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Review Article

Cuprous oxide (Cu_2O) photoelectrodes for photoelectrochemical solar cells: Materials properties, fabrication techniques and device architectures: A Review

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ABSTRACT: The increasing global demand for sustainable energy has intensified research into solar-driven fuel generation technologies. Photoelectrochemical (PEC) solar cells represent a promising pathway for direct conversion of solar energy into chemical fuels such as hydrogen through water splitting. Among various semiconductor materials investigated for PEC applications, cuprous oxide (Cu_2O) has attracted significant attention owing to its suitable direct band gap (~2.0 eV), high absorption coefficient in the visible spectrum, earth abundance, and low toxicity. However, the practical deployment of Cu_2O-based PEC devices remains limited by challenges including photocorrosion, short minority-carrier diffusion lengths, and defect-mediated recombination. This review provides a comprehensive overview of Cu_2O as a photoelectrode material for PEC solar cells. The fundamental electronic and optical properties of Cu_2O are discussed together with intrinsic defect chemistry and charge transport characteristics relevant to PEC operation. Various fabrication techniques for Cu_2O thin films such as immersion deposition, boiling-assisted deposition, electrodeposition, thermal oxidation, and sputtering are critically reviewed with emphasis on their influence on film morphology, crystallinity, and electronic properties. In addition, different PEC device architectures such as regenerative PEC cells, photocatalytic PEC cells, single-photoelectrode systems, and tandem configurations are examined. Finally, key strategies for improving the performance and stability of Cu_2O photoelectrodes, including surface passivation, catalyst integration, and heterojunction engineering, are highlighted. The review concludes with perspectives on future research directions aimed at enabling efficient and durable Cu_2O-based PEC solar energy conversion systems.

Keywords: Electrodeposition, morphology, photoelectrochemical (PEC), photoelectrode, solar cells, sputtering, thermal oxidation.

INTRODUCTION

With increasing global energy demand and mounting environmental concerns, the pursuit of clean, renewable, and efficient energy conversion systems has never been more urgent. Photoelectrochemical (PEC) solar cells, which convert solar energy directly into chemical energy, often hydrogen or electrical energy, are one of the promising clean-energy technologies (Fu *et al*., 2024). However, their widespread adoption hinges on finding stable, efficient, earth-abundant semiconductors for the photoelectrodes (Harris-Lee *et al*., 2023).

Cuprous oxide (Cu_2O), which can be synthesised as a p-type or n-type semiconductor, is particularly attractive for PEC applications because of its favourable bandgap (~2.0 eV), excellent visible light absorption, and relatively benign environmental footprint (Baran *et al*., 2021). Its direct bandgap and strong absorption coefficient allow efficient

harvesting of sunlight in the visible region.

Despite these advantages, the performance of Cu_2O-based PEC systems is limited by several intrinsic challenges. These include rapid charge-carrier recombination, short minority-carrier diffusion lengths, and poor stability due to photocorrosion under aqueous operating conditions. These limitations have motivated extensive research aimed at improving Cu_2O photoelectrodes through strategies such as heterojunction formation, protective coatings, surface catalyst integration, and nanostructuring.

This review provides a comprehensive discussion of Cu_2O materials for PEC solar cell applications. The fundamental properties of Cu_2O relevant to photoelectrochemical processes are first examined, followed by an overview of commonly used deposition techniques for Cu_2O thin films. Different PEC device architectures incorporating Cu_2O are then discussed, highlighting recent advances and remaining challenges in the development of efficient solar fuel generation systems.

PROPERTIES OF Cu_2O RELEVANT FOR PEC APPLICATIONS

Electronic band structure and optical absorption

Cuprous oxide (Cu_2O) is a direct band gap semiconductor with a band gap energy generally in the range of 1.9–2.2 eV. Because of its direct band gap, Cu_2O can absorb visible light efficiently via direct electronic transitions, eliminating the requirement for phonon participation. As a result, Cu_2O exhibits strong absorption in the visible region of the solar spectrum, with an absorption coefficient exceeding 10^5 cm^{-1}. The band gap of Cu_2O corresponds to an absorption edge around 600–620 nm, enabling the material to utilise a substantial fraction of solar radiation. This characteristic makes Cu_2O particularly attractive for PEC photocathodes intended for hydrogen generation through water reduction.

Another important factor in PEC applications is the relative position of the semiconductor band edges with respect to electrochemical redox potentials. In Cu_2O, the conduction band minimum is sufficiently negative relative to the hydrogen evolution potential, allowing photoexcited electrons to reduce protons to hydrogen under suitable conditions. This alignment makes Cu_2O suitable for use as a photocathode in PEC water-splitting systems. The conduction-band minimum (CBM) of Cu_2O lies at a more negative potential than the hydrogen evolution potential in many reports, which means photoexcited electrons can, in principle, reduce protons to H_2, making Cu_2O a natural p-type photocathode candidate for PEC hydrogen generation (Cheng *et al*., 2023).

Cu_2O high absorption coefficient in the visible region, prompting its thin films, hundreds of nm to ~1 µm, to capture most incident visible light. This is attractive for thin-film PEC architectures where minimising bulk recombination and material usage matters (Gonçalves *et al*., 2023).

Moreover, other realities like photocorrosion, short carrier diffusion lengths and fast recombination require protective overlayers, catalyst integration, and tailored nanostructures to translate Cu_2O spectral advantages into good PEC performance (Zhu *et al*., 2023).

