

**PEROVSKITE SODIUM NIOBATE ( $\text{NaNbO}_3$ )  
NANOSTRUCTURES BASED NANOCOMPOSITES  
FOR ENHANCED PHOTOELECTROCHEMICAL  
WATER SPLITTING APPLICATION**

**DHEERAJ KUMAR**



**DEPARTMENT OF PHYSICS  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
NOVEMBER 2021**

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*by*

**DHEERAJ KUMAR**

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**Submitted**

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

**to the**



**DEPARTMENT OF PHYSICS  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
NOVEMBER 2021**

**Dedication**

*I want to dedicate this thesis work*

*To the Supreme Almighty God, Parents,*

*And to my beloved Grandparents*

*(Late. Shri Jaswant Singh and Late. Smt. Kela Devi)*

*And*

*(Late. Shri Babulal Sagar and Late. Smt. Maya Devi)*

## **Certificate**

This is to certify that, the thesis entitled “**Perovskite Sodium Niobate (NaNbO<sub>3</sub>) Nanostructures Based Nanocomposites for Enhanced Photoelectrochemical Water Splitting Application**” being submitted by **Dheeraj Kumar** to the Department of Physics, **Indian Institute of Technology Delhi** is worthy of consideration for the award of the degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under my guidance and supervision. The results contained in it have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

**Prof. Neeraj Khare**

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## Abstract

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The potential of solar energy harvesting strategy using semiconductor materials has received a lot of research interest to overcome the increasing demands for renewable energy production. In this regard, hydrogen is considered a clean fuel in the development of renewable and sustainable energy sources. The solar light-driven photoelectrochemical water splitting into hydrogen and oxygen is considered a promising strategy for renewable energy as both solar energy and water are limitless natural resources. In recent times, various novel semiconductor materials are being used, although the majority of the materials have significant drawbacks. The present thesis focuses on fabricating semiconductor nanostructures photoanodes and employing different strategies to enhance the solar light-driven PEC water splitting activity.

In order to perform work in this direction, a facile hydrothermal method has been utilized to synthesize the sodium niobate ( $\text{NaNbO}_3$ ) in different morphologies such as nanorods and nanofibers. The structural, morphological, and optical analysis have been performed of the synthesized  $\text{NaNbO}_3$  nanostructures. Moreover, a comparative study among the prepared  $\text{NaNbO}_3$  nanorods and  $\text{NaNbO}_3$  nanofibers photoanodes for the photoelectrochemical (PEC) water splitting application has been carried out. The PEC performance of the  $\text{NaNbO}_3$  nanofibers photoanode has been observed to be higher as compared to  $\text{NaNbO}_3$  nanorods photoanode. The photocurrent density of  $\text{NaNbO}_3$  nanofibers photoanode is observed to be  $2.75 \text{ mA/cm}^2$  at  $0.9 \text{ V vs. Ag/AgCl}$ , which is  $\sim 3$  fold enhanced in comparison to  $\text{NaNbO}_3$  nanorods photoanode. Furthermore, the  $\text{NaNbO}_3$  nanofibers photoanode exhibits an incident photon to current conversion efficiency (IPCE) value of  $7.2 \%$ , which is  $\sim 2$  times higher than that of  $\text{NaNbO}_3$  nanorods photoanode. This comparative study demonstrates that the variation in the morphology of the nanostructures is extremely favourable for achieving efficient solar light-driven PEC water splitting application.

In order to enhance the PEC performance of  $\text{NaNbO}_3$ , metal silver (Ag) nanoparticles have been decorated by a simple chemical solution method onto the surface of hydrothermally grown  $\text{NaNbO}_3$  nanorods for the fabrication of efficient visible light active Ag decorated  $\text{NaNbO}_3$  nanorods photoanode over fluorine-doped tin oxide (FTO) substrates by a spray coating method. Presence of Ag nanoparticles in the nanocomposite affects the optical properties of  $\text{NaNbO}_3$  nanorods and significantly shifts the photoresponse to the visible light region, which is attributed to the plasmonic effect of Ag nanoparticles. The PEC performance of the prepared photoanodes has been studied. The Ag decorated  $\text{NaNbO}_3$  nanorods

photoanode exhibits ~4 fold higher photocurrent density ( $3.54 \text{ mA/cm}^2$  at  $0.9 \text{ V vs. Ag/AgCl}$ ) as compared to the  $\text{NaNbO}_3$  nanorods photoanode. This enhancement in PEC activity of Ag decorated  $\text{NaNbO}_3$  nanorods photoanode has been attributed to the stronger visible light absorption due to the plasmonic effect of Ag, low recombination of photogenerated charge carriers, and high charge carrier concentration as compared to  $\text{NaNbO}_3$  nanorods photoanode.

