



Indian Institute of  
Technology Delhi

**RATIONAL DESIGN OF HIGHLY EFFICIENT  
VISIBLE-LIGHT-DRIVEN PHOTOCATALYSTS  
FOR CO<sub>2</sub> CONVERSION TO FUELS**

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**DOCTOR OF PHILOSOPHY**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI  
&  
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**Rational Design of Highly Efficient Visible-Light-driven  
Photocatalysts for CO<sub>2</sub> Conversion to Fuels**

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*“Try and leave this world a little better than you found it, and when your turn comes to die, you can die happy in feeling that at any rate, you have not wasted your time but have done your best.”*

*~ Sir Robert Baden-Powell*

*Founder of the World Scouting movement*

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## Supervisor Certification

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This is to certify that the thesis entitled “**Rational Design of Highly Efficient Visible-Light-Driven Photocatalysts for CO<sub>2</sub> Conversion to Fuels**” being submitted by **Mr. Aloka Kumar Sahu** to the **Indian Institute of Technology Delhi** and **The University of Queensland** for the award of a joint degree of **Doctor of Philosophy** is a record of *bonafide* research work carried out by him. **Aloka** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.



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## **ABSTRACT**

Photocatalytic CO<sub>2</sub> conversion to solar fuels is considered to be a clean and sustainable way to generate renewable energy. This green energy technology draws inspiration from the photosynthesis process in plants, representing a remarkable innovation that captures sunlight, CO<sub>2</sub>, and H<sub>2</sub>O and converts it into viable fuel sources such as CO, CH<sub>4</sub>, and CH<sub>3</sub>OH. At present, this concept remains in the realm of fundamental research, with catalyst design as its central focus for advancing the photocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). However, designing efficient photocatalysts for selective photoreduction of CO<sub>2</sub>, all while avoiding the need for sacrificial reagents or external electrical bias, remains a formidable challenge. It is mainly due to the limited light-harvesting capacity, high bulk charge recombination, and insufficient surface-active sites of existing photocatalysts.

This thesis focuses on developing highly efficient visible-light-driven photocatalysts based on metal oxide semiconductors for converting CO<sub>2</sub> to hydrocarbons and alcohols. Chapter 1 introduces CO<sub>2</sub> utilization, solar fuel production, and the thesis objectives and scope. Chapter 2 provides an understanding of photocatalytic CO<sub>2</sub> reduction processes and reviews metal oxide and perovskite oxide-based photocatalysts and various strategies adopted by these materials to enhance the performance of photocatalytic CO<sub>2</sub>RR. Chapter 3 describes the materials synthesis procedures and experimental protocols.

The core studies and innovations of this thesis are delineated across three consecutive research chapters. In Chapter 4, I investigated the dynamics of photogenerated charge carriers using a model photocatalyst of edge-truncated cubic Cu<sub>2</sub>O, with exposed {110} and {100} facets, employing both computational and experimental approaches. I found that edge-truncated cubic Cu<sub>2</sub>O microcrystals show an enhanced charge separation upon illumination, attributed to the in-built potential difference induced by band bending at the {110}/{100} facet junctions. When the model edge-truncated cubic Cu<sub>2</sub>O microcrystals were synthesized and tested for photocatalytic CO<sub>2</sub>RR, they showed a superior CH<sub>3</sub>OH yield, around 5.5 times better than the reference simple cubic Cu<sub>2</sub>O photocatalysts. This experiment result validates my computational prediction that controlling photocatalyst morphology through crystal facet engineering increases overall CO<sub>2</sub>RR activity by improving the separation of photogenerated electron-hole pairs across two different facets. However, the difficulty in controlling the growth of crystal structures for synthesizing edge-truncated cubic Cu<sub>2</sub>O microcrystals on a

mass scale and the inherent self-redox capability of Cu<sub>2</sub>O pose constraints on its applicability in photocatalytic CO<sub>2</sub>RR.