Quantitatively, Cu_2O exhibits a very high absorption coefficient in the visible region. Reports such as those by Kartha *et al*. (2022) indicate that even sub-micron-thick films can absorb a substantial fraction of incident visible light. This enables the design of thin photoelectrodes capable of efficient photon harvesting while minimising bulk recombination losses and material consumption, making Cu_2O particularly attractive for scalable photoelectrochemical (PEC) device architectures.

Carrier transport and diffusion

Although Cu_2O exhibits excellent light absorption properties, its performance in PEC systems is strongly influenced by charge carrier transport. Minority-carrier diffusion lengths in polycrystalline Cu_2O films are often relatively short, typically below 200–300 nm. However, efficient light absorption often requires film thicknesses on the order of several hundred nanometers to a few micrometres.

This mismatch between optical absorption depth and carrier diffusion length results in significant recombination losses before photogenerated carriers can reach the reaction interface. Consequently, many studies have focused on nanostructuring or reducing film thickness to improve carrier extraction efficiency.

Recent investigations have demonstrated that high-quality single-crystal or preferentially oriented Cu_2O films can exhibit significantly improved carrier mobility and longer diffusion lengths. In particular, Cu_2O films oriented along the (111) crystallographic plane have been reported to exhibit enhanced charge transport properties, resulting in improved photoelectrochemical performance.

Recent studies by Pan *et al*. (2024) have demonstrated that carrier mobility and charge transport can be substantially improved in high-quality, preferentially oriented single-crystal Cu_2O films. In particular, films oriented along the (111) crystallographic plane exhibited enhanced charge extraction efficiency, leading to improved overall device performance.

In contrast, many polycrystalline and electrodeposited Cu_2O films are characterised by short minority-carrier electron diffusion lengths and pronounced bulk or interfacial recombination. This results in a fundamental compromise: while thicker films are required for complete light absorption, their thickness often surpasses the carrier diffusion length, leading to recombination losses before charge carriers can reach the reaction interface. Its suitable band gap and a wide range of carrier concentrations of 10^9–10^{16} cm^{-3} according to literature made it suitable for applications like photovoltaics, photo-

catalysis, thin-film transistors, or resistive switching devices. However, Cu_2O is only stable at room temperature and ambient pressure and shows a tendency to form precipitates of secondary phases. The formation of secondary phases is typically controlled by process parameters, which influence the thermodynamics and kinetics of the deposition (Deuermeier *et al*., 2018).

Defect chemistry and recombination

Copper vacancies are common in Cu_2O and are responsible for its p-type conductivity. Oxygen vacancies and interstitials may also appear depending on growth conditions. These point defects introduce shallow or deep levels that affect carrier densities and trapping (Zivkovic *et al*., 2022).

Polycrystalline films prepared by electrodeposition or sputtering typically contain structural defects such as grain boundaries, dislocations, and stacking faults. These defects can serve as recombination centres and, in PEC environments, may also provide pathways for electrolyte penetration. Grain-boundary defect states can locally pin the Fermi level, enhance non-radiative recombination, and ultimately reduce charge collection efficiency (Deuermeier *et al*., 2018).

The semiconductor/electrolyte and semiconductor/transport-layer interfaces can contain chemical defects such as dangling bonds, native oxide layers, and mixed CuO_x phases. These interfacial defects act as recombination centres and can induce Fermi-level pinning, thereby limiting efficient charge transfer. Such effects are particularly critical in PEC systems, where electrochemical reactions occur directly at the semiconductor surface (Kafi *et al*., 2020).

Surface states present at the Cu_2O/electrolyte interface act as carrier trapping centres, promoting recombination before effective interfacial charge transfer can take place. This process reduces the apparent quantum efficiency and shifts the onset potential of the photoelectrochemical reaction to more positive values (Heo *et al*., 2023).

Many experimental studies reported minority-carrier diffusion lengths in polycrystalline Cu_2O well below 200–300 nm, while optical absorption requires thicknesses of several hundred nm to microns for complete absorption; this mismatch is a primary driver of recombination losses. Meanwhile, single-crystal, epitaxial films can show much longer diffusion lengths and better carrier transport (Pan *et al*., 2024).

FABRICATION METHODS FOR Cu_2O THIN FILMS

The performance of Cu_2O photoelectrodes depends strongly on the synthesis method used to prepare the material. Various deposition techniques have been developed for Cu_2O thin-film fabrication, each offering different advantages in terms of cost, scalability, and control over material properties. Several techniques have been reported for the deposition of Cu_2O thin films. These include the boiling-assisted immersion technique, electrochemical deposition, thermal oxidation, sputtering, chemical bath deposition, chemical vapour deposition, and atomic layer deposition (Musa *et al*., 2017; Kafi *et al*., 2020; Košiček *et al*., 2022; Lakshmanan *et al*., 2022; Hildebrandt *et al*., 2023; Singh *et al*., 2023; Iivonen *et al*., 2019). Each of these techniques offers distinct advantages in terms of film quality, cost, scalability, and level of control over material properties.

However, this review focuses primarily on boiling-assisted deposition, immersion techniques, electrodeposition, thermal oxidation, and sputtering. These methods were selected because they are among the most widely employed and experimentally validated approaches for the fabrication of Cu_2O thin films used in photoelectrochemical (PEC) applications. In particular, they represent two important classes of deposition strategies: low-cost solution-based processes (such as boiling-assisted methods, immersion techniques, and electrodeposition) and controlled physical deposition methods (such as thermal oxidation and sputtering).

Focusing on these techniques enables a more detailed and systematic comparison of their influence on structural properties, defect density, film morphology, and photoelectrochemical performance of Cu_2O photoelectrodes. Including a broader range of deposition techniques would likely dilute the depth of analysis and reduce the clarity of the comparative evaluation presented in this review.