In order to further improve the PEC activity, another strategy for efficient separation and slow the faster recombination of photogenerated charge carriers of the silver (Ag) nanoparticles grafted onto  $\text{NaNbO}_3$  nanorods (Ag- $\text{NaNbO}_3$  nanocomposite) is to combine two effects simultaneously, i.e., coupling of plasmonic effect and piezophototronic effect. Efficient coupling between semiconducting, optical, and piezoelectric properties such as coupling of piezo-phototronic and plasmonic effects in as-prepared photoelectrodes has been demonstrated to improve the efficiency of PEC water splitting performance. It is noteworthy that the Ag- $\text{NaNbO}_3$  (under light with ultra-sonic vibration) nanocomposite photoelectrode exhibits significantly higher PEC water splitting performance. A ~9 fold and ~5 fold enhancement in photocurrent density ( $9.65 \text{ mA/cm}^2$  at  $1 \text{ V vs. Ag/AgCl}$ ) and IPCE photoresponse (29.6%) for Ag- $\text{NaNbO}_3$  (under light with ultra-sonic vibration) photoelectrode as compared to bare  $\text{NaNbO}_3$  (under light without ultra-sonic vibration) is achieved, respectively in PEC water splitting activity. The enhancement in the PEC performance of Ag- $\text{NaNbO}_3$  (under light with ultra-sonic vibration) has been attributed to the coupling of piezo-phototronic and plasmonic effects together. The surface plasmonic effect due to the presence of Ag nanoparticles expands the visible-light absorption part, and an alternating built-in potential is generated under periodic mechanical strain (piezo-phototronic effect) in  $\text{NaNbO}_3$  material enhances the drift and separation of the photogenerated charge carriers. This method has been demonstrated as a novel strategy for enhancing the performance of silver decorated semiconducting/piezoelectric material for achieving efficient solar light-driven hydrogen generation.

Finally, in order to increase the efficiency of a single semiconductor, the formation of semiconductor-semiconductor-based nanocomposites has also been attempted. A visible light active graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) nanosheets coupled with hydrothermally grown sodium niobate nanofibers ( $\text{NaNbO}_3\text{-NF}$ ) photoanode have been fabricated using the spray coating method. The  $\text{g-C}_3\text{N}_4/\text{NaNbO}_3\text{-NF}$  (4-CN) nanocomposite photoanode exhibits ~3 times higher photocurrent density as compared to  $\text{NaNbO}_3\text{-NF}$  photoanode under light illumination. The formation of type-II heterojunction among them has induced a built-in electric field in the depletion region, resulting in faster separation of photogenerated charge carriers and enhanced charge transfer efficiency at the semiconductor/electrolyte interface. The

strategy of coupling visible light active g-C<sub>3</sub>N<sub>4</sub> with UV active materials has been demonstrated to be a favourable method for visible-light-driven hydrogen generation.

## सारांश

अक्षय ऊर्जा उत्पादन की बढ़ती माँगों को दूर करने के लिए अर्धचालक पदार्थों का उपयोग करके सौर ऊर्जा संचयन रणनीति की क्षमता ने बहुत अधिक शोध रुचि प्राप्त की है। इस संबंध में, अक्षय और टिकाऊ ऊर्जा स्रोतों के विकास में हाइड्रोजन को एक स्वच्छ ईंधन माना जाता है। सौर प्रकाश-चालित (PEC) जल को हाइड्रोजन और ऑक्सीजन में विभाजित करना अक्षय ऊर्जा के लिए एक आशाजनक रणनीति माना जाता है क्योंकि सौर ऊर्जा और जल दोनों ही असीमित प्राकृतिक संसाधन हैं। हाल के दिनों में, विभिन्न श्रेष्ठ अर्धचालक पदार्थों का उपयोग किया जा रहा है, हालांकि अधिकांश पदार्थों में महत्वपूर्ण कमियाँ हैं। वर्तमान थीसिस (Thesis) PEC जल विभाजन गतिविधि को बढ़ाने के लिए अर्धचालक नैनोस्ट्रक्चर फोटोएनोड्स बनाने और विभिन्न रणनीतियों को नियोजित करने पर केंद्रित है।