In Chapter 5 of my research, I explored more stable materials to use as photocatalysts for CO<sub>2</sub> reduction. Specifically, I synthesized Ga-doped NiTiO<sub>3</sub> photocatalysts using Pechini methods and functionalized their surfaces with Ru nanoparticles. I found that doping Ga into NiTiO<sub>3</sub> helps to prolong the lifespan of photogenerated electron-hole pairs by increasing the electrons' diffusion length. Furthermore, loading Ru cocatalysts on the photocatalysts enhances the electron-hole separation by forming a metal-semiconductor Schottky junction. To test the photocatalysts' efficiency, I conducted the CO<sub>2</sub> photoreduction reaction under varying pressures from 1 to 4.5 bar in a batch photoreactor. I found that an optimal concentration of 1.0 wt.% of Ru loaded over Ga-doped NiTiO<sub>3</sub> photocatalysts suspended in 0.1 M NaHCO<sub>3</sub> aqueous solution under 3.5 bar CO<sub>2</sub> pressure achieved the highest CH<sub>3</sub>OH yield at a rate of 84.48 μmol g<sup>-1</sup> h<sup>-1</sup>. A small amount of CH<sub>4</sub> was also produced as a side product, evolving at a 21.35 μmol g<sup>-1</sup> h<sup>-1</sup> rate. This superior activity was achieved due to the synergetic combination of Ga doping and Ru loading onto NiTiO<sub>3</sub>, which accelerated the charge transfer and provided more surface-active sites. Additionally, the pressurized microenvironment facilitated more efficient CO<sub>2</sub> solubility and absorption at the catalyst surface. Nevertheless, the Brownian motion of the suspended particulate photocatalysts made continuous sunlight harvesting difficult, resulting in low energy efficiency. Moreover, the nanoscale size of the suspended photocatalyst materials rendered post-reaction separation challenging, thereby limiting catalyst reusability.

In Chapter 6, I explored the concept of fabricating a photocatalyst sheet through the immobilization of photocatalyst materials onto a substrate. I synthesized a heterostructure photocatalyst sheet using Cu-loaded Al-doped SrTiO<sub>3</sub> as the CO<sub>2</sub> reduction catalyst and CoO<sub>x</sub>-WO<sub>3</sub> as the H<sub>2</sub>O oxidation catalyst, with a gold nanolayer electron mediator. This composite structure exhibited multiple photo-excitations and excellent charge separation efficiency through an indirect Z-scheme charge transfer mechanism. I tested the photocatalyst sheet's CO<sub>2</sub> reduction performance in both indoor experiments using a solar simulator and outdoor experiments under natural sunlight. I observed that this photocatalyst sheet primarily converts CO<sub>2</sub> to CH<sub>4</sub> and CH<sub>3</sub>OH, with a slight trace of CO. During the indoor experiment, the total carbon product formation rate achieved by this system was 3.237 μmol cm<sup>-2</sup> h<sup>-1</sup>, while during the outdoor experiment, it reached up to 0.384 μmol cm<sup>-2</sup> h<sup>-1</sup>. Furthermore, I

tested the photocatalyst sheet over five consecutive CO<sub>2</sub>RR cycles, during which it exhibited outstanding performance with minimal efficiency changes, demonstrating its robustness and reusability. The key factors contributing to the high activity and stability of the photocatalyst sheet were attributed to the innovative fabrication method employed and the enhanced charge separation facilitated by the indirect Z-scheme heterostructure.

In conclusion, this research offers a variety of strategies for developing highly efficient photocatalyst materials capable of harnessing a broad spectrum of solar energy, enhancing the separation of photogenerated charges, and optimizing CO<sub>2</sub> reduction sites. These findings hold promise for driving the progress of durable and scalable photocatalytic CO<sub>2</sub> reduction systems. By leveraging the insights gained from this study, future endeavors can strive towards realizing more sustainable and practical approaches for CO<sub>2</sub> photoreduction and solar fuel production.

