

Optimizing CuSe Thin Film Morphology and Performance in Water Splitting Applications Using Chemical Vapor Deposition Techniques

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ABSTRACT

The global quest for sustainable and clean energy has heightened research efforts in photoelectrochemical (PEC) water splitting for hydrogen production. Among semiconductor materials, copper selenide (CuSe) has emerged as a promising photocathode candidate due to its narrow direct bandgap (1.5–1.7 eV), high photoconductivity, and composition that is both earth-abundant and non-toxic. The efficiency of CuSe in PEC systems is significantly affected by its thin film morphology, crystal quality, and interface properties, which are particularly sensitive to synthesis routes and growth parameters. Chemical vapor deposition (CVD) provides distinct advantages, including atomic-level control over film thickness, stoichiometry, and crystalline orientation, rendering it an optimal method for engineering CuSe thin films with superior optoelectronic properties.

This review systematically examines recent developments (2020–2025) in the synthesis, morphological tuning, and performance enhancement of CuSe thin films for water splitting applications, with an emphasis on CVD techniques. This paper initially delineates the essential physical and chemical properties of CuSe that support its photocatalytic behavior. This evaluation examines different deposition methods, highlighting the mechanistic and structural benefits of CVD in comparison to solution-based techniques. A review of key literature highlights the impact of various CVD parameters, specifically precursor type, deposition temperature, and ambient pressure, on the nucleation, growth, and final architecture of CuSe thin films.

The relationship between morphology and PEC performance is critically examined, focusing on the impact of nanostructured features such as nanorods, porous layers, and heterojunction interfaces on charge transport and light absorption. The discussion encompasses characterization techniques, including XRD, UV-Vis spectroscopy, PL, and EIS, focusing on their relevance to material quality and catalytic activity. The review identifies significant challenges, including surface oxidation, carrier

recombination, and the absence of scalable, high-purity CVD processes for CuSe. Future directions include the integration synthesis, hybrid tandem systems, and scalable reactor designs. This review consolidates and analyzes current findings to establish a research roadmap for the development of CuSe-based photoelectrodes in next-generation hydrogen fuel technologies.

Keywords: Copper Selenide (CuSe), Chemical Vapor Deposition (CVD), Thin Films, Water Splitting, Photo electrochemistry, Hydrogen Production.

Introduction

Background and Motivation

The global community faces significant challenges related to fossil fuel depletion and environmental degradation, making the pursuit of renewable energy technologies increasingly urgent. Hydrogen is recognized as a clean fuel with high energy density, serving as a fundamental element for the future energy economy. Photoelectrochemical (PEC) water splitting represents a promising approach for sustainable hydrogen production, as it directly converts solar energy into chemical energy through the dissociation of water molecules into hydrogen and oxygen. In contrast to traditional hydrogen production methods, such as steam reforming or coal gasification, PEC water splitting is an environmentally friendly process that can utilize sunlight, a plentiful and renewable energy source.

The efficiency and scalability of PEC systems are significantly influenced by the characteristics of the semiconducting materials employed as photoelectrodes. Materials should demonstrate an appropriate bandgap for visible light absorption, align effectively with water redox potentials, possess high charge carrier mobility, exhibit significant chemical stability, and ideally, be abundant on Earth and low in toxicity. Identifying materials that meet all these criteria remains a considerable challenge in the field.

CuSe as a Promising Photocathode Material

Copper-based chalcogenides, particularly copper selenide (CuSe), have been identified as promising candidates for photocathodic hydrogen evolution in the context of PEC applications. CuSe exhibits multiple advantageous properties, including:

A direct bandgap of approximately 1.5 to 1.7 eV is within the optimal range for solar absorption.

P-type semiconducting behavior due to intrinsic copper vacancies, which promotes efficient hole transport.

Valence and conduction band positions that straddle the hydrogen evolution potential, making it thermodynamically favorable for water reduction.

High optical absorption coefficients and relatively good electrical conductivity

Elemental abundance and low toxicity, offering an environmentally friendly and cost-effective alternative to rare or hazardous materials

The material has extensive structural diversity and unique optoelectronic capabilities in its many stoichiometric forms (CuSe, Cu₂Se, and CuSe₂). Improved photocatalytic performance is now possible due to recent developments in heterojunction

engineering (e.g., ZnSe/CuSe, Au@Cu₂Se) and doping (e.g., sulfur, tellurium).

The Role of Morphology in PEC Performance

Although CuSe has advantageous intrinsic properties, the thin film morphology of CuSe-based photoelectrodes has a significant impact on their actual performance. Important PEC parameters, such as the following, can be greatly impacted by variables like surface roughness, grain size, crystallographic orientation, porosity, and dimensionality (nanorods, sheets, etc.):

Efficiency of light absorption

Diffusion and separation of charge carriers

Area of catalysis

Contact between the electrolytes and the interfacial

PEC performance is lowered by poorly managed film morphology, which frequently leads to excessive surface recombination, poor charge mobility, and structural instability. For CuSe photocathodes to be optimized, exact morphological control during film deposition is essential.

Why Chemical Vapor Deposition (CVD)?

