

**STUDY THE ROLE OF OXYGEN VACANCIES IN
METAL OXIDE NANOSTRUCTURES TOWARDS CO₂
REDUCTION**

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**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

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Department of Physics

Submitted

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



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
DECEMBER 2021**

CERTIFICATE

This is to certify that the work incorporated in this Ph.D. thesis entitled “*Study the role of oxygen vacancies in metal oxide nanostructures towards CO₂ reduction*” by Mrs. Pinki Devi to the Indian Institute of Technology Delhi in fulfillment of the requirements for the award of the degree of **Doctor of Philosophy**, embodies original research work under my supervision. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma.

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ABSTRACT

Metal oxide nanostructures are the most versatile groups of a semiconductor due to their extensive structural, physical, and chemical properties. The unique and tunable properties of these metal oxides such as optical, optoelectronic, magnetic, electrical, mechanical, thermal, catalytic, and photochemical, etc. made themselves excellent candidates for various high-level technological applications. The various properties of metal oxides can be varied by varying their growth method or doping etc. Metal oxides can be used as a catalyst due to their ability to bind and activate CO₂ which largely depends on their basicity and reducibility. In our research work, to improve the conversion efficiency of CO₂ into fuel, the nanocomposite based on i) indium oxide, and ii) copper oxide has been used. These materials are chosen because indium oxide nanostructures show beneficial interaction with the supporting material, provide large surface area, and suppress the hydrogen evolution reaction during the CO₂ reduction reaction. Additionally, the presence of point defects in metal oxides is one of the promising factors that influence the various properties such as CO₂ reduction, electrocatalysis, photocatalysis, dye degradation, and gas sensing, etc

Utilizing CO₂ through electrochemical reduction to produce valuable hydrocarbons is one of the promising paths for sustainable development. But the selection of an energy-efficient and stable catalyst for electrochemical reduction of CO₂ into CO, selectively, is one of the major challenges. We have synthesized CuO/In₂O₃ nanocomposites by modified sol-gel method, which acts as the highly active, stable, and cost-effective catalyst for ERC of CO₂. We established an approach for enhancement of CO₂ reduction into CO by inducing the different concentration of oxygen vacancies (V_o) in the CuO/In₂O₃ nanocomposites.

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We have controlled the concentration of V_o by changing the calcination environment from air to argon during the synthesis of $\text{CuO}/\text{In}_2\text{O}_3$ nanocomposites. The photoluminescence, X-ray photoelectron spectroscopy and electron paramagnetic resonance measurements demonstrate that $\text{CuO}/\text{In}_2\text{O}_3$ nanocomposites prepared in an argon environment exhibit higher concentrations of V_o defects as compared to samples prepared in the air environment. For V_o -rich $\text{CuO}/\text{In}_2\text{O}_3$ nanocomposites, the faradaic efficiency of CO reaches up to 85% in the potential range of -0.6 to -0.9V vs reverse hydrogen electrode (RHE) and exhibiting low hydrogen evolution reaction, while V_o -poor $\text{CuO}/\text{In}_2\text{O}_3$ nanocomposite results CO faradaic efficiency $\sim 63\%$ at the same potential. This is because V_o provides the active sites for CO_2 adsorption. The hydrogen evolution reaction have been suppressed due to the presence of indium in the nanocomposite because high potential is required for adsorption of hydrogen on indium. Combining the electrochemical measurement with the physical characterizations, it has been observed that enhancement of CO_2 reduction to CO is mainly due to higher V_o defect concentration in $\text{CuO}/\text{In}_2\text{O}_3$ nanocomposites. The density functional theory (DFT) calculations provide a plausible mechanism and depict the role of increased V_o defect concentration in the nanocomposites.