## सारांश

सौर ईंधन में फोटोकैटलिटिक  $\text{CO}_2$  रूपांतरण को नवीकरणीय ऊर्जा उत्पन्न करने का एक स्वच्छ और टिकाऊ तरीका माना जाता है। यह हरित ऊर्जा तकनीक पौधों में प्रकाश संश्लेषण प्रक्रिया से प्रेरणा लेती है, जो एक उल्लेखनीय नवाचार का प्रतिनिधित्व करती है जो सूर्य के प्रकाश,  $\text{CO}_2$  और  $\text{H}_2\text{O}$  को पकड़ती है और इसे  $\text{CO}$ ,  $\text{CH}_4$  और  $\text{CH}_3\text{OH}$  जैसे व्यवहार्य ईंधन स्रोतों में परिवर्तित करती है। वर्तमान में, यह अवधारणा मौलिक अनुसंधान के दायरे में बनी हुई है, जिसमें फोटोकैटलिटिक  $\text{CO}_2$  कमी प्रतिक्रिया ( $\text{CO}_2\text{RR}$ ) को आगे बढ़ाने के लिए उत्प्रेरक डिजाइन इसका केंद्रीय फोकस है। हालाँकि, बलि अभिकर्मकों या बाहरी विद्युत पूर्वाग्रह की आवश्यकता से बचते हुए,  $\text{CO}_2$  के चयनात्मक फोटोरिडक्शन के लिए कुशल फोटोकैटलिस्ट को डिजाइन करना एक कठिन चुनौती बनी हुई है। यह मुख्य रूप से सीमित प्रकाश-संचयन क्षमता, उच्च थोक चार्ज पुनर्संयोजन और मौजूदा फोटोकैटलिस्ट की अपर्याप्त सतह-सक्रिय साइटों के कारण है।

यह थीसिस  $\text{CO}_2$  को हाइड्रोकार्बन और अल्कोहल में परिवर्तित करने के लिए धातु ऑक्साइड अर्धचालकों पर आधारित अत्यधिक कुशल दृश्य-प्रकाश-चालित फोटोकैटलिस्ट विकसित करने पर केंद्रित है। अध्याय 1 में,  $\text{CO}_2$  उपयोग और सौर ईंधन उत्पादन, साथ ही थीसिस उद्देश्यों और दायरे का परिचय देता है। अध्याय 2 फोटोकैटलिटिक  $\text{CO}_2$  कटौती प्रक्रियाओं की समझ प्रदान करता है और फोटोकैटलिटिक  $\text{CO}_2\text{RR}$  के प्रदर्शन को बढ़ाने के लिए धातु ऑक्साइड और पेरोव्स्काइट ऑक्साइड-आधारित फोटोकैटलिस्ट और इन सामग्रियों द्वारा अपनाई गई विभिन्न रणनीतियों की समीक्षा करता है। अध्याय 3 सामग्री संश्लेषण प्रक्रियाओं और प्रयोगात्मक प्रोटोकॉल का वर्णन करता है।

इस थीसिस के मुख्य अध्ययन और नवाचारों को लगातार तीन शोध अध्यायों में चित्रित किया गया है। अध्याय 4 में, मैंने एज-ट्रंकेटेड क्यूबिक  $\text{Cu}_2\text{O}$  के एक मॉडल फोटोकैटलिस्ट का उपयोग करके फोटोजेनरेटेड चार्ज कैरियर्स की गतिशीलता की जांच की, जिसमें एक्सपोज़्ड {110} और {100} पहलुओं के साथ, कम्प्यूटेशनल और प्रयोगात्मक दोनों दृष्टिकोणों को नियोजित किया गया। मैंने पाया कि किनारे से काटे गए क्यूबिक  $\text{Cu}_2\text{O}$  माइक्रोक्रिस्टल रोशनी पर एक बढ़ा हुआ चार्ज पृथक्करण दिखाते हैं, जो कि {110}/{100} पहलू जंक्शनों पर बैंड झुकने से प्रेरित अंतर्निहित संभावित अंतर के कारण होता है। जब मॉडल एज-ट्रंकेटेड क्यूबिक  $\text{Cu}_2\text{O}$  माइक्रोक्रिस्टल को संश्लेषित किया गया और फोटोकैटलिटिक  $\text{CO}_2\text{RR}$  के लिए परीक्षण किया गया, तो उन्होंने बेहतर  $\text{CH}_3\text{OH}$  उपज दिखाई, जो संदर्भ सरल क्यूबिक  $\text{Cu}_2\text{O}$  फोटोकैटलिस्ट से लगभग 5.5 गुना बेहतर थी। यह प्रयोग परिणाम मेरी कम्प्यूटेशनल भविष्यवाणी को मान्य करता है कि क्रिस्टल पहलू इंजीनियरिंग के माध्यम से फोटोकैटलिस्ट आकृति विज्ञान को नियंत्रित करने से दो अलग-अलग पहलुओं में फोटोजेनरेटेड इलेक्ट्रॉन-छेद जोड़े के पृथक्करण में सुधार करके समग्र  $\text{CO}_2\text{RR}$