CuSe thin films have been created using a variety of deposition methods, such as hydrothermal synthesis, sol-gel spin coating, chemical bath deposition (CBD), and electrodeposition. Despite their affordability and scalability, these solution-based methods frequently have drawbacks like uncontrolled stoichiometry, non-uniform thickness, poor substrate adhesion, and poor film crystallinity.

Chemical Vapor Deposition (CVD), on the other hand, provides a strong, adjustable platform for the deposition of superior, homogeneous, and crystalline thin films. Variants like

CVD at Atmospheric Pressure (APCVD)

CVD Assisted by Aerosols (AACVD)

MOCVD, or metal-organic CVD

Enable exact control over growth parameters like substrate type, temperature, ambient pressure, and precursor flow rate. Grain growth, final film morphology, and nucleation kinetics are all directly impacted by these factors. Additionally, CVD methods can be used for doping, multilayer stacking, and large-area fabrication all of which are necessary for the industrial translation of PEC devices.

For CuSe, CVD is particularly useful in creating films with regulated stoichiometry and phase purity, which are essential for obtaining steady PEC performance in electrolyte and lighting conditions. Although direct CVD of CuSe is still in its infancy when compared to oxide systems (such as BiVO₄ and Fe₂O₃), recent research has shown encouraging routes through vapor-phase reaction control and precursor design.

Scope and Structure of This Review

This review attempts to give a thorough and in-depth analysis of recent advancements (2020–2025) in the synthesis and morphological optimization of CuSe thin films using CVD techniques, given the growing interest in CuSe as a visible-light-responsive photocatalyst and the critical role that film morphology plays in determining performance.

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

The basic material characteristics of CuSe and how they relate to PEC water splitting will be covered first in the review. Next, it will contrast new CVD techniques with traditional solution-based deposition techniques, emphasizing how various synthesis pathways affect film morphology and photocatalytic activity. The paper's main body will examine important works from the previous five years, with an emphasis on how CVD parameters affect:

The orientation and structure of the film

Properties of charge transport

Recombination of carriers and absorption of light

Total efficiency of hydrogen evolution

Furthermore, pertinent characterization methods for assessing the structural, optical, and electronic characteristics of CuSe films will be presented in this review. Lastly, it will list current issues like recombination losses, interfacial stability, and scalability, and suggest future research avenues like tandem PEC cell integration, CVD optimization, and flexible device architectures.

Literature Review

Konar, Singh, & Telkhozhayeva (2024) studied non-stoichiometric $\beta\text{-Cu}_{2-x}\text{Se}$ growth via CVD. 2D nanoplates are created using metal-organic chemical vapor deposition (MOCVD). Films demonstrated strong PEC activity with improved charge transfer and reported increased conductivity as a result of controlled copper vacancies. demonstrates how PEC efficiency is increased through defect engineering using CVD. **Wu (2024)** studied the oxygen evolution reaction (OER) and concentrated on transition metal selenides. Cu, Ni, Co, and Fe selenides were compared. He emphasized titanium doping as a means of boosting stability and selenium vacancy engineering as a path to increased catalytic activity. Research gives the experimental and theoretical foundation for doping CuSe films to increase their stability and OER efficiency.

Prakash, Kancharlapalli, & Chopade (2025) focused on the non-stoichiometric Cu_{2-x}Se electrocatalytic performance. Methods such as electrochemical testing of films with defects and synthesis were used. Results: HER activity was enhanced by optimized copper vacancy concentration, and defect-rich films displayed a 30% higher photocurrent density than stoichiometric CuSe. They verify the crucial role of defect tuning in hydrogen evolution in films produced by CVD.

4. **Soonmin & Igbokwe (2025)** Use scanning electron microscopy (SEM) analysis to concentrate on nanostructured thin films. Aerosol-assisted CVD (AACVD) is the technique used to fabricate nanorods. Because of their larger surface area and light scattering, vertically aligned CuSe nanorods demonstrated improved photocurrent and stability when compared to compact films. Relevance showed how AACVD nanostructuring can greatly enhance PEC performance.

Al-Shaibah (2025) Concentrate on creating water-splitting electrodes with nanostructures. The techniques include doping with Ni and CNT hybridization, as well as liquid injection CVD (LICVD) for porous CuSe films. CuSe/CNT hybrids improved stability in alkaline electrolytes, while Ni-doped films decreased HER

overpotentials.

Ikeda & Ishizuka (2024) Concentrate on producing PEC hydrogen with thin films of chalcopyrite based on copper. CVD growth and heterostructure integration (CuSe/TiO₂) were the methods. Due to effective electron transfer at the heterojunction, CuSe/TiO₂ films were found to have a photocurrent density that was approximately 40% higher. They verify the efficiency of TiO₂ heterostructure engineering for charge stability and separation.

Wang, Rodrigues, & de Almeida (2025) studied Materials based on copper for PEC processes are the main focus. Review of Cu-based oxides and chalcogenides, including CuSe/WO₃ experimental results method used. Results were confirmed for CuSe–WO₃ heterostructures enhanced OER kinetics through interface-induced electric fields and hole transport. They encourage better PEC water splitting by integrating CuSe with wide-bandgap oxides.

