किया जा सकता है।

कार्य के प्रारंभिक भाग में, हमने GLAD और उसके बाद सल्फ्यूराइजेशन का उपयोग करके Ag_2S के ज़िग-ज़ैग नैनोरोड का निर्माण किया है। PEC प्रदर्शन का अध्ययन Ag_2S की ज़िग-ज़ैग भुजाओं की संख्या को अलग-अलग करके किया गया था। Ag_2S के ज़िग-ज़ैग नैनोरोड्स लंबवत नैनोरोड सरणियों की तुलना में बेहतर ऑप्टिकल अवशोषण प्रदान करते हैं। इसे लंबवत नैनोरोड्स में सबस्ट्रेट से प्रतिबिंब द्वारा महत्वपूर्ण फोटॉन हानि के लिए जिम्मेदार ठहराया जा सकता है। कठोर युग्मित तरंग विश्लेषण [आरसीडब्ल्यूए] सिमुलेशन का उपयोग करके ऑप्टिकल अवशोषण की भी सैद्धांतिक रूप से जांच की गई थी। सेमीकंडक्टिंग इलेक्ट्रोड/इलेक्ट्रोलाइट इंटरफेस पर न्यूनतम चार्ज ट्रांसफर प्रतिरोध वाले एक हाथ वाले Ag_2S नैनोरोड की तुलना में पहले से तैयार चार बांह वाले एजी2एस ज़िग-ज़ैग इलेक्ट्रोड ने 3.04 एमए/सेमी^2 (1 वी बनाम एजी/एजीसीएल पर) की उच्चतम फोटोक्रेट घनत्व प्रदर्शित की। चार भुजा वाले Ag_2S ज़िग-ज़ैग नैनोरोड्स इलेक्ट्रोड के बेहतर फोटोक्रेट घनत्व को ऑप्टिकल ट्रैपिंग में वृद्धि के लिए जिम्मेदार ठहराया गया था और इसलिए, इसकी लहरदार संरचना के कारण प्रकाश का प्रभावी अवशोषण हुआ।

एक अन्य दृष्टिकोण हेटेरोजंक्शन आधारित प्रणाली का निर्माण है। यह सबसे व्यवहार्य तरीकों में से एक है क्योंकि यह सेमीकंडक्टर इंटरफेस पर चार्ज वाहकों के प्रभावी पृथक्करण के साथ आधार सामग्री के बैंड गैप को ट्यून करके प्रकाश अवशोषण को बढ़ाता है। $\text{WO}_3/\text{Ag}_2\text{S}$ आधारित हेटेरोजंक्शन के कार्यशील इलेक्ट्रोड तैयार करने के लिए, दो-चरणीय विधि अपनाई गई जिसमें डीसी स्पटरिंग का उपयोग करके जमा की गई WO_3 की एक पतली फिल्म और ग्लैसिंग कोण जमाव द्वारा निर्मित अच्छी तरह से अलग किए गए Ag_2S नैनोरोड शामिल हैं। PEC प्रतिक्रिया का अध्ययन नंगे WO_3 , Ag_2S और $\text{WO}_3/\text{Ag}_2\text{S}$ हेटेरोजंक्शन के लिए किया गया था। पूर्व-तैयार $\text{WO}_3/\text{Ag}_2\text{S}$ हेटेरोजंक्शन नमूनों में नंगे WO_3 पतली फिल्म (0.34 mA/cm^2) की तुलना में उच्च अवशोषण के साथ-साथ 2.40 mA/cm^2 (1 V Ag/AgCl पर) की उच्च फोटोक्रेट घनत्व का पता चला। $\text{WO}_3/\text{Ag}_2\text{S}$ इलेक्ट्रोड के फोटोक्रेट घनत्व में वृद्धि को WO_3 और Ag_2S के बीच टाइप-II हेटेरोजंक्शन के गठन के लिए जिम्मेदार ठहराया जा सकता है जो इंटरफेस पर चार्ज वाहक को प्रभावी ढंग से अलग और स्थानांतरित करता है। इसके अलावा, लंबवत झुके हुए Ag_2S नैनोरोड्स संरचनाओं के कारण प्रकाश के फंसने में वृद्धि के परिणामस्वरूप प्रकाश का प्रभावी अवशोषण होता है।