गतिविधि बढ़ जाती है। हालाँकि, बड़े पैमाने पर किनारे-काटे गए क्यूबिक  $\text{Cu}_2\text{O}$  माइक्रोक्रीस्टल को संश्लेषित करने के लिए क्रिस्टल संरचनाओं के विकास को नियंत्रित करने में कठिनाई और  $\text{Cu}_2\text{O}$  की अंतर्निहित स्व-रेडॉक्स क्षमता फोटोकैटलिटिक  $\text{CO}_2\text{RR}$  में इसकी प्रयोज्यता पर बाधा उत्पन्न करती है।

अपने शोध के अध्याय 5 में, मैंने  $\text{CO}_2$  कटौती के लिए फोटोकैटलिस्ट के रूप में उपयोग करने के लिए अधिक स्थिर सामग्रियों की खोज की। विशेष रूप से, मैंने पेचिनी विधियों का उपयोग करके गा-डोप्ड  $\text{NiTiO}_3$  फोटोकैटलिस्ट को संश्लेषित किया और आरयू नैनोकणों के साथ उनकी सतहों को कार्यात्मक बनाया। मैंने पाया कि Ga को  $\text{NiTiO}_3$  में डोपिंग करने से इलेक्ट्रॉनों की प्रसार लंबाई को बढ़ाकर फोटोजेनरेटेड इलेक्ट्रॉन-होल जोड़े के जीवनकाल को बढ़ाने में मदद मिलती है। इसके अलावा, फोटोकैटलिस्ट पर आरयू कोकैटलिस्ट को लोड करने से धातु-अर्धचालक शोटकी जंक्शन बनाकर इलेक्ट्रॉन-छेद पृथक्करण बढ़ जाता है। फोटोकैटलिस्ट की दक्षता का परीक्षण करने के लिए, मैंने एक बैच फोटोरिएक्टर में 1 से 4.5 बार तक के विभिन्न दबावों के तहत  $\text{CO}_2$  फोटोरिडक्शन प्रतिक्रिया का संचालन किया। मैंने पाया कि 3.5 बार  $\text{CO}_2$  दबाव के तहत 0.1 M  $\text{NaHCO}_3$  जलीय घोल में निलंबित Ga-doped  $\text{NiTiO}_3$  फोटोकैटलिस्ट पर लोड किए गए 1.0 wt.% Ru की इष्टतम सांद्रता ने  $84.48 \mu\text{mol g}^{-1} \text{h}^{-1}$  की दर पर उच्चतम  $\text{CH}_3\text{OH}$  उपज प्राप्त की।  $21.35 \mu\text{mol g}^{-1} \text{h}^{-1}$  की दर से विकसित होते हुए,  $\text{CH}_4$  की एक छोटी मात्रा को एक साइड उत्पाद के रूप में भी उत्पादित किया गया था। यह बेहतर गतिविधि  $\text{NiTiO}_3$  पर Ga डोपिंग और Ru लोडिंग के सहक्रियात्मक संयोजन के कारण हासिल की गई, जिसने चार्ज ट्रांसफर को तेज किया और अधिक सतह-सक्रिय साइटें प्रदान कीं। इसके अतिरिक्त, दबावयुक्त सूक्ष्म वातावरण ने उत्प्रेरक सतह पर अधिक कुशल  $\text{CO}_2$  घुलनशीलता और अवशोषण की सुविधा प्रदान की। फिर भी, निलंबित कण फोटोकैटलिस्ट की ब्राउनियन गति ने निरंतर सूर्य के प्रकाश की कटाई को कठिन बना दिया, जिसके परिणामस्वरूप कम ऊर्जा दक्षता हुई। इसके अलावा, निलंबित फोटोकैटलिस्ट सामग्रियों के नैनोस्केल आकार ने प्रतिक्रिया के बाद पृथक्करण को चुनौतीपूर्ण बना दिया, जिससे उत्प्रेरक की पुनः प्रयोज्यता सीमित हो गई।