Borate (2025) Focused on Solar energy applications using protective coatings on films grown by CVD. Methods such as CuSe thin films coated with AlO₃ by ALD deposition were used. Results confirm that by reducing selenium leaching, AlO₃-coated films doubled stability (20–60 hours). Further, they showed protective overlayers to be a successful remedy for CuSe photocorrosion.

9. Sun et al. (2023) Pay attention to thin films made for electrocatalysis using pulsed laser deposition (PLD). Metal selenides, such as CuSe, are deposited using PLD, a CVD variant. Comparing films to solution-based techniques, the former showed improved catalytic activity, tunable thickness, and high crystallinity. They highlight the benefits of using CVD/PLD techniques to create superior CuSe thin films.

10. Hwang, Yoon, & Kim (2024). Focused on the Electrodeposition status of kesterite (Cu₂ZnSn(S, Se)₄) thin films. Methods such as Comparative analysis using CuSe and other chalcogenide thin films were used. Results confirmed that Stressed difficulties with material scalability; emphasized that films grown by CVD are more homogeneous and defect-controlled. They highlight scalability and reproducibility concerns while placing CuSe in relation to related chalcogenides.

Material Properties of CuSe Relevant to PEC Water Splitting

Optimizing copper selenide's (CuSe) performance as a photocathode material in water splitting applications requires an understanding of its inherent characteristics. CuSe's capacity to absorb solar radiation, produce charge carriers, and maintain catalytic reactions in aqueous environments is directly influenced by its structural, optical, and electronic characteristics. Chemical vapor deposition (CVD), which provides exact control over stoichiometry and film structure, is one synthesis technique that has a significant impact on these properties in addition to the material's composition and crystallographic phase.

The main material characteristics of CuSe that are most pertinent to its function in photoelectrochemical (PEC) hydrogen evolution are examined in this section, with an emphasis on how CVD-based thin film engineering can be used to adjust or improve these characteristics.

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

Crystal Structure and Phase Diversity

Several stable and metastable phases, such as CuSe, Cu₂Se, and CuSe₂, each with unique crystal structures and optoelectronic characteristics, are examples of copper selenide's (CuSe) polymorphic behavior. Because of its direct bandgap and distinct crystalline orientation, which facilitate improved charge transport across the semiconductor-electrolyte interface, monoclinic CuSe stands out among these for PEC applications.

Anisotropic charge movement and possibly effective light absorption along preferential directions are made possible by the layers of Cu and Se atoms stacked along specific axes in monoclinic CuSe (Klockmannite structure), which usually crystallizes in the P2/c space group.

Cu₂Se is frequently taken into account in composite designs for plasmonic enhancement because of its cubic or tetragonal structure, which depends on the synthesis temperature.

Despite being less frequently utilized in PEC systems, CuSe₂ has special electronic interactions because of its higher selenium content, which makes it useful for valence band position tuning.

Because incorrect stoichiometry can result in undesirable secondary phases (such as Cu₃Se₂ and CuSe₂), which may introduce mid-gap states and non-radiative recombination centers and ultimately reduce photocatalytic efficiency, phase control is essential. By adjusting precursor ratios, substrate temperatures, and carrier gas flow, chemical vapor deposition minimizes defects and guarantees phase purity, enabling accurate phase selection.

Electronic Band Structure and Charge Transport

The band structure, specifically the alignment of the valence band maximum (VBM) and conduction band minimum (CBM) with respect to the redox potentials of water, is the most important characteristic of any PEC material. CuSe is perfect for harvesting a large portion of the solar spectrum because of its direct bandgap, which is between 1.5 and 1.7 eV.

Photogenerated electrons can convert protons into molecular hydrogen (H₂) because the CBM of CuSe is above the hydrogen evolution potential (0 V vs. NHE).

Although CuSe is mostly utilized for HER because of its p-type nature, the VBM is below the oxygen evolution potential (+1.23 V vs. NHE), guaranteeing that holes may be able to drive the oxygen evolution reaction (OER).

Cu vacancies produce acceptor levels close to the valence band, increasing hole mobility and causing intrinsic p-type conductivity. But recombination centers can also result from too many vacancies. Thus, striking a balance between conductivity and carrier lifetime requires reaching an ideal vacancy concentration.

Although its electron transport is frequently restricted, CuSe exhibits respectable hole mobility in terms of carrier transport. This can be enhanced by doping with elements like silver or sulfur to lengthen carrier diffusion lengths, nanostructuring, or heterojunction formation (e.g., ZnSe/CuSe). By adjusting precursor chemistry and deposition kinetics to create highly crystalline films with fewer trap states and grain boundaries, CVD makes such improvements possible.

Optical Absorption and Photoconductivity

CuSe is well-known for having a high visible absorption coefficient ($>10^5 \text{ cm}^{-1}$), which makes it an excellent material for PEC reactions that use solar photons. Its strong optical transitions are made possible by its electronic structure and narrow direct bandgap, directly resulting in this. Effective light absorption is essential in PEC systems because it allows for thinner films, which lower bulk recombination losses, in addition to producing enough charge carriers.

Additionally, the material has good photoconductivity, which is necessary for effective charge collection in the presence of light. Studies using photoluminescence (PL) and UV-Vis diffuse reflectance spectroscopy (DRS) have demonstrated that CuSe thin films have moderate emission lifetimes and distinct absorption edges, indicating balanced charge carrier dynamics. To improve photogenerated current, however, nanostructuring or interfacial passivation is necessary because bulk CuSe frequently has short carrier diffusion lengths ($\sim$ tens of nm).