उत्कृष्ट धातु नैनोकण की स्थानीयकृत सतह प्लास्मोनिक अनुनाद (एलएसपीआर) घटना प्रकाश के प्रति संवेदनशील है जो स्थानीय विद्युत चुम्बकीय क्षेत्र को बढ़ाती है, सौर प्रकाश अवशोषण सीमा का विस्तार करती है, और आंतरिक रूप से इलेक्ट्रॉन-छेद जोड़े को उत्तेजित करती है। इसलिए, पीईसी में प्लास्मोनिक्स की भूमिका का अध्ययन करने के लिए, हमने आरएफ स्पटरिंग और परमाणु परत जमाव (एएलडी) के बाद ग्लैसिंग कोण जमाव (जीएलएडी) विधि का उपयोग करके $\text{Ag}_2\text{S}/\text{Au}/\text{Al}_2\text{O}_3$ फोटोइलेक्ट्रोड का निर्माण किया है। हालाँकि, फोटोस्टेबिलिटी में सुधार करने और सतह चार्ज पुनर्संयोजन को कम करने के लिए, Al_2O_3 की एक निष्क्रिय परत जमा की गई थी। पहले से तैयार किए गए $\text{Ag}_2\text{S}/\text{Au}/\text{Al}_2\text{O}_3$ नमूनों में सेमीकंडक्टिंग इंटरफेस पर कम चार्ज ट्रांसफर प्रतिरोध के साथ नंगे Ag_2S (1.70 mA/cm^2) की तुलना में 2.50 mA/cm^2 (0.95 V Ag/AgCl पर) की उच्च फोटोक्रेट घनत्व का पता चला। एयू नैनोकणों का प्लास्मोनिक प्रभाव Ag_2S की दृश्य-प्रकाश प्रतिक्रिया को बढ़ाता है और साथ ही फोटोक्रेट घनत्व को बढ़ाने के लिए गर्म इलेक्ट्रॉन प्रदान करता है। इसके अलावा, Ag_2S नैनोरोड्स की झुकी हुई वास्तुकला के कारण प्रकाश के फँसने

में वृद्धि के परिणामस्वरूप प्रकाश का प्रभावी अवशोषण हुआ। Ag_2S और $\text{Ag}_2\text{S}/\text{Au}$ के नैनोरोड्स के बीच विद्युत-क्षेत्र की तीव्रता और प्रकाश के ऑप्टिकल ट्रैपिंग के वितरण का पता लगाने के लिए परिमित अंतर समय डोमेन पर आधारित सैद्धांतिक सिमुलेशन भी किए गए थे।