इस दिशा में काम करने के लिए, नैनोरोड्स और नैनोफाइबर्स जैसे विभिन्न आकारिकी में सोडियम नायोबेट ( $\text{NaNbO}_3$ ) को संश्लेषित करने के लिए एक आसान जलतापीय विधि का उपयोग किया गया है। संश्लेषित  $\text{NaNbO}_3$  नैनोस्ट्रक्चर का संरचनात्मक, रूपात्मक और प्रकाशिक विश्लेषण किया गया है। इसके अलावा, प्रकाशविद्युत रासायनिक जल विभाजन अनुप्रयोग के लिए तैयार  $\text{NaNbO}_3$  नैनोरोड्स और  $\text{NaNbO}_3$  नैनोफाइबर्स फोटोएनोड्स के बीच एक तुलनात्मक अध्ययन किया गया है।  $\text{NaNbO}_3$  नैनोफाइबर्स फोटोएनोड का PEC प्रदर्शन  $\text{NaNbO}_3$  नैनोरोड्स फोटोएनोड की तुलना में अधिक देखा गया है।  $\text{NaNbO}_3$  नैनोफाइबर्स फोटोएनोड का प्रकाश धारा घनत्व  $2.75 \text{ mA/cm}^2$  at  $0.9 \text{ V vs. Ag/AgCl}$  पर देखा गया है, जो  $\text{NaNbO}_3$  नैनोरोड्स फोटोएनोड की तुलना में  $\sim 3$  गुना बढ़ा हुआ है। इसके अलावा,  $\text{NaNbO}_3$  नैनोफाइबर्स फोटोएनोड 7.2 % आपतित फोटोन से विद्युत धारा में परिवर्तन की क्षमता (IPCE) प्रदर्शित करता है, जो  $\text{NaNbO}_3$  नैनोरोड्स फोटोएनोड की तुलना में  $\sim 2$  गुना अधिक है। यह तुलनात्मक अध्ययन दर्शाता है कि कुशल PEC जल विभाजन अनुप्रयोग को प्राप्त करने के लिए नैनोस्ट्रक्चर के आकारिकी में भिन्नता अत्यंत अनुकूल है।

$\text{NaNbO}_3$  के PEC प्रदर्शन को बढ़ाने के लिए, जलतापीय-विकसित  $\text{NaNbO}_3$  नैनोरोड्स की सतह पर धातु, सिल्वर (Ag) नैनोकणों को एक साधारण रासायनिक विलयन विधि द्वारा बनाया गया और कुशल द्रश्य प्रकाश सक्रिय Ag सजाए गए  $\text{NaNbO}_3$  नैनोरोड्स को फ्लोरीन-डॉप्ड टिन ऑक्साइड (FTO) सबस्ट्रेट की सतह पर स्प्रे कोटिंग विधि द्वारा फोटोएनोड बनाया गया है। नैनोकम्पोजिट में Ag नैनोकणों की उपस्थिति  $\text{NaNbO}_3$  नैनोरोड्स

के प्रकाशिक गुणों को प्रभावित करती है और द्रश्य प्रकाश क्षेत्र में प्रकाशप्रतिक्रिया को महत्वपूर्ण रूप से स्थानांतरित कर देती है, जिसे Ag नैनोकणों के प्लास्मोनिक प्रभाव के लिए जिम्मेदार ठहराया जाता है। तैयार फोटोएनोड्स के PEC प्रदर्शन का अध्ययन किया गया है। Ag सजाए गए  $\text{NaNbO}_3$  नैनोरोड्स फोटोएनोड,  $\text{NaNbO}_3$  नैनोरोड्स फोटोएनोड की तुलना में  $\sim 4$  गुना अधिक प्रकाश धारा घनत्व ( $3.54 \text{ mA/cm}^2$   $0.9 \text{ V vs. Ag/AgCl}$ ) प्रदर्शित करता है। Ag सजाए गए  $\text{NaNbO}_3$  नैनोरोड्स फोटोएनोड की PEC गतिविधि में इस वृद्धि को Ag के प्लास्मोनिक प्रभाव, फोटोजेनरेटेड चार्ज कैरियर्स के कम पुनर्संयोजन और  $\text{NaNbO}_3$  नैनोरोड्स फोटोएनोड की तुलना में उच्च चार्ज वाहक सांद्रता के कारण मजबूत द्रश्य प्रकाश अवशोषण के लिए जिम्मेदार ठहराया गया है।