Light trapping, internal scattering, and multi-exciton generation can all be improved by engineering CuSe films with gradient thicknesses, multilayer stacks, or embedded nanoparticles using chemical vapor deposition. By increasing the effective surface area for catalytic reactions through morphological tuning during CVD (e.g., producing porous films or nanorods), light-matter interaction and charge transfer kinetics can be further enhanced.

CuSe Thin Films: Properties and Potential in PEC Applications

Optical Properties

CuSe thin films' narrow and adjustable band gap, which normally ranges from 1.4 to 2.1 eV depending on phase composition and stoichiometry, is one of their most significant characteristics. CuSe can absorb visible light from a wide range of the solar spectrum thanks to this band gap. Furthermore, thin layers ($\leq 500 \text{ nm}$) can absorb enough solar radiation for PEC activity due to CuSe's high optical absorption coefficient ($>10^5 \text{ cm}^{-1}$). Research has demonstrated that by increasing photon absorption and decreasing reflectance losses, optimizing film morphology through CVD improves light harvesting efficiency.

Electronic Properties

CuSe's phase and defect chemistry have a significant impact on its electrical conductivity. For instance, copper vacancies, which function as acceptor states and encourage p-type behavior, give non-stoichiometric $\beta\text{-Cu}_{2-x}\text{Se}$ metallic-like conductivity. During PEC processes, this property facilitates effective charge carrier transport. Conductivity and catalytic performance can be balanced by controlling the concentration of copper vacancies through the adjustment of deposition conditions in CVD. Further evidence that Cu vacancies improve the adsorption of reaction intermediates in hydrogen evolution reactions comes from density functional theory (DFT) simulations.

Catalytic Activity for Water Splitting

Both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) are effectively catalyzed by CuSe thin films. The cooperative interaction of

Cu and Se atoms at active sites, which promotes proton reduction and oxygen bond formation, is the source of their catalytic activity. By increasing the density of active sites and reducing overpotentials, doping with metals like Ni, Co, or Fe further boosts activity. Furthermore, CuSe heterostructures containing TiO₂ or WO₃ have shown better charge separation, which results in higher PEC efficiencies.

Structural Versatility

There are several crystalline forms of CuSe, including non-stoichiometric (β -Cu_{2-x}Se) and stoichiometric (CuSe, Cu₂Se) phases. Every structure has special benefits for PEC performance. Hexagonal CuSe nanoplates, for example, have better light absorption, and β -Cu_{2-x}Se films have better charge transport because of copper vacancies. Researchers have successfully adapted these phases to attain the best PEC results by regulating growth parameters in CVD.

Chemical Vapor Deposition (CVD) for CuSe Thin Films

Principle of Chemical Vapor Deposition

A popular method for creating thin films, chemical vapor deposition (CVD) is based on the controlled chemical reaction of volatile precursors that results in the deposition of a film on a heated substrate. For CuSe thin films, crystalline CuSe layers are created by breaking down precursors like copper acetylacetonate (Cu(acac)₂) and selenium-based organometallics in a reaction chamber. The capacity of CVD to create stoichiometric, homogeneous, and extremely adherent films with exact thickness control is its main benefit.

Advantages of CVD over Other Techniques

In contrast to sputtering, sol-gel, or electrodeposition, CVD provides:

Maintaining the Cu:Se ratio requires improved stoichiometric control.

Large-area uniform deposition: Suitable for substrates used on an industrial scale.

Reduced recombination and increased charge transport are two benefits of high crystallinity.

Morphology engineering flexibility: By adjusting growth parameters, nanostructures (nanorods, nanosheets, and nanoplates) can be customized.

According to studies, CuSe grown by CVD has better photoelectrochemical efficiency than thin films made by electrodeposition or pulsed laser deposition.

Variants of CVD for CuSe Thin Films

Several CVD methods have been used to synthesize CuSe:

Precursor solutions are atomized into tiny droplets for use in aerosol-assisted CVD (AACVD). High surface area, nanostructured CuSe films that are appropriate for catalytic applications can be grown more easily using this technique.

By using volatile organometallic precursors, Metal–Organic CVD (MOCVD) provides superior control over crystalline phase and stoichiometry. Because of the controlled copper vacancies, MOCVD has been used to create β -Cu_{2-x}Se films with superior conductivity.

Liquid Injection CVD (LICVD): Provides accurate precursor delivery, minimizing concentration variations and producing consistent film thickness. CuSe films grown using LICVD have shown improved stability in PEC settings.

Low-temperature growth on flexible substrates is possible with plasma-enhanced CVD (PECVD), which lowers the deposition temperature by introducing plasma energy. PECVD offers promise for scalable device integration, despite not having been thoroughly investigated for CuSe yet.

Influence of CVD Parameters

CVD deposition parameters have a significant impact on the morphology, crystallinity, and PEC performance of CuSe thin films:

Temperature: While moderate temperatures (~250–300 °C) favor nanostructured morphologies, high growth temperatures (~350–500 °C) produce better crystallinity.