दृश्य प्रकाश का उपयोग करने के अलावा, ठोस पदार्थों की इलेक्ट्रॉनिक बैंड संरचना को बदलना महत्वपूर्ण है। डोपिंग बेहतर पीईसी प्रतिक्रिया के लिए ऊर्जा स्तर और इलेक्ट्रॉनिक बैंड संरचना की स्थिति को समायोजित करने का एक तरीका हो सकता है। यहां, MoS_2 फोटोएनोड के साथ WO_3 नैनोकम्पोजिट की फोटोइलेक्ट्रोकेमिकल जल-विभाजन प्रतिक्रिया पर Ti और Co डोपिंग के प्रभाव की प्रयोगात्मक और सैद्धांतिक अध्ययनों का उपयोग करके जांच की जा रही है। कार्यशील इलेक्ट्रोडों की वृद्धि के लिए एक सरल हाइड्रोथर्मल और सोल-जेल विधि अपनाई गई। सभी नमूनों में, Ti-doped WO_3 - MoS_2 नमूने ने 1.6 V बनाम Ag/AgCl पर $1.15 \text{ mA}/\text{cm}^2$ के फोटोकंट घनत्व के साथ अधिकतम ऑप्टिकल अवशोषण दिखाया। फोटोकंट घनत्व में सुधार MoS_2 में बड़ी संख्या में सक्रिय साइटों की उपस्थिति के साथ-साथ चालन बैंड किनारे के H^+/H_2 रेडॉक्स क्षमता की ओर ऊपर की ओर बढ़ने के कारण हो सकता है जिसके परिणामस्वरूप चार्ज वाहक का बेहतर स्थानांतरण और पृथक्करण होता है। इसके अलावा, घनत्व कार्यात्मक सिद्धांत गणना से संकेत मिलता है कि Ti और Co के साथ WO_3 को डोपिंग करने पर, फर्मी स्तर के संबंध में, वैलेंस बैंड अधिकतम में किसी भी महत्वपूर्ण बदलाव के बिना, चालन बैंड न्यूनतम में थोड़ा ऊपर की ओर बदलाव होता है। परिणामस्वरूप, WO_3 का चालन बैंड न्यूनतम H^+/H_2 रिडॉक्स क्षमता के करीब ऊपर की ओर स्थानांतरित हो जाता है।

हाल के वर्षों में, बाहरी क्षेत्र-समर्थित तकनीकें फोटोइलेक्ट्रोकेमिकल प्रदर्शन में सुधार के लिए एक प्रभावी रणनीति के रूप में उभरी हैं। बाहरी क्षेत्र-सहायता प्राप्त पीईसी जल-विभाजन प्रक्रिया में मुख्य चरण हेरफेर किए गए वाहकों का पुनर्संयोजन है, जो एक गर्म मुद्दा रहा है। मूल कारण यह है कि बाहरी क्षेत्र इलेक्ट्रोड प्रणाली को अधिक ऊर्जा की आपूर्ति करता है और अधिक इलेक्ट्रॉन-छेद जोड़ी पृथक्करण को बढ़ावा देता है, जिससे पीईसी जल-विभाजन दक्षता में सुधार होता है। वर्तमान अध्ययन में, हम एक चुंबकीय क्षेत्र की उपस्थिति में उन्नत फोटोइलेक्ट्रोकेमिकल जल विभाजन प्रदर्शन को प्राप्त करने के लिए Co_3O_4 NRs और TF के निर्माण की रिपोर्ट करते हैं। Co_3O_4 NRs और TF के कार्यशील इलेक्ट्रोड दो-चरणीय प्रक्रिया का उपयोग करके जमा किए गए थे। रासायनिक वाष्प जमाव के बाद ग्लॉसिंग कोण इलेक्ट्रॉन बीम वाष्पीकरण विधि का उपयोग करके संश्लेषण किया गया था। चुंबकीय क्षेत्र की उपस्थिति में Co_3O_4 NRs और TF के लिए PEC प्रदर्शन का अध्ययन किया गया था। Co_3O_4 NRs नमूने Co_3O_4 के TF की तुलना में बेहतर ऑप्टिकल अवशोषण प्रदर्शित करते हैं। सभी नमूनों में, Co_3O_4 NRs ने चुंबकीय क्षेत्र की उपस्थिति में $0.12 \text{ mA}/\text{cm}^2$ का उच्चतम फोटोकंट घनत्व दिखाया। चुंबकीय क्षेत्र की उपस्थिति में Co_3O_4 NRs के फोटोकंट घनत्व में वृद्धि लोरेन्ज़ बल द्वारा संचालित वाहकों के गैर-विकिरणीय पुनर्संयोजन की सीमा और आकार अनिसोट्रॉपी के कारण हो सकती है। चुंबकीय क्षेत्र की उपस्थिति में Co_3O_4 NRs का विद्युत रासायनिक प्रतिबाधा स्पेक्ट्रा अर्धचालक इलेक्ट्रोलाइट इंटरफ़ेस पर सबसे कम चार्ज स्थानांतरण प्रतिरोध दिखाता है। यह कार्य एक कुशल पीईसी इलेक्ट्रोड बनाने के लिए बाहरी चुंबकीय क्षेत्र का उपयोग करके नैनोसंरचित सामग्रियों की आकृति विज्ञान को संशोधित करने के लिए एक सीधी और व्यावहारिक विधि प्रदान करता है।