Immersion deposition

Immersion deposition is a simple solution-based technique in which a copper substrate is immersed in a chemical solution containing copper ions, as in Figure 1. Under appropriate conditions, a Cu_2O layer forms on the substrate surface through redox reactions occurring at the solid–liquid interface.

Parameters such as solution pH, temperature, and deposition time significantly influence film formation. Experimental studies have shown that Cu_2O films begin to form at moderately alkaline pH conditions, while highly alkaline solutions may lead to the formation of CuO instead.

Although immersion deposition is relatively simple and cost-effective, the long deposition times required and limited control over film uniformity restrict its application in high-performance PEC devices.

The experimental procedure employed in this study followed the immersion deposition method reported by Musa *et al*. (2017). In this approach, 100 cm^3 of copper sulfate ($CuSO_4$) solution was prepared, and the pH of the solution was adjusted to 5.5, as recommended in earlier

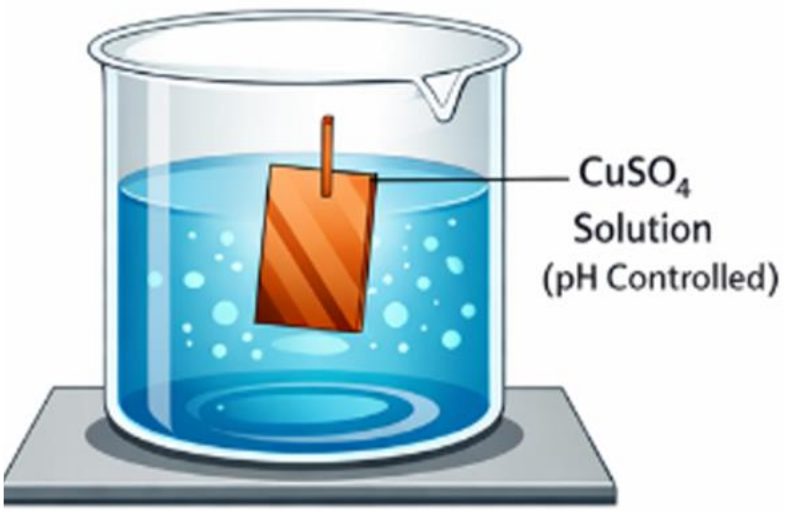

Figure 1. Schematic diagram of the immersion deposition technique for Cu_2O thin-film growth, where a copper foil substrate is immersed in a $CuSO_4$ solution at controlled pH (AI Generated).

studies. The prepared solution was transferred into a beaker, after which a properly cleaned copper foil substrate was immersed in the solution and left undisturbed for a period of 30 days to facilitate film growth on the substrate surface.

To investigate the influence of solution pH on film formation, the same procedure was repeated at higher pH values of 8.05, 9.83, and 12.30, with each sample maintained under identical deposition conditions and exposure duration, as reported in related studies. The authors also indicated that the deposition period can be adjusted depending on the specific objectives of the investigation. At the end of the designated immersion period, the copper substrates were carefully removed from the solution, rinsed thoroughly with deionised water to eliminate residual impurities, and subsequently dried using tissue paper.

The reported results indicated that the formation of n-type Cu_2O films began to appear at pH 5.5 and became more pronounced at pH 8.05. At pH 9.83, the film was fully developed and exhibited a distinct reddish-brown colouration, which is characteristic of Cu_2O formation. However, at pH 12.30, the deposited layer appeared black, suggesting the formation of CuO rather than Cu_2O. In contrast, solutions with pH values below 5.5 produced no observable film deposition on the copper substrate.

Boiling-assisted deposition

Boiling-assisted deposition is a variation of immersion deposition in which the precursor solution is heated to boiling temperatures during film formation, as shown in Figure 2. Elevated temperatures accelerate chemical reactions and improve film growth rates.

Studies have shown that deposition time plays a critical role in determining film stability and thickness. Excessively long deposition times may lead to film dissolution or mechanical instability. Consequently, optimisation of deposition parameters is necessary to obtain uniform and adherent Cu_2O films.

Musa *et al*. (2017) reported the synthesis of n-type cuprous oxide (Cu_2O) thin films using an immersion-boiling assisted deposition technique based on a copper sulfate ($CuSO_4$) precursor solution. In their experimental procedure, 100 cm^3 of $CuSO_4$ solution was prepared in a beaker, and the pH of the solution was measured using a pH meter. The pH could be adjusted depending on the required deposition conditions. The prepared solution was subsequently heated to the boiling point using a magnetic heating stirrer. Once boiling commenced, a pre-cleaned copper foil substrate was immersed in the solution and maintained under continuous heating for a specified deposition period.

The authors reported that 60 minutes was the optimum deposition time for achieving stable and well-adhered Cu_2O film formation. Nevertheless, the study emphasised that deposition time plays a critical role in determining the structural and physical properties of the resulting thin films. Musa *et al*. (2016) also observed that variations in the solution pH produced no visible film deposition within the boiling durations investigated. Furthermore, when the boiling time exceeded 60 minutes, the deposited layer gradually weakened and eventually dissolved or detached from the substrate, indicating reduced film stability beyond the optimal deposition period.