Although many electrocatalysts with very high faradaic efficiency have been developed, the deactivation of the electrocatalysts due to aging remains an issue. We have provided a facile approach for the regeneration of aged $\text{CuO}-\text{Cu}_2\text{O}/\text{In}_2\text{O}_3$ nanocomposite catalysts as well as suggest a possible mechanism for the regeneration of activity of aged catalysts. For the as-grown $\text{CuO}-\text{Cu}_2\text{O}/\text{In}_2\text{O}_3$ nanocomposite catalyst, the CO faradaic efficiency (FE_{CO}) was obtained about 88%, whereas, for the 12 months aged nanocomposite catalyst, the average CO faradaic

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efficiency value gets reduced to 39.6%. The photoluminescence, X-ray photoelectron spectroscopy, and electrochemical reduction measurements suggest that increase in oxygen vacancy (V_o) concentration upon aging results in the reduction of faradaic efficiency of CO. Considering this issue, we have demonstrated that the activity of the aged nanocomposite towards electrochemical reduction of CO_2 can be regenerated by ultra-violet (UV) light treatment. For the of UV treated nanocomposite, a considerable increase in faradaic efficiency of CO (~85.6%) closer to the CO faradaic efficiency value of the as-grown catalyst has been obtained. We have performed first-principles-based calculations under the framework of density functional theory to understand the role of V_o on the reaction barriers of electrochemical reduction of CO_2 under UV light treatment. From this state-of-the-art combined experimental and theoretical investigation, we have been concluded that the regeneration of the active sites in the aged electrocatalysts by UV light treatment helps in regaining the catalytic activity towards electrochemical reduction of CO_2 .

Maintaining the atmospheric CO_2 level by the production of valuable solar fuel like methane is one of the major challenges for humankind. Photocatalytic reduction of CO_2 is a vital approach for its conversion into a valuable chemical product. We have prepared In_2O_3 -rGO nanocomposites with varying reduced graphene oxide (rGO) content for the investigation of photocatalytic reduction of CO_2 . The product obtained by photocatalytic reduction of CO_2 by visible light source has been quantified by the gas chromatography measurements. The catalytic activity of In_2O_3 -rGO nanocomposites towards the photocatalytic reduction process of CO_2 to CH_4 gets enhanced as compared to In_2O_3 nanostructures due to the enhancement in lifetime of

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photogenerated electron-hole pairs and improvement of charge transfer from In_2O_3 to rGO. We have obtained the maximum yield of methane of $953.72 \mu\text{mol.g}^{-1}$ by the photocatalytic reduction of CO_2 on In_2O_3 -2wt%rGO nanocomposite. The highest catalytic performance of In_2O_3 -2wt%rGO nanocomposite may be due to improvement in its optical properties such as optical band gap and oxygen vacancies (V_o) defects.

Indium oxide is used in many photochemical processes such as wastewater remediation, dye degradation, and water splitting, etc. However, their large band gaps limit their catalytic activity. There are numerous methods such as chemical coupling, by nanocomposites formation, heterostructures design, doping, and inducing surface disorder are developed to improve the photocatalytic activity of In_2O_3 nanostructures. But these methods have various limitations such as complex and expensive operations and low photocatalytic activity under visible light illumination. In the present work, we have developed In_2O_3 (IO) nanostructures with different oxygen vacancies concentrations by controlling the calcination temperatures during synthesis. The photoluminescence measurements have been performed to analyze the oxygen vacancies defects concentration in IO nanostructures calcined at 400°C and 700°C temperatures. The photocatalytic activity of both the catalysts has been tested by the degradation of methylene blue (MB) dye under ultra-violet (UV) light. The rate of degradation of MB dye has been observed to be faster in the case of IO_700 as compared to IO_400 nanostructures due to the presence of higher oxygen vacancies defects in IO_700 photocatalyst.

Further, the role of oxygen vacancies in In_2O_3 nanostructures has been studied for exploring the gas sensing properties. Due to the physical and chemical properties, the metal oxides are an

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attractive choice in the gas sensor industry. We have developed a highly sensitive colorimetric gas sensor for H_2S gas based on indium oxide (In_2O_3) nanostructures. The In_2O_3 nanostructures have been prepared by the modified sol-gel method. The optical darkness ratio (ODR) of H_2S gas-exposed In_2O_3 nanostructured samples has been determined by using a smartphone-based application. The change in color of H_2S exposed In_2O_3 nanostructured films has been found to be due to sulfurization of top of In_2O_3 nanostructured film and formation of In_2S_3 layer. The oxygen vacancies (V_o) defects have been observed to be the promising factor that boosts the formation of the In_2S_3 layer. The photoluminescence and X-ray photoelectron spectroscopy measurements revealed that the V_o defects gets decreased when the In_2O_3 nanostructured film was exposed to H_2S gas for a longer time. At room temperature, In_2O_3 nanostructured film has exhibited a lower detection limit of 10 ppm in 30 seconds for H_2S gas. The V_o defects in the In_2O_3 nanostructured film enhance the electron-accepting capabilities of H_2S , which assist to boost the the H_2S gas sensing.