PEC गतिविधि को और बेहतर बनाने के लिए,  $\text{NaNbO}_3$  नैनोरोड्स (Ag- $\text{NaNbO}_3$  nanocomposite) पर सजाये गए Ag नैनोकणों के फोटोजेनरेटेड चार्ज कैरियर्स के कुशल पृथक्करण और तेजी से पुनर्संयोजन को धीमा करने के लिए एक और रणनीति एक साथ दो प्रभावों को संयोजित करना है, अर्थात् युग्मन प्लास्मोनिक प्रभाव और पीजो-फोटोट्रॉनिक प्रभाव। PEC जल विभाजन प्रदर्शन की दक्षता में सुधार करने के लिए तैयार फोटोइलेक्ट्रोड में पीजो-फोटोट्रॉनिक और प्लास्मोनिक प्रभावों के युग्मन जैसे अर्धचालक, प्रकाशिक और पीजोइलेक्ट्रिक गुणों के बीच कुशल युग्मन का प्रदर्शन किया गया है। यह उल्लेखनीय है कि, Ag- $\text{NaNbO}_3$  (अल्ट्रा-सोनिक कंपन के साथ प्रकाश में) नैनोकम्पोजिट फोटोइलेक्ट्रोड काफी उच्च PEC जल विभाजन क्षमता प्रदर्शित करता है। मौलिक  $\text{NaNbO}_3$  (अल्ट्रा-सोनिक कंपन के बिना प्रकाश के तहत) की तुलना में Ag- $\text{NaNbO}_3$  (अल्ट्रा-सोनिक कंपन के साथ प्रकाश के तहत) फोटोइलेक्ट्रोड के लिए प्रकाश धारा घनत्व में  $\sim 9$  गुना ( $9.65 \text{ mA/cm}^2$  at  $1 \text{ V vs. Ag/AgCl}$  पर) और IPCE प्रकाशप्रतिक्रिया (29.6 %) PEC जल विभाजन गतिविधि में  $\sim 5$  गुना वृद्धि प्राप्त की गयी है। Ag- $\text{NaNbO}_3$  (अल्ट्रा-सोनिक कंपन के साथ प्रकाश के तहत) के PEC प्रदर्शन में वृद्धि को पीजो-फोटोट्रॉनिक और प्लास्मोनिक प्रभावों के एक साथ युग्मन के लिए जिम्मेदार ठहराया गया है। Ag नैनोकणों की उपस्थिति के कारण सतह प्लास्मोनिक प्रभाव द्रश्य-प्रकाश अवशोषण भाग का विस्तार करता है, और  $\text{NaNbO}_3$  सामग्री में आवधिक यांत्रिक तनाव (पीजो-फोटोट्रॉनिक प्रभाव) के तहत एक वैकल्पिक अंतर्निहित विभव उत्पन्न होता है, जो फोटोजेनरेटेड चार्ज के बहाव और पृथक्करण को बढ़ाता है। उच्च सौर प्रकाश-चालित हाइड्रोजन उत्पादन प्राप्त करने के लिए Ag से सजाए गए अर्धचालक/पीजोइलेक्ट्रिक पदार्थों के प्रदर्शन को बढ़ाने के लिए इस पद्धति को एक नई रणनीति के रूप में प्रदर्शित किया गया है।