Following deposition, the samples were removed from the solution, rinsed thoroughly with deionised water, and dried using tissue paper. To further evaluate the influence of deposition time on film formation, additional experiments

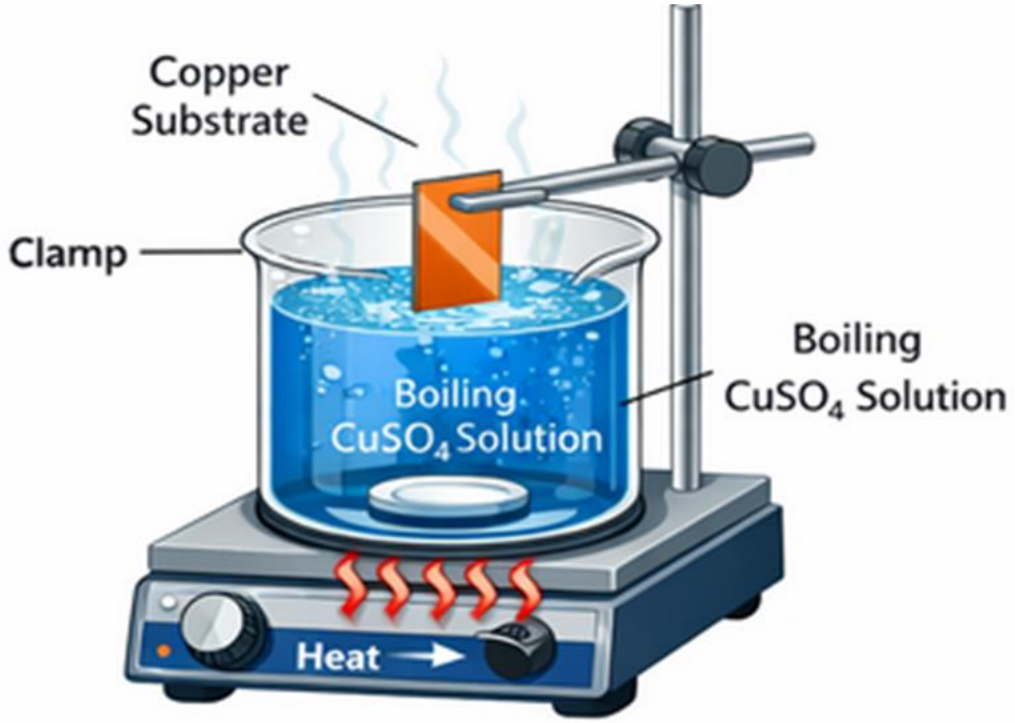

Figure 2. Schematic experimental setup for the boiling-assisted immersion deposition of Cu_2O thin films, showing a copper substrate immersed in boiling $CuSO_4$ solution on a magnetic heating stirrer (AI Generated).

were conducted using freshly prepared solutions, with boiling durations systematically varied to 50, 40, 30, 20, and 10 minutes. The resulting films were subsequently characterised using surface morphology analysis and X-ray diffraction (XRD) in order to investigate their structural properties and phase composition.

Electrodeposition

Electrodeposition is one of the most widely used methods for preparing Cu_2O thin films for PEC applications. In this technique, Cu_2O is deposited electrochemically from an aqueous solution containing copper salts using a three-electrode configuration.

The process typically involves a working electrode substrate, a counter electrode (often platinum), and a reference electrode such as Ag/AgCl. By controlling parameters such as deposition potential, solution pH, and temperature, the structural and electronic properties of Cu_2O films can be tailored.

Electrodeposition offers several advantages, including low processing temperature, scalability, and precise control over film thickness and morphology. Consequently, many high-performance Cu_2O photocathodes reported in the literature are fabricated using this method.

Electrodeposition is one of the most widely used techniques for the fabrication of Cu_2O thin films due to its simplicity, low processing temperature, cost-effectiveness, and ability to precisely control film properties through electrochemical parameters. In this technique, copper foil or conductive substrates serve as the working electrode, while a graphite or platinum rod acts as the counter electrode. Cu_2O thin films are deposited under controlled potentials and deposition durations. After deposition, the films are typically rinsed with deionised (DI) water and allowed to dry in air to remove residual electrolyte and impurities (Binghao *et al*., 2023).

Budi *et al*. reported that electrodeposition enables the synthesis of Cu_2O thin films at relatively low temperatures while allowing their microstructure, optical properties, and photocatalytic performance to be easily tuned by adjusting deposition parameters such as applied potential, current density, and solution pH. This level of control makes electrodeposition particularly suitable for tailoring Cu_2O films for photoelectrochemical (PEC) applications.

Kafi *et al*. (2020) successfully fabricated n-type Cu_2O thin films via potentiostatic electrodeposition using an aqueous bath containing 0.1 M sodium acetate and 0.01 M cupric acetate. The deposition process was performed in a three-electrode electrochemical cell consisting of the substrate as the working electrode, a platinum plate as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The films were deposited at a potential of −200 mV vs. Ag/AgCl, with the electrolyte maintained at 55°C for a deposition time of 60 minutes.

Similarly, Jrajri *et al*. (2022) synthesised Cu_2O thin films through a simple and cost-effective electrodeposition approach using the linear sweep voltammetry (LSV) method at a bath temperature of 50°C and a short deposition time of 10 minutes. Citric acid was employed as a complexing agent to stabilise the copper ions in solution. X-ray diffraction analysis revealed that films deposited at pH values of 9.5, 10.5, and 11.5 corresponded well with the cubic Cu_2O structure (Pn3m), with improved crystallinity observed near pH 10.5. Raman spectroscopy further confirmed the cubic phase of the deposited films. The resulting thin films exhibited a high absorption coefficient in the visible region, with an estimated band gap energy of approximately 1.8 eV, indicating strong potential for solar energy applications.