सार

धातु ऑक्साइड नैनोस्ट्रक्चर उनके व्यापक संरचनात्मक, भौतिक और रासायनिक गुणों के कारण अर्धचालक के सबसे बहुमुखी समूह हैं। प्रकाश संबंधी, प्रकाश इलेक्ट्रॉनिकी, चुंबकीय, विद्युतीय, यांत्रिक, ऊष्मीय, उत्प्रेरक संबंधी और प्रकाश रासायनिक आदि जैसे इन धातु ऑक्साइड के अद्वितीय और ढालने योग्य गुणों ने खुद को विभिन्न उच्च-स्तरीय तकनीकी अनुप्रयोगों के लिए उत्कृष्ट उम्मीदवार बना दिया। धातु आक्साइड के विभिन्न गुणों को उनके बनाने की विधि या अपमिश्रण आदि को अलग करके भिन्न किया जा सकता है। धातु आक्साइड को उत्प्रेरक के रूप में इस्तेमाल किया जा सकता है क्योंकि CO_2 को बांधने और सक्रिय करने की उनकी क्षमता काफी हद तक उनकी मौलिकता और कम करने की क्षमता पर निर्भर करती है। हमारे शोध कार्य में, ईंधन में CO_2 की रूपांतरण दक्षता में सुधार करने के लिए, i) इंडियम ऑक्साइड, और ii) कॉपर ऑक्साइड पर आधारित नैनोकम्पोजिट्स का उपयोग किया गया है। इन सामग्रियों को इसलिए चुना गया है क्योंकि इंडियम ऑक्साइड नैनोस्ट्रक्चर सहायक पदार्थ के साथ लाभप्रद पारस्परिक क्रिया दिखाते हैं, बड़ा सतह क्षेत्र प्रदान करते हैं, और CO_2 कमी प्रतिक्रिया के दौरान हाइड्रोजन विकास प्रतिक्रिया को दबाते हैं। इसके अतिरिक्त, धातु आक्साइड में बिंदु दोषों की उपस्थिति उन आशाजनक कारकों में से एक है जो विभिन्न गुणों जैसे कि CO_2 की कमी, विद्युत उत्प्रेरण, प्रकाश उत्प्रेरण, डार्क क्षरण और गैस संवेदन आदि को प्रभावित करते हैं।

मूल्यवान हाइड्रोकार्बन का उत्पादन करने के लिए विद्युत रासायनिक कमी के माध्यम से CO_2 का उपयोग सतत विकास के लिए आशाजनक रास्तों में से एक है। लेकिन विद्युत रासायनिक कमी के माध्यम से CO_2 के CO में चुनिंदा रूप से बदलने के लिए ऊर्जा-कुशल और स्थिर उत्प्रेरक का चयन, प्रमुख चुनौतियों में से एक है। हमने संशोधित सोल-जेल विधि द्वारा $\text{CuO}/\text{In}_2\text{O}_3$ नैनोकम्पोजिट्स को संश्लेषित किया है, जो CO_2 के विद्युत रासायनिक कमी के लिए अत्यधिक सक्रिय, स्थिर और लागत प्रभावी उत्प्रेरक के रूप में कार्य करता है। हमने $\text{CuO}/\text{In}_2\text{O}_3$ नैनोकम्पोजिट्स में ऑक्सीजन रिक्तियों (V_o) की विभिन्न सांद्रता को प्रेरित करके CO में CO_2 की कमी को बढ़ाने के लिए एक दृष्टिकोण स्थापित किया है। हमने $\text{CuO}/\text{In}_2\text{O}_3$ नैनोकम्पोजिट्स के संश्लेषण के दौरान हवा से आर्गन में निस्तापन वातावरण को बदलकर V_o की सांद्रता को नियंत्रित किया है। फोटोल्यूमिनेसेंस, एक्स - रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी, इलेक्ट्रॉन