अंत में, एकल अर्धचालक की दक्षता बढ़ाने के लिए, अर्धचालक-अर्धचालक आधारित नैनोकम्पोजिट के गठन का भी प्रयास किया गया है। एक द्रश्य प्रकाश सक्रिय ग्रेफाइटिक कार्बन नाइट्राइड ( $g-C_3N_4$ ) नैनोशीट्स को जलतापीय रूप से विकसित सोडियम नाइओबेट नैनोफाइबर्स ( $NaNbO_3-NF$ ) के साथ मिलाकर, स्प्रे कोटिंग विधि का उपयोग करके, फोटोएनोड बनाया गया है। प्रकाश रोशनी में  $NaNbO_3-NF$  फोटोएनोड की तुलना में  $g-C_3N_4/NaNbO_3-NF$  (4-CN) नैनोकम्पोजिट फोटोएनोड,  $\sim 3$  गुना अधिक प्रकाश धारा घनत्व प्रदर्शित करता है। उनके बीच टाइप- II हेटेरोजंक्शन के गठन ने कमी क्षेत्र में एक अंतर्निर्मित विद्युत क्षेत्र को प्रेरित किया है, जिसके परिणामस्वरूप फोटोजेनरेटेड चार्ज कैरियर्स का तेजी से पृथक्करण और अर्धचालक/इलेक्ट्रोलाइट इंटरफेस में चार्ज ट्रांसफर दक्षता में वृद्धि हुई है। द्रश्यमान प्रकाश सक्रिय  $g-C_3N_4$  को UV सक्रिय पदार्थों के साथ युग्मित करने की रणनीति को द्रश्य प्रकाश-चालित हाइड्रोजन उत्पन्न करने के लिए एक अनुकूल विधि के रूप में प्रदर्शित किया गया है।

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## Nomenclature

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### Symbols

$\Delta G$	Gibbs free energy
$d$	Interplanar spacing between the diffracting planes
$\theta$	Bragg diffraction angle
$\phi_m$	Work function of metal
$\phi_s$	Work function of semiconductor
$n$	Integer
$E$	Energy of emission lines
$Z$	Atomic number
$\alpha$	Absorption coefficient
$h$	Planck's constant
$\nu$	Frequency of the incident photons
$E_g$	Optical band gap
$T$	Transmittance
$I_0$	Initial light intensity
$I$	Transmitted intensity
$\epsilon$	Molar absorptivity
$c$	Concentration
$l$	Path length of light
$\theta_i$	Angle of incidence
$\theta_R$	Angle of refraction
$\theta_c$	Critical angle
$C_{sc}$	Space charge capacitance of semiconductor

$C_H$	Helmholtz layer capacitance
$e$	Electronic charge
$\epsilon_0$	Permittivity of vacuum
$\epsilon_r$	Dielectric constant
$N_D$	Donor density
$V$	Applied potential
$V_{FB}$	Flat band potential
$K_B$	Boltzmann constant
$T$	Absolute temperature
$V(t)$	Sinusoidal ac voltage
$I(t)$	Sinusoidal ac current
$V_0$	dc bias potential
$I_0$	Steady state current
$V_m$	Maximum amplitude of $V(t)$
$I_m$	Maximum amplitude of $I(t)$
$\omega$	Angular frequency
$\theta$	Phase angle
$Z(\omega)$	Impedance
$Z'$	Real part of the impedance
$Z''$	Imaginary part of the impedance
$R_s$	Solution resistance
$R_{ct}$	Charge transfer resistance
$C_{dl}$	Double layer capacitance
$J_p$	Photocurrent density
$J_{dark}$	Dark current density

$J_{\text{light}}$	Light current density
$\lambda$	Wavelength of the incident monochromatic light
P	Incident power density

### **Abbreviations**

AES	Auger electron spectroscopy
AM	Air mass
CB	Conduction band
CCD	Charged coupled device
DI	Deionized
EDS	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FTO	Fluorine doped tin oxide
HRTEM	High resolution transmission electron microscopy
IPA	Isopropanol
IPCE	Incident photon to current conversion efficiency
IR	Infrared
JCPDS	Joint committee on powder diffraction standards
LEDs	Light emitting diodes
LSV	Linear sweep voltammetry
NF	Nanoflowers
NHE	Normal hydrogen electrode
NIR	Near infrared
NPs	Nanoparticles
NR	Nanorods

NW	Nanowires
MS	Mott-Schottky
OER	Oxygen evolution reactions
PCB	Printed circuit board
PEC	Photoelectrochemical
PL	Photoluminescence spectroscopy
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
SPR	Surface plasmon resonance
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
UV	Ultraviolet
UV-vis	UV-vis spectroscopy
VB	Valence band
XRD	X-ray diffraction