Mohd Hanif *et al*. (2015) fabricated Cu_2O thin films on fluorine-doped tin oxide (FTO) glass substrates using electrodeposition in an electrolyte containing copper (II) acetate monohydrate and lactic acid. During the deposition process, the solution temperature (40 °C), pH (6.5), and current density (−0.3 mA cm^{-2}) were maintained, while the deposition time was varied up to 80 minutes. X-ray diffraction results indicated that the intensity of the Cu_2O (111) diffraction peak increased with increasing deposition time, suggesting improved crystallinity. Atomic force microscopy (AFM) analysis revealed that the surface roughness initially increased with deposition time from 5 to 60 minutes, but decreased slightly when the deposition time reached 70 and 80 minutes. Electrical characterisation through I–V measurements showed Ohmic behaviour, confirming the successful fabrication of n-type Cu_2O thin films. The study demonstrated that deposition time significantly influences the growth mechanism, morphology, and electrical properties of the films.

Mohamad *et al*. (2020) also reported the fabrication of n-type Cu_2O thin films on FTO substrates through potentiostatic electrodeposition using a copper acetate-based electrolyte. The films were deposited at pH 6.3, with an applied potential of −0.125 V vs. Ag/AgCl and a deposition time of 30 minutes. Post-deposition annealing treatment was introduced to enhance film quality. Optical characterisation revealed that all samples exhibited a band gap of approximately 1.9 eV, which remained largely unaffected by the annealing process. However, the electrical resistivity of the Cu_2O films decreased after annealing, indicating improved charge transport properties.

More recently, Gonçalves *et al*. (2023) conducted a comprehensive investigation of the morphology, microstructure, and optical properties of electrodeposited Cu_2O thin films on SnO_2:F (FTO) substrates using the galvanostatic deposition method. The films were synthesised at different pH values (9 and 12) and temperatures ranging from 40 to 65 °C. The deposited films exhibited good uniformity, reproducibility, stability, high purity (single Cu_2O phase), and improved crystallinity, demonstrating the reliability of electrodeposition for producing high-quality Cu_2O films.

Overall, electrodeposition offers significant advantages for Cu_2O thin-film fabrication, including low temperature processing, tunable structural properties, and scalability, making it a highly attractive technique for photovoltaic and photoelectrochemical device applications.

Thermal oxidation

Thermal oxidation is commonly employed for fabricating p-type Cu_2O photocathodes, especially via direct oxidation of copper foils at high temperatures. During this technique, copper substrates are annealed between 600–1000°C, as illustrated in Figure 3. Subsequent chemical etching with reagents such as aqueous ammonia, NaCl, $FeCl_3$, or HCl is then performed to eliminate secondary oxide phases and enhance the quality of the Cu_2O film.

According to Bae *et al*. (2025), the formation of thermally oxidised Cu_2O was confirmed through cross-sectional scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis. Their measurements showed that untreated copper foil contained approximately 61.2% Cu and 4.5% O, whereas the oxidised sample exhibited 54.6% Cu and 25.3% O, closely matching the expected 2:1 atomic ratio of Cu to O in Cu_2O. These findings confirm that thermal oxidation can effectively produce stoichiometric Cu_2O layers.

Morariu *et al*. (2024) investigated the growth of Cu_2O/CuO nanowires via a one-step thermal oxidation process using flexible copper mesh substrates. The oxidation process was conducted within the temperature range of 300–600 °C in a controlled atmosphere consisting of mixed argon and oxygen gases. The authors highlighted that thermal oxidation is among the simplest and most economical approaches for producing metal oxide nanostructures on conductive substrates. The resulting Cu/Cu_2O/CuO nanowire electrodes demonstrated promising electrochemical performance when evaluated using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS). At a scan rate of 5 mV s^{-1}, the electrode oxidised at 300°C exhibited the highest capacitance value of 26.158 mF cm^{-2}, while GCD measurements revealed a maximum specific capacitance of 21.198 mF cm^{-2} at a current density of 0.5 mA cm^{-2}. The electrodes also maintained good electrochemical stability over 500 charge–discharge cycles.

Košiček *et al*. (2022) further investigated the growth mechanisms of copper oxide layers formed during thermal oxidation. Their study revealed that during annealing in air, a Cu_2O layer with randomly oriented column grains forms initially, followed by the development of preferentially oriented CuO grains that eventually evolve into CuO nanowires. The formation process is strongly influenced by copper and oxygen diffusion dynamics and the equilibrium between the Cu_2O and CuO phases. The authors reported

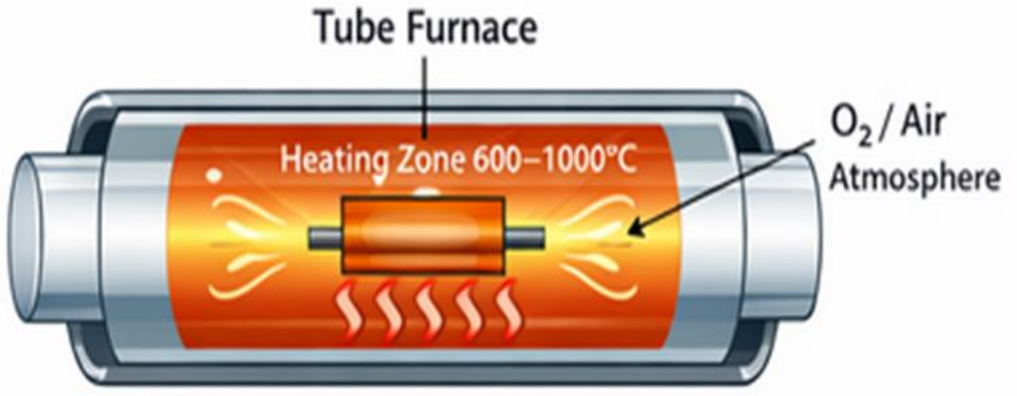

Figure 3. Schematic representation of the thermal oxidation setup for Cu_2O synthesis, where copper foil is heated in a furnace under an oxygen-containing atmosphere (Holm *et al.,* 2026).

that CuO nanowires originate from twinned CuO grains, which elongate due to the instability of the twin boundaries.