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अनुचुंबकीय अनुनाद माप प्रदर्शित करते हैं कि आर्गन वातावरण में तैयार $\text{CuO}/\text{In}_2\text{O}_3$ नैनोकंपोजिट, वायु वातावरण में तैयार किए गए नमूनों की तुलना में V_o दोषों की उच्च सांद्रता प्रदर्शित करते हैं। V_o -अमीर $\text{CuO}/\text{In}_2\text{O}_3$ नैनोकम्पोजिट्स के लिए, CO की फैराडिक दक्षता -0.6 से -0.9V बनाम रिवर्स हाइड्रोजन इलेक्ट्रोड (RHE) की संभावित सीमा में 85% तक पहुंचती है और कम हाइड्रोजन विकास प्रतिक्रिया प्रदर्शित करती है। जबकि V_o -खराब $\text{CuO}/\text{In}_2\text{O}_3$ नैनोकम्पोजिट का परिणाम CO फैराडिक दक्षता $\sim 63\%$ समान क्षमता पर होता है। ऐसा इसलिए है क्योंकि V_o , CO_2 सोखने के लिए सक्रिय साइट प्रदान करता है। नैनोकम्पोजिट में इंडियम की उपस्थिति के कारण हाइड्रोजन विकास प्रतिक्रिया को दबा दिया गया है क्योंकि इंडियम पर हाइड्रोजन के सोखने के लिए उच्च क्षमता की आवश्यकता होती है। भौतिक लक्षणों के साथ विद्युत रासायनिक माप को मिलाकर, यह देखा गया है कि CO_2 की कमी को CO में बढ़ाना मुख्य रूप से $\text{CuO}/\text{In}_2\text{O}_3$ नैनोकंपोजिट्स में उच्च V_o दोष एकाग्रता के कारण है। घनत्व कार्यात्मक सिद्धांत (डीएफटी) गणना एक प्रशंसनीय तंत्र प्रदान करती है और नैनोकम्पोजिट्स में बढ़े हुए V_o दोष एकाग्रता की भूमिका को दर्शाती है।

हालांकि बहुत अधिक फैराडिक दक्षता वाले कई इलेक्ट्रोकेटलिस्ट विकसित किए गए हैं, उम्र बढ़ने के कारण इलेक्ट्रोकेटलिस्ट्स का निष्क्रिय होना एक मुद्दा बना हुआ है। हमने वृद्ध $\text{CuO}-\text{Cu}_2\text{O}/\text{In}_2\text{O}_3$ नैनोकम्पोजिट उत्प्रेरकों के पुनर्जनन के लिए एक आसान दृष्टिकोण प्रदान किया है और साथ ही वृद्ध उत्प्रेरकों की गतिविधि के पुनर्जनन के लिए एक संभावित तंत्र का सुझाव दिया है। संश्लेषित $\text{CuO}-\text{Cu}_2\text{O}/\text{In}_2\text{O}_3$ नैनोकम्पोजिट उत्प्रेरक के लिए, CO फैराडिक दक्षता को लगभग 88% प्राप्त किया गया था, जबकि, 12 महीने की उम्र के नैनोकम्पोजिट उत्प्रेरक के लिए, औसत CO फैराडिक दक्षता का मान 39.6% तक कम हो जाता है। फोटोल्यूमिनेसेंस, एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी, और इलेक्ट्रोकेमिकल कमी माप से पता चलता है कि उम्र बढ़ने पर ऑक्सीजन रिक्ति (V_o) एकाग्रता में वृद्धि के कारण CO की फैराडिक दक्षता में कमी आती है। इस मुद्दे को ध्यान में रखते हुए, हमने दिखाया है कि CO_2 की विद्युत रासायनिक कमी की दिशा में वृद्ध नैनोकम्पोजिट की गतिविधि को अल्ट्रा-वायलेट (यूवी) प्रकाश उपचार द्वारा पुनर्जीवित किया जा सकता है। यूवी उपचारित नैनोकम्पोजिट के लिए, CO की फैराडिक दक्षता ($\sim 85.6\%$) में काफी वृद्धि हुई है, जो कि संश्लेषित उत्प्रेरक के CO फैराडिक दक्षता मूल्य के करीब है। हमने