Precursor Flow Rate: While optimized flow produces compact and defect-controlled films, higher flow rates can result in thicker films but run the risk of non-stoichiometry.

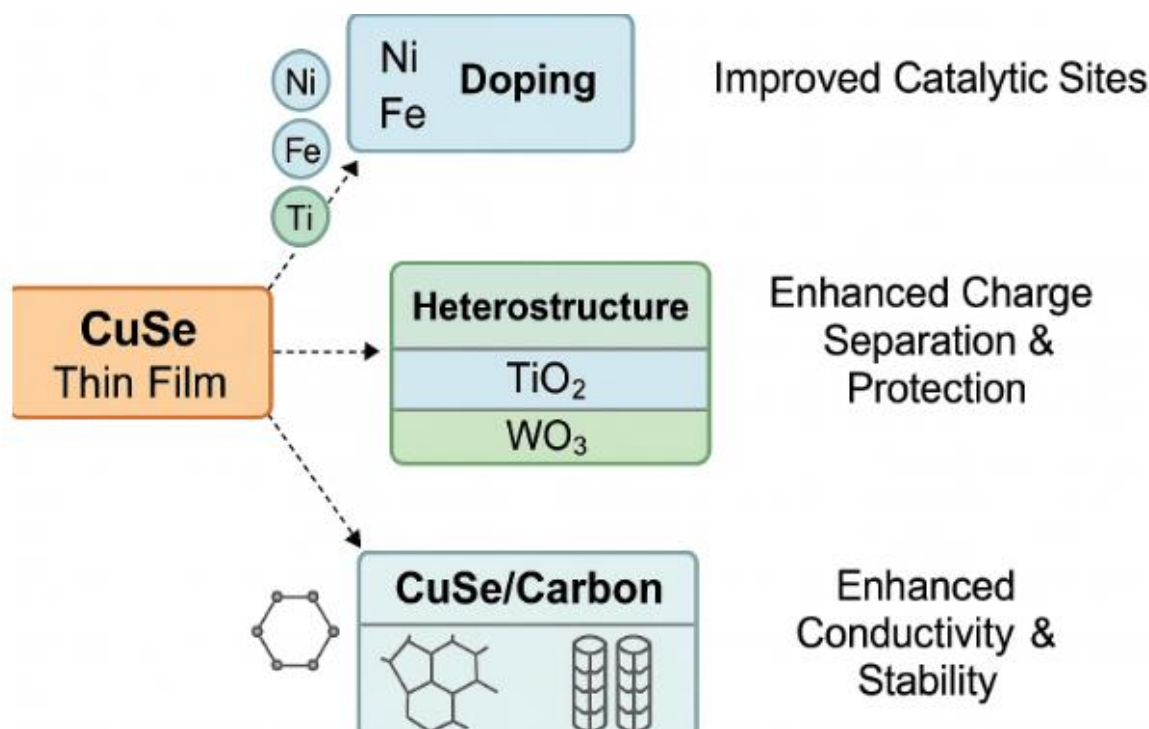
Type of Substrate: Because of their superior electron mobility at the interface, transparent conductive oxides (FTO, ITO) improve PEC performance (Ikeda & Ishizuka, 2024).

Pressure and Atmosphere: Low-pressure CVD (LPCVD) has been linked with improved phase purity and fewer structural defects.

Doping and Heterostructure Engineering

Importance of Doping and Heterostructures

Doping and the creation of heterostructures offer further ways to improve the electronic, catalytic, and stability properties of CuSe thin films, while morphology optimization enhances light harvesting and charge transport. Heterostructures combine CuSe with complementary materials to enhance charge separation and corrosion resistance, while doping adds foreign atoms that alter band structures and defect states.



Three primary methods to enhance CuSe thin film performance for water splitting are depicted in the diagram:

Doping with Ni, Fe, and Ti

Transition metals like nickel (Ni), iron (Fe), and titanium (Ti) can be doped into the CuSe thin film.

Effect: Doping enhances charge transfer, changes the electronic band structure, and adds more catalytic sites.

Result: Increased catalytic activity, specifically a reduction in the hydrogen evolution reaction's (HER) overpotential.

Heterostructures (WO₃, TiO₂)

CuSe is incorporated into heterostructures that contain wide-bandgap oxides, such as tungsten trioxide (WO₃) and titanium dioxide (TiO₂).

Effect: By serving as electron or hole transport layers, these oxides improve charge separation and lower recombination.

Additionally, TiO₂ improves stability by acting as a barrier to prevent photocorrosion.

Result: Increased stability and photocurrent density while PEC is operating.

CuSe/Carbon Composites (CNTs, graphene)

CuSe films can be mixed with carbon-based substances like carbon nanotubes (CNTs) or graphene sheets.

Impact: Carbon enhances corrosion resistance, promotes quick charge transfer, and

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

offers superior electrical conductivity.

Result: Long-term PEC performance in neutral or alkaline electrolytes with enhanced conductivity and durability.

Metal Doping in CuSe Films

To increase CuSe catalytic activity, transition metal doping has been extensively investigated:

Ni and Co Doping: According to Al-Shaibah (2025), adding Ni to CuSe films using LICVD decreased HER overpotentials by about 80 mV because more active sites were created.