These findings highlight the effectiveness of thermal oxidation as a simple, scalable, and cost-effective technique for synthesising Cu_2O-based structures with potential applications in energy storage and photoelectrochemical devices.

Sputtering

Sputtering is a physical vapour deposition (PVD) technique widely used for the fabrication of high-quality thin films under high-vacuum conditions. In direct current (DC) sputtering, the target material acts as the cathode, while a glow discharge is generated in an inert gas—typically argon, at low pressures ranging from 10^{-1} to 10^{-2} Torr, using applied voltages of several kilovolts (Arun *et al*., 2025). The substrate intended for film deposition is placed near the anode, where sputtered atoms condense to form a thin film.

During the sputtering process, positively charged gas ions accelerate toward the cathode, impacting the target surface and causing the ejection of atoms or clusters, as shown in Figure 4. These sputtered species travel through the vacuum environment and subsequently deposit onto the substrate surface, forming a thin film.

For the synthesis of Cu_2O films, reactive sputtering is commonly employed, where a copper target is exposed to oxygen introduced into the sputtering chamber. By carefully controlling the oxygen partial pressure, the electrical and structural properties of the resulting Cu_2O films can be tuned over a wide range. Drobny and Pulfrey (1979) demonstrated that this approach allows the fabrication of Cu_2O films with resistivities as low as 25 Ω·cm.

Kim *et al*. (2023) deposited Cu_2O films on glass substrate via RF (radio frequency) magnetron sputtering under substrate temperature conditions that ranged from room temperature (RT, 25 °C) to 400°C. The substrate

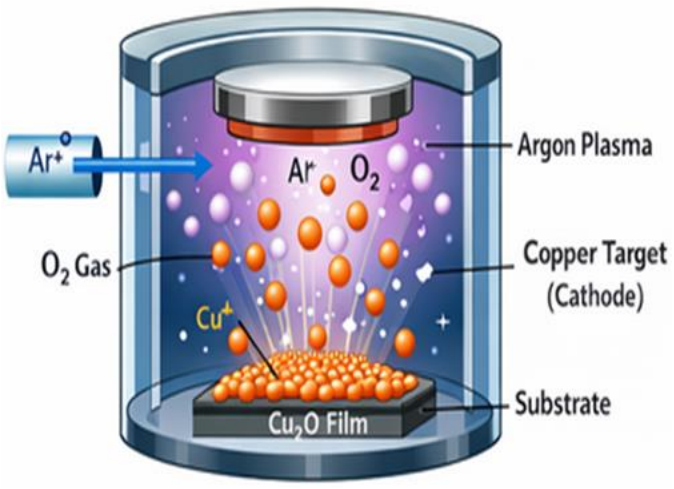

Figure 4. Schematic illustration of the reactive magnetron sputtering system used for Cu_2O thin-film deposition, showing the copper target, plasma region, and substrate (Aghilizadeh *et al*., 2017).

temperature was a crucial factor in shaping the structural, compositional, and optical properties of the Cu_2O films that were synthesised via RF-magnetron sputtering. Their findings revealed that the Cu_2O films exhibited a cubic structure, which was confirmed by XRD analysis. It was also reported that the (111) and (200) planes showed different trends with respect to the substrate temperature. The intensity of the (111) peak increased at 250 °C, and above 300 °C, the preferred orientation of the (111) plane was maintained. The grain size, which was determined via FE-SEM, displayed a positive correlation with the substrate temperature. Additionally, XPS analysis revealed that the binding energy (BE) of the Cu_2O film sputtered at 400 °C was similar to that which was previously reported. The results, therefore, indicate that the as-deposited Cu_2O film exhibited the maximum visible-light transmittance of 15.9%, which progressively declined

as the substrate temperature increased. In addition, the optical band gap (Eg) remained unchanged at about 2.51 eV for films grown at lower substrate temperatures (25–200 °C), but showed a modest increase at elevated temperatures, reaching 2.57 eV at 400 °C.

Lakshmanan *et al*. (2022) deposited Cu_2O thin films by reactive magnetron sputtering at different substrate temperatures ranging from 300 to 673 K. X-ray diffraction and Raman studies confirmed the cubic phase of Cu_2O. X-ray photoelectron spectroscopy shows the presence of a minority CuO phase at the surface. The optical band gap obtained from the transmittance spectroscopy is found to be in the range of 1.82–2.07 eV. All the films were reported to exhibit p-type conductivity with a typical carrier concentration of ~1014 cm^{-3}.

Li (2018) produced cuprous oxide (Cu_2O) thin films from metallic Cu targets on α-Al_2O_3 (000l) substrate by radio frequency magnetron sputtering technology. Three batches of samples were deposited under various sputtering parameters by modulating substrate temperature, gas flow and sputtering power, respectively. It was reported that the crystallisation extent and the crystal orientation in Cu_2O thin films mainly depend on the temperature exchange, which contributes to the variation of the film morphology. Moreover, the gas flow was also noticed to have an effect on the valence of the copper ion in the film, and the sputtering power mainly affects the growth rate of the films. This research promotes a more specific scheme to deposit proper Cu_2O thin films with proper morphology and useful properties.

The sputtering techniques most relevant to Cu_2O thin-film synthesis include reactive Direct Current and Radio Frequency sputtering, their magnetron-enhanced variants, pulsed DC sputtering, and High-Power Impulse Magnetron Sputtering (HiPIMS). These methods enable precise control of oxygen incorporation, phase formation, and electrical properties, which are critical for optimising Cu_2O for photovoltaic and photoelectrochemical applications.