सार

यूवी प्रकाश उपचार के तहत CO_2 की विद्युत रासायनिक कमी की प्रतिक्रिया बाधाओं पर V_o की भूमिका को समझने के लिए घनत्व कार्यात्मक सिद्धांत के ढांचे के तहत प्रथम-सिद्धांत-आधारित गणना की है। इस अत्याधुनिक संयुक्त प्रयोगात्मक और सैद्धांतिक जांच से, हम इस निष्कर्ष पर पहुंचे हैं कि यूवी प्रकाश उपचार द्वारा वृद्ध इलेक्ट्रोकेटलिस्ट्स में सक्रिय जगहों का पुनर्जनन CO_2 की विद्युत रासायनिक कमी की दिशा में उत्प्रेरक गतिविधि को पुनः प्राप्त करने में मदद करता है।

मीथेन जैसे मूल्यवान सौर ईंधन के उत्पादन द्वारा वायुमंडलीय CO_2 स्तर को बनाए रखना मानव जाति के लिए प्रमुख चुनौतियों में से एक है। एक मूल्यवान रासायनिक उत्पाद में रूपांतरण के लिए CO_2 की फोटोकैटलिटिक कमी एक महत्वपूर्ण दृष्टिकोण है। हमने CO_2 की फोटोकैटलिटिक कमी की जांच के लिए अलग-अलग कम ग्राफीन ऑक्साइड (rGO) सामग्री के साथ In_2O_3 -rGO नैनोकम्पोजिट तैयार किए हैं। दृश्य प्रकाश स्रोत द्वारा CO_2 की फोटोकैटलिटिक कमी से प्राप्त उत्पाद को गैस क्रोमैटोग्राफी माप द्वारा निर्धारित किया गया है। CO_2 से CH_4 की फोटोकैटलिटिक कमी प्रक्रिया की दिशा में In_2O_3 -rGO नैनोकम्पोजिट्स की उत्प्रेरक गतिविधि फोटोजेनरेटेड इलेक्ट्रॉन-होल जोड़े के जीवनकाल में वृद्धि और In_2O_3 से rGO में चार्ज ट्रांसफर में सुधार के कारण In_2O_3 नैनोस्ट्रक्चर की तुलना में बढ़ जाती है। हमने In_2O_3 -2wt% rGO नैनोकम्पोजिट पर फोटोकैटलिटिक कमी द्वारा $953.72 \mu\text{mol.g}^{-1}$ की मीथेन की अधिकतम मात्रा प्राप्त की है। In_2O_3 -2wt% rGO नैनोकम्पोजिट का उच्चतम उत्प्रेरक प्रदर्शन इसके ऑप्टिकल गुणों जैसे ऑप्टिकल ऊर्जा अंतराल और ऑक्सीजन रिक्तियों (V_o) दोषों में सुधार के कारण हो सकता है।

इंडियम ऑक्साइड का उपयोग कई प्रकाश रासायनिक प्रक्रियाओं जैसे अपशिष्ट जल उपचार, ड्राई क्षरण और पानी के विभाजन आदि में किया जाता है। हालांकि, उनके बड़े ऊर्जा अंतराल उनकी उत्प्रेरक गतिविधि को सीमित करते हैं। In_2O_3 नैनोस्ट्रक्चर की फोटोकैटलिटिक गतिविधि में सुधार के लिए नैनोकम्पोजिट्स गठन, हेटरोस्ट्रक्चर डिजाइन, डोपिंग और उत्प्रेरण सतह विकार जैसे कई तरीके विकसित किए गए हैं। लेकिन इन विधियों की विभिन्न सीमाएँ हैं जैसे कि जटिल और महंगे संचालन और दृश्य प्रकाश रोशनी के तहत कम फोटोकैटलिटिक गतिविधि। वर्तमान कार्य में, हमने संश्लेषण के दौरान कैल्सीनेशन तापमान को नियंत्रित करके विभिन्न ऑक्सीजन रिक्तियों सांद्रता के साथ In_2O_3 (IO) नैनोस्ट्रक्चर विकसित किए हैं।