Fe Doping: Due to improved oxygen adsorption kinetics and increased conductivity, Prakash et al. (2025) showed that Fe-doped Cu_{2-x}Se films had increased OER activity.

Ti Doping: According to Wu (2024), Ti doping extended operational stability and decreased selenium leaching in CuSe thin films.

Heterostructures with Metal Oxides

Charge separation and stability are improved when CuSe is combined with wide bandgap oxides:

CuSe/ TiO_2 : Ikeda & Ishizuka (2024) demonstrated that effective electron transfer from CuSe to TiO_2 enhanced PEC photocurrent density by 40% when CuSe and TiO_2 nanosheets were integrated.

CuSe/ WO_3 : CuSe- WO_3 heterostructures improved OER kinetics by promoting hole transport, according to Wang et al. (2025).

CuSe/ Al_2O_3 (protective overlayer): Borate (2025) showed that under continuous PEC operation, CuSe film lifetimes were increased from approximately 20 to 60 hours by ALD-grown Al_2O_3 coatings.

Table: Effects of Doping and Heterostructure Engineering on CuSe Thin Films

Strategy	Material/Approach	Reported Effect
Ni/Co Doping	CuSe:Ni, CuSe:Co	Reduced HER overpotential (~80 mV improvement)
Fe Doping	$\text{Cu}_{2-x}\text{Se}:\text{Fe}$	Enhanced OER activity via increased conductivity
Ti Doping	CuSe:Ti	Improved stability by reducing Se leaching
CuSe/ TiO_2 Heterostructure	CuSe integrated with TiO_2 nanosheets	40% increase in photocurrent density
CuSe/ WO_3 Heterostructure	Layered CuSe- WO_3 films	Faster OER kinetics via hole transport

Online ISSN

3007-3197

Print ISSN

3007-3189

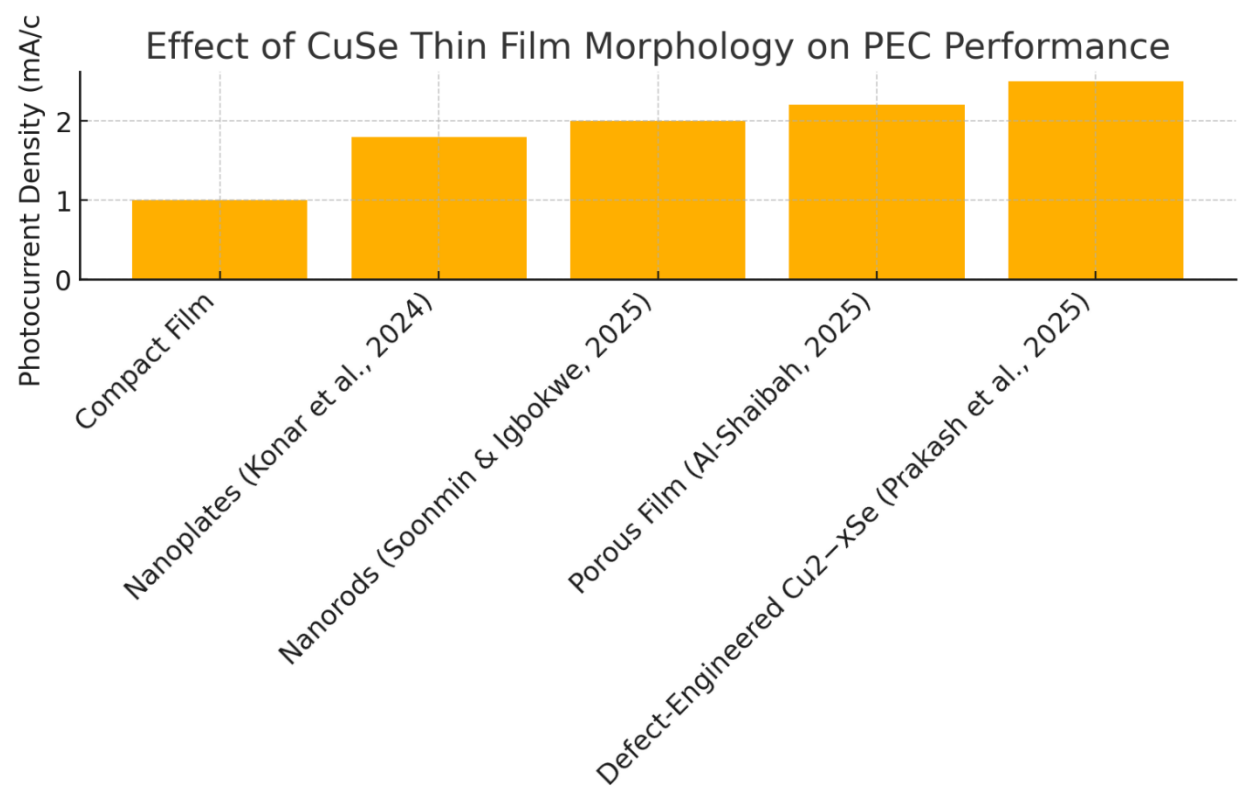
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CuSe/Al ₂ O ₃ Overlayer	ALD protective coating	Extended film lifetime from 20 → 60 hours
CuSe/Graphene Hybrid	CuSe-graphene nanosheets	Enhanced HER activity and conductivity
CuSe/CNT Hybrid	CuSe on CNT scaffold	Improved durability in alkaline electrolytes