FABRICATION OF A PHOTOELECTROCHEMICAL (PEC) SOLAR CELL

A photoelectrochemical (PEC) solar cell is an energy conversion device that utilises light-absorbing semiconductor electrodes in contact with an electrolyte to convert solar energy directly into electrical energy or chemical fuels such as hydrogen through water splitting. Unlike conventional solid-state photovoltaic (PV) cells, PEC cells rely on semiconductor–electrolyte interfaces where photogenerated charge carriers participate in electrochemical reactions (Fu *et al*., 2024).

The concept of PEC water splitting was first demonstrated through the landmark Honda–Fujishima effect in 1972 by Akira Fujishima and Kenichi Honda. In this discovery, ultraviolet illumination of a TiO_2 electrode produced electron–hole pairs capable of driving the oxidation and reduction reactions necessary for water splitting. Photogenerated holes at the TiO_2 photoanode oxidised water to produce oxygen, while electrons flowed through an external circuit to the counter electrode, where hydrogen evolution occurred. This breakthrough provided the first clear demonstration of solar-driven photocatalytic water splitting and laid the foundation for modern PEC technologies.

A typical PEC system consists of a semiconductor photoelectrode (photoanode or photocathode), a counter electrode, an electrolyte solution, and an external circuit. When the semiconductor absorbs photons with energy equal to or greater than its band gap, electron–hole pairs are generated. These charge carriers are separated by the internal electric field at the semiconductor–electrolyte interface. The electrons migrate toward the cathode to reduce protons to hydrogen, while the holes migrate toward the anode to oxidise water and produce oxygen.

Key components of the PEC setup

1. Working electrode (Photoelectrode): A semiconductor material (e.g., TiO_2, Cu_2O, ZnO) deposited on a conductive substrate such as FTO or ITO glass.
2. Counter electrode: Usually, an inert metal such as platinum, graphite, or carbon is used to complete the circuit.
3. Reference electrode (in three-electrode systems): Commonly, an Ag/AgCl or saturated calomel electrode (SCE) is used to control and measure electrode potential.
4. Electrolyte solution: Provides ionic conduction and participates in redox reactions (e.g., Na_2SO_4, KOH, or acidic solutions).
5. Light source: Simulated sunlight or a solar lamp used to illuminate the semiconductor electrode.
6. External circuit/potentiostat: Allows measurement of photocurrent, voltage, and electrochemical performance.

Types of photoelectrochemical (PEC) solar cells

Photoelectrochemical (PEC) solar cells can be broadly classified based on the type of semiconductor electrode responsible for the photo-reaction. The two most common configurations are photoanode PEC cells and photocathode PEC cells. These configurations determine the direction of charge carrier movement and the type of electrochemical reaction occurring at the semiconductor–electrolyte interface.

Photoanode PEC solar Cell (n-type semiconductor)

In a photoanode PEC cell, as in Figure 5, an n-type semiconductor acts as the working electrode and is responsible for the oxidation reaction. When sunlight illuminates the semiconductor, photons with energy equal

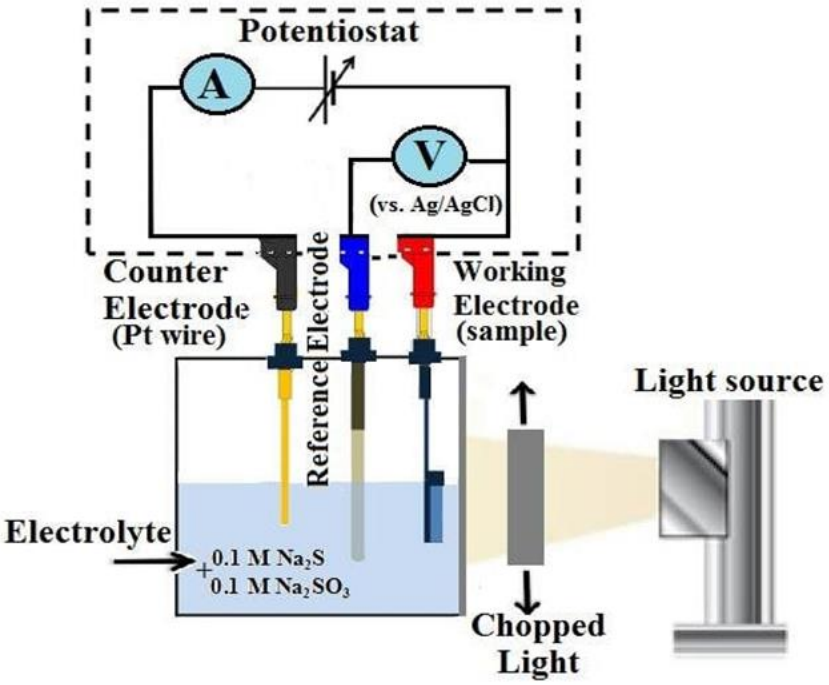

Figure 5. Schematic representation of a photoanode PEC cell showing an n-type semiconductor photoanode where oxidation occurs and hydrogen is produced at the counter electrode (Luo *et al*., 2012).

to or greater than the bandgap excite electrons from the valence band to the conduction band, creating electron–hole pairs.

The photogenerated holes migrate to the semiconductor surface, where they oxidise water molecules to produce oxygen. Meanwhile, the electrons travel through the external circuit to the counter electrode, where they reduce protons to form hydrogen. Common materials used for photoanodes include: (i) Titanium dioxide (ii)Zinc oxide (iii) Hematite. These materials are typically n-type semiconductors and are widely studied for solar water splitting due to their stability in aqueous electrolytes.