अध्याय 6 में, मैंने एक सबस्ट्रेट पर फोटोकैटलिस्ट सामग्री को स्थिर करके एक फोटोकैटलिस्ट शीट की इंजीनियरिंग के विचार का पता लगाया। मैंने एक सोने के नैनोलेयर इलेक्ट्रॉन मध्यस्थ के साथ,  $\text{CO}_2$  कटौती उत्प्रेरक के रूप में Cu-लोडेड Al-doped  $\text{SrTiO}_3$  और  $\text{H}_2\text{O}$  ऑक्सीकरण उत्प्रेरक के रूप में  $\text{CoO}_x\text{-WO}_3$  का उपयोग करके एक हेटरोस्ट्रक्चर फोटोकैटलिस्ट शीट को संश्लेषित किया। इस समग्र संरचना ने अप्रत्यक्ष जेड-स्कीम चार्ज ट्रांसफर तंत्र के माध्यम से कई फोटो-उत्तेजना और उत्कृष्ट चार्ज पृथक्करण दक्षता प्रदर्शित की। मैंने सौर सिम्युलेटर का उपयोग करके इनडोर प्रयोगों और प्राकृतिक सूर्य के प्रकाश के तहत बाहरी प्रयोगों दोनों में फोटोकैटलिस्ट शीट के  $\text{CO}_2$  कटौती प्रदर्शन का परीक्षण किया। मैंने

देखा कि यह फोटोकैटलिस्ट शीट मुख्य रूप से CO<sub>2</sub> को थोड़े से CO के अंश के साथ CH<sub>4</sub> और CH<sub>3</sub>OH में बदल देती है। इनडोर प्रयोग के दौरान, इस प्रणाली द्वारा प्राप्त कुल कार्बन उत्पाद निर्माण दर 3.237  $\mu\text{mol cm}^{-2} \text{ h}^{-1}$  थी, जबकि आउटडोर के दौरान प्रयोग, यह 0.384  $\mu\text{mol cm}^{-2} \text{ h}^{-1}$  तक पहुंच गया। मैंने लगातार पांच चक्रों तक फोटोकैटलिस्ट शीट का भी परीक्षण किया और इसने प्रदर्शन में न्यूनतम बदलाव के साथ उत्कृष्ट प्रदर्शन दिखाया, जिससे फोटोकैटलिस्ट शीट की मजबूती और पुनः प्रयोज्यता प्रदर्शित हुई। फोटोकैटलिस्ट शीट की उच्च गतिविधि और स्थिरता के पीछे मुख्य कारण नवीन निर्माण विधि और अप्रत्यक्ष जेड-स्कीम हेटरोस्ट्रक्चर के माध्यम से बेहतर चार्ज पृथक्करण थे।

निष्कर्ष में, यह शोध सौर ऊर्जा के व्यापक स्पेक्ट्रम का उपयोग करने, फोटोजेनरेटेड चार्ज के पृथक्करण को बढ़ाने और CO<sub>2</sub> कटौती साइटों को अनुकूलित करने में सक्षम अत्यधिक कुशल फोटोकैटलिस्ट सामग्रियों को विकसित करने के लिए विभिन्न प्रकार की रणनीतियों की पेशकश करता है। ये निष्कर्ष टिकाऊ और स्केलेबल फोटोकैटलिटिक CO<sub>2</sub> कमी प्रणालियों की प्रगति को आगे बढ़ाने का वादा करते हैं। इस अध्ययन से प्राप्त अंतर्दृष्टि का लाभ उठाकर, भविष्य के प्रयास CO<sub>2</sub> कटौती और सौर ईंधन उत्पादन के लिए अधिक टिकाऊ और प्रभावी दृष्टिकोण को साकार करने की दिशा में प्रयास कर सकते हैं।

## **Declaration by Author**

This thesis is composed of my original work and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution of others to jointly authored works that I have included in my thesis.