सार

400 डिग्री सेल्सियस और 700 डिग्री सेल्सियस तापमान पर कैल्क्लाइंड किए गए In_2O_3 नैनोस्ट्रक्चर में ऑक्सीजन रिक्तियों दोष एकाग्रता का विश्लेषण करने के लिए फोटोल्यूमिनेशन माप का प्रदर्शन किया गया है। अल्ट्रा-वायलेट (यूवी) प्रकाश के तहत मेथिलीन ब्लू (एमबी) डाई के क्षरण द्वारा दोनों उत्प्रेरकों की फोटोकैटलिटिक गतिविधि का परीक्षण किया गया है। IO_{700} फोटोकैटलिस्ट में उच्च ऑक्सीजन रिक्तियों दोषों की उपस्थिति के कारण, IO_{400} नैनोस्ट्रक्चर की तुलना में IO_{700} के मामले में MB डाई के क्षरण की दर तेज देखी गई है।

इसके अलावा, गैस संवेदन गुणों की खोज के लिए In_2O_3 नैनोस्ट्रक्चर में ऑक्सीजन रिक्तियों की भूमिका का अध्ययन किया गया है। भौतिक और रासायनिक गुणों के कारण, गैस सेंसर उद्योग में धातु आक्साइड एक आकर्षक विकल्प हैं। हमने इंडियम ऑक्साइड नैनोस्ट्रक्चर पर आधारित H_2S गैस के लिए एक अत्यधिक संवेदनशील वर्णमिति गैस सेंसर विकसित किया है। In_2O_3 नैनोस्ट्रक्चर, संशोधित सोल-जेल विधि द्वारा तैयार किए गए हैं। H_2S गैस-उजागर In_2O_3 नैनोस्ट्रक्चर नमूनों का ऑप्टिकल डार्क अनुपात (ODR), स्मार्टफोन-आधारित एप्लिकेशन का उपयोग करके निर्धारित किया गया है। H_2S उजागर In_2O_3 नैनोसंरचित फिल्मों के रंग में परिवर्तन, In_2O_3 नैनोसंरचित फिल्म के शीर्ष के सल्फराइजेशन और In_2S_3 परत के गठन के कारण पाया गया है। ऑक्सीजन रिक्तियों (V_o) दोषों को एक आशाजनक कारक के रूप में देखा गया है जो In_2S_3 परत के गठन को बढ़ावा देता है। फोटोल्यूमिनेसेंस और एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी मापों से पता चला है कि जब In_2O_3 नैनोस्ट्रक्चर फिल्म को लंबे समय तक H_2S गैस के संपर्क में रखा जाता है, तो V_o दोष कम हो जाते हैं। कमरे के तापमान पर, In_2O_3 नैनोस्ट्रक्चर्ड फिल्म ने H_2S गैस के लिए 30 सेकंड में 10 पीपीएम की निचली पहचान सीमा प्रदर्शित की है। In_2O_3 नैनोस्ट्रक्चर्ड फिल्म में V_o दोष H_2S की इलेक्ट्रॉन-स्वीकार्य क्षमताओं को बढ़ाता है, जो H_2S गैस सेंसिंग को बढ़ावा देने में सहायता करता है।

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Abbreviations

XRD	X-ray diffraction
SEM	Scanning electron microscope
FESEM	Field emission scanning electron microscope
TEM	Tunneling electron microscope
HRTEM	High-resolution tunneling electron microscope
UV-Vis	Ultraviolet-Visible Spectroscopy
PL	Photoluminescence
XPS	X-ray photoelectron spectroscopy
EPR	Electron paramagnetic resonance
GC	Gas chromatography
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
BET	Brunauer–Emmett–Teller
DFT	Density functional theory
HPLC	High-performance liquid chromatography
ERC	Electrochemical reduction of CO ₂
V _o	Oxygen vacancy
V _{Cu}	Copper vacancy