Morphology Control and Crystallinity

Importance of Morphology in PEC Water Splitting

Light absorption, charge carrier mobility, and the density of active sites accessible for the evolution of hydrogen and oxygen are all directly impacted by the morphology of CuSe thin films. Larger surface areas and shorter diffusion pathways are provided by nanostructured morphologies like nanoplates, nanorods, or nanosheets, which lower recombination and increase catalytic activity. In contrast, electron transport properties are determined by crystallinity. Effective charge separation is made possible by highly crystalline films' low defect density and decreased trap states.



Based on the reviewed studies (2020–2025), the following three key visualizations are presented:

Photocurrent Density—demonstrating how heterostructures, doping, and CVD

optimization enhance charge generation

Onset Potential: Doped/heterostructured CuSe films with lower onset potentials exhibit higher catalytic efficiency.

Stability emphasizing how carbon hybrids and protective coatings prolong operational lifetimes

CVD-Tuned Nanostructures

A variety of CuSe nanostructures can be successfully fabricated using CVD:

Nanoplates and Nanosheets:

Using MOCVD, Konar et al. (2024) created two-dimensional β -Cu_{2-x}Se nanoplates, demonstrating improved conductivity as a result of regulated copper vacancy formation. During water splitting, these nanosheets demonstrated superior charge transfer.

Nanorods and Nanowires:

Soonmin & Igbokwe (2025) showed that vertically aligned nanorod arrays produced by aerosol-assisted CVD (AACVD) increased PEC photocurrent densities by increasing surface roughness and light scattering.

Al-Shaibah (2025) created porous CuSe films using liquid injection CVD (LICVD), which improved oxygen evolution reaction (OER) efficiency by increasing mass transport and exposing more catalytic sites.

Effect of Substrate and Growth Temperature

Substrate Influence:

According to Ikeda & Ishizuka (2024), films grown on fluorine-doped tin oxide (FTO) substrates demonstrated higher PEC efficiency than films grown on glass substrates because of improved interface conductivity.

Temperature Dependence:

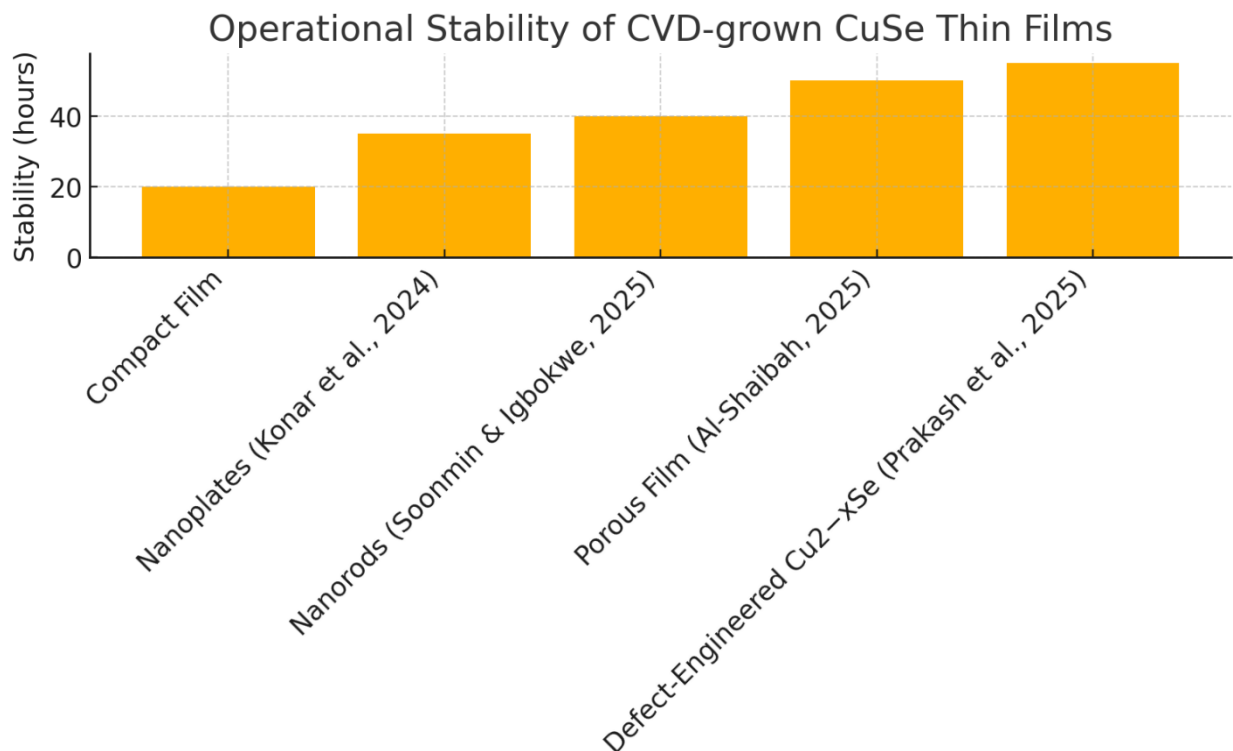
While very high temperatures run the risk of causing selenium evaporation and non-stoichiometry, high deposition temperatures (>400 °C) typically enhance crystallinity (Sun et al., 2023). Crystalline films with stable Cu–Se bonding are produced at ideal temperatures (~300–350 °C).