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Nomenclature

List of Symbols

α	Polarizability of a molecule
β	Inclination of nano-columns
$\text{\AA}$	Angstrom
D	Diffusion coefficient
E	Electric field
E_a	Energy barrier of the diffusion process
k_b	Boltzmann's constant
ϕ	Substrate rotation angle
C	Space-charge capacitance
ϵ_o	Dielectric permittivity in vacuum
ϵ_s	Relative permittivity of the semiconductor
q	Electronic charge
N_D	Donor density
W	Width of space charge layer
A	Active area
V_{app}	Applied potential,
V_{fb}	Flat-band potential,
T	Temperature
Z'	Real impedance
Z''	Imaginary impedance
X	Absolute electronegativity
E_g	Bandgap
ν	Frequency
ΔG°	Standard Gibbs free energy per mole
N_A	Avogadro number
E_{th}	Threshold energy

σ	Electrical conductivity
η	Photoconversion efficiency

Abbreviations

AgNRs	Ag nanorods
Ar	Argon
RF	Radio-frequency
nm	Nanometer
TF	Thin film
NRs	Nanorods
ITO	Indium doped tin oxide
FTO	Fluorine doped tin oxide
STH	Solar-to-hydrogen
NPs	Nanoparticles
LSPR	Localized surface plasmonic resonance
TFSF	Total field scattered field
PML	Perfectly matched layer
TE	Transverse electric mode
TM	Transverse magnetic mode
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
IPA	Isopropyl alcohol
DFT	Density functional theory
PBE	Perdew-Burke-Ernzerhof
GGA	Generalized gradient approximation
VASP	Vienna ab initio simulation package
PAW	Projected augmented wave
GGA	Generalized gradient approximation
HSE	Heyd-Scuseria-Ernzerhof
LSV	linear sweep voltammogram

DOS	Density of states
CB	Conduction band
VB	Valance band
VBE	Valance band edge
CBE	Conduction band edge
CBM	Conduction band minimum
VBM	Valance band maximum
NHE	Normal hydrogen electrode
SHE	Standard hydrogen electrode
GAXRD	Glancing angle X-ray diffraction
JCPDS	Joint committee on powder diffraction standards
PVD	Physical vapor deposition
CVD	Chemical vapor deposition
GLAD	Glancing angle deposition
ALD	Atomic layer deposition
e-beam GLAD	Electron beam glancing angle deposition
XRD	X-ray diffraction
EDX	Energy dispersive X-ray
HRTEM	High-resolution transmission electron microscope
SAED	Selective area electron diffraction
FESEM	Field emission scanning electron microscope
XPS	X-ray photoelectron spectroscopy
VSM	Vibrating sample magnetometer
AM	Air mass
PEC	Photoelectrochemical
IPCE	Incident photon to electron conversion efficiency
EIS	Electrochemical impedance spectra
Ag ₂ S	Silver sulfide
WO ₃	Tungsten oxide

MoS_2	Molybdenum sulfide
MoO_3	Molybdenum oxide
Au	Gold
Ti	Titanium
Co	Cobalt
Co_3O_4	Cobalt oxide
Al_2O_3	Aluminium oxide
Na_2SO_4	Sodium sulfate
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	Sodium tungstate