I have clearly stated the contributions of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support, and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

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Aloka Kumar Sahu

Signature

Aloka Kumar Sahu

Date: 24/07/2024

## Publications

### Publications included in this thesis

1. **Sahu, A. K.**; Pokhriyal, M.; Zhao, X. S.; Upadhyayula, S.; Modulating photogenerated charge carrier dynamics among anisotropic crystal facets of Cu<sub>2</sub>O for enhanced CO<sub>2</sub> photoreduction, *J. Phys. Chem. C* **2022**, 126, 13094-13104. (Incorporated in Chapters 3 and 4)

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Xiu Song Zhao	Concept and design (5%) Analysis and interpretation (10%) Drafting and production (15%)
Sreedevi Upadhyayula	Concept and design (10%) Analysis and interpretation (10%) Drafting and production (10%)

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2. Banerjee, D.; **Sahu, A. K.**; Upadhyayula, S.; Clegg J. K.; Recent advances in 2-methylfuran production via catalytic transfer hydrogenation of biomass-derived furfural, *Chem. Eng. J.* **2024**, 493, 152552.
3. Banerjee, D.; Yadav, S.; **Sahu, A. K.**; Upadhyayula, S.; Clegg J. K.; Transfer hydrogenation of furfural to 2-methylfuran over a Cu-BTC-derived catalyst with isopropanol as a hydrogen donor, *Energy & Fuels* **2024**, 38, 11, 9814–9826.

## Conferences

1. Photo- and electrocatalytic CO<sub>2</sub> reduction based on Ga-doped NiTiO<sub>3</sub> perovskite nanoparticles; orally presented at **International Symposium on Green Transformation of Carbon Dioxide-2023**, Brisbane, Queensland, Australia.
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3. Modulating charge carrier dynamics among anisotropic crystal facets of Cu<sub>2</sub>O for enhanced CO<sub>2</sub> photoreduction; poster presented at **International Conference on Nanomaterials for Electro-Catalysis Technology-2023**, Indian Institute of Technology Delhi, New Delhi, India.
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## **List of Abbreviations**

CO <sub>2</sub> RR	–	CO <sub>2</sub> RR – CO <sub>2</sub> reduction reaction
WOR	–	Water Oxidation reaction
VLD	–	Visible-light-driven
CB	–	Conduction band
VB	–	Valance band
CBM	–	Conduction band minima
VBM	–	Valance band maxima
XRD	–	X-ray diffraction
XPS	–	X-ray photoelectron spectroscopy
TEM	–	Transmission electron microscopy
FESEM	–	Field-emission scanning microscopy
EDS	–	Energy dispersive X-ray spectroscopy
SSPL	–	Steady-state photoluminescence
TRPL	–	Time-resolved photoluminescence
EPR	–	Electron paramagnetic resonance spectroscopy
FTIR	–	Fourier-transform infrared spectroscopy
EIS	–	Electrochemical impedance spectroscopy
ESR	–	Electrochemical spin resonance
KPFM	–	Kelvin probe force microscopy
SPS	–	Surface photovoltage spectroscopy
TAS	–	Transient absorption spectroscopy
O <sub>v</sub>	–	Oxygen vacancy
O <sub>vs</sub>	–	Surface oxygen vacancy
NTO	–	NiTiO <sub>3</sub>
GNTO	–	Ga-doped NiTiO <sub>3</sub>
Ru-GNTO	–	Ru-loaded Ga-doped NiTiO <sub>3</sub>
STO	–	SrTiO <sub>3</sub>
ASTO	–	Al-doped SrTiO <sub>3</sub>
Cu-ASTO	–	Cu-loaded Al-doped SrTiO <sub>3</sub>
CoO <sub>x</sub> -WO <sub>3</sub>	–	CoO <sub>x</sub> -loaded WO <sub>3</sub>