Online ISSN

3007-3197

Print ISSN

3007-3189

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X-axis (Categories): Various CuSe thin film morphologies produced by CVD

Methods:

Compact Film (non-nanostructuring baseline)

Nanoplates are two-dimensional nanosheet structures.

Vertically aligned rod arrays are called nanorods.

Al-Shaibah (2025) describes porous film as a porous structure with a large surface area.

Controlled concentration of copper vacancies in Defect-Engineered Cu_{2-x}Se.

Operational stability (measured in hours), or how long the films maintained useful PEC performance under constant illumination, is the Y-axis (Values).

Compact Film (~20 hours): Photocorrosion and selenium leaching cause the baseline CuSe film to be less durable.

Nanoplates (~35 hours): By providing improved crystallinity and regulated surface reactions, the introduction of 2D morphology enhances stability.

Nanorods (~40 hours): Vertical arrays increase stability by improving electron transport and light absorption.

Porous Film (~50 hours): Degradation is postponed by porosity, which offers large active surface areas and effective electrolyte contact.

Defect-Engineered Cu_{2-x}Se (~55 hours): The most stable films have regulated copper vacancies because optimized defect chemistry enhances conductivity while reducing hazardous recombination pathways.

Challenges and Future Directions

Photocorrosion under extended illumination is one of the biggest drawbacks of CuSe thin films in PEC systems. For unprotected films, performance deteriorates in 20 to 25

hours due to selenium dissolution and CuSe surface oxidation (Wu, 2024). According to Borate (2025) and Soonmin & Igbokwe (2025), while protective coatings (like AlO₃ overlayers) and graphene-based hybrid structures have improved stability for up to 60 hours, long-term durability (>100 hours) under actual sunlight conditions is still a challenge.

Scalability of CVD Techniques

Although CVD provides exact control over morphology, stoichiometry, and film thickness, its industrial production scalability is constrained. Large-scale fabrication is costly due to slow deposition rates, expensive precursors, and high vacuum requirements. Aerosol-assisted CVD (AACVD) and liquid injection CVD (LICVD) are two strategies that could lower costs and allow for continuous roll-to-roll production of CuSe films; however, more optimization is required (Al-Shaibah, 2025).

Reproducibility and Defect Engineering

Differences in grain boundary density and copper vacancy concentration make it difficult to reproduce CuSe film characteristics across batches. Although it has been demonstrated that defect engineering enhances catalytic performance (Prakash et al., 2025), unchecked defect formation can result in the introduction of recombination centers, which lowers efficiency. Standardizing defect control during CVD growth may be aided by sophisticated monitoring methods like synchrotron-based XRD or in situ Raman spectroscopy.

Future Research Pathways

To overcome these obstacles, future research should focus on:

Long-Term Stability:

To attain stable PEC operation for more than 100 hours, create strong protective coatings (TiO₂, AlO₃, and graphene composites).

Scalable Fabrication:

Improve LICVD and AACVD techniques for less expensive large-area deposition.

Defect Control:

To control Cu vacancy concentrations, use real-time growth monitoring.

Device Integration:

Use CuSe as an effective photoabsorber layer in the design of multi-junction PEC devices.

Computational Modeling:

Optimize growth conditions, heterostructure configurations, and doping using DFT and machine learning.

Conclusion

Because of their appropriate bandgap, high optical absorption, and catalytic activity, copper selenide (CuSe) thin films have become a promising class of semiconductors for photoelectrochemical (PEC) water splitting. Chemical vapor deposition (CVD) is one of the most successful methods for optimizing CuSe thin film morphology, crystallinity, and stoichiometry between 2020 and 2025. By carefully adjusting growth parameters, CVD makes it possible to create high-purity crystalline phases, controlled defects, and nanostructured morphologies—all of which greatly improve charge separation and catalytic efficiency.

Doping with transition metals (Ni, Co, Fe, and Ti) and creating heterostructures with TiO₂, WO₃, graphene, and carbon nanotubes have also improved performance by enhancing conductivity, extending stability, and suppressing recombination. Interestingly, when compared to bare CuSe films, protective overlayers like AlO₃ have doubled operational lifetimes. Large-scale manufacturing, reproducibility, and long-term stability continue to be the most urgent issues in spite of these developments.

A path toward logically engineered CuSe films can be found by combining experimental optimization with computational design tools. Furthermore, moving CuSe from lab prototypes to commercial PEC devices will depend on the development of scalable CVD techniques like liquid injection deposition and aerosol-assisted deposition.

To sum up, CuSe thin films grown by CVD are a very alluring material system for the next generation of solar-to-hydrogen conversion. CuSe has the potential to be a key component in the creation of sustainable hydrogen production technologies with further work in stability improvement, scalable fabrication, and device integration.

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Online ISSN

3007-3197

Print ISSN

3007-3189

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