Photocathode PEC solar Cell (p-type semiconductor)

In a photocathode PEC cell, as shown in Figure 6, a p-type semiconductor functions as the working electrode and drives the reduction reaction. Upon illumination, electrons are excited to the conduction band and move toward the surface of the semiconductor.

At the semiconductor–electrolyte interface, these electrons reduce protons (H^+) to form hydrogen gas, while the holes move through the external circuit to the counter electrode, where oxidation reactions occur. Typical photocathode materials include: (i) Cuprous oxide (ii) Gallium phosphide (iii) Silicon. Among these materials, Cu_2O is particularly attractive because of its direct bandgap (~2.0 eV), strong visible light absorption, and low cost, making it suitable for solar hydrogen generation.

Tandem or dual PEC solar cell (advanced configuration)

A more advanced PEC system is the tandem PEC cell, which combines both photoanode and photocathode materials to improve solar energy conversion efficiency. In this configuration, two semiconductor electrodes with complementary band gaps, as shown in Figure 7, are used to maximise light absorption across the solar spectrum.

The tandem configuration offers several advantages: (i) improved solar spectrum utilisation, (ii) Higher photovoltage generation (iii) increased overall water splitting efficiency

For example, a tandem PEC device may combine: Cuprous oxide photocathode and Titanium dioxide photoanode

Regenerative PEC solar cell

A regenerative cell transforms incident light into electrical energy without producing any permanent chemical alteration. When photons with energies greater than the semiconductor band gap are absorbed, electron–hole pairs are created and subsequently separated by the electric field within the space-charge region. The electrons then migrate through the semiconductor bulk to the current collector and into the external circuit (Bard and Faulkner, 2001). Positive holes are driven to the surface where they are scavenged by the reduced form of the redox relay

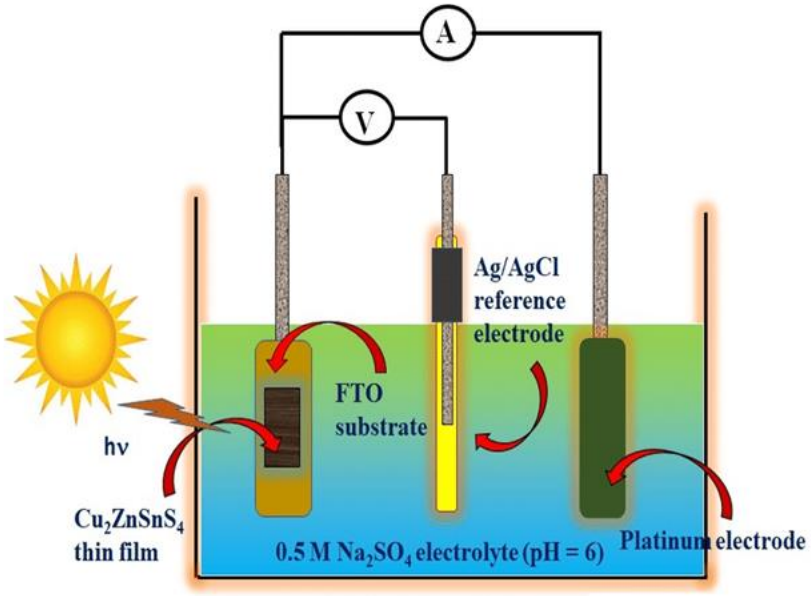

Figure 6. Schematic illustration of a photocathode PEC cell where a p-type semiconductor absorbs light and produces hydrogen at the electrode surface (Krishnan *et al*., 2020).

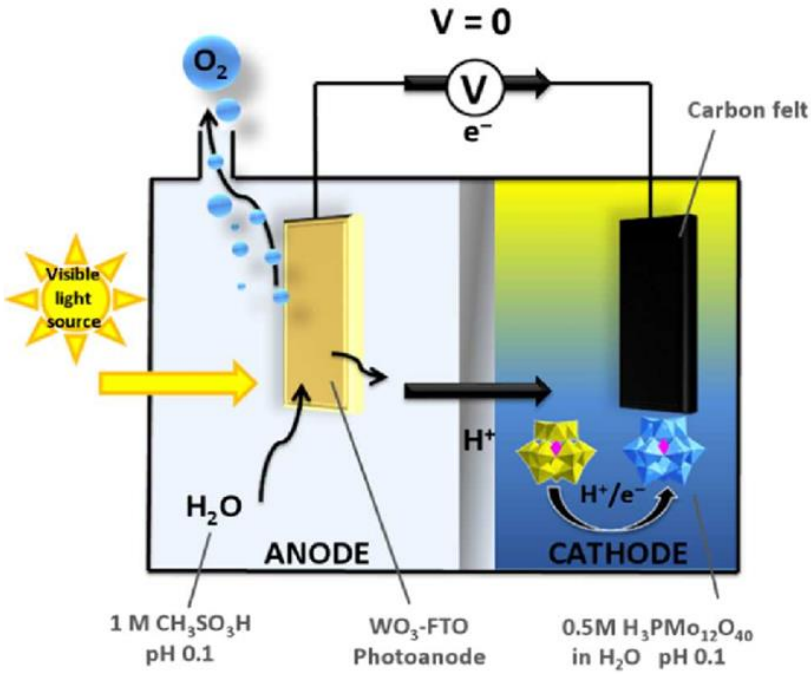

Figure 7. Schematic representation of a tandem PEC cell employing both photoanode and photocathode for efficient solar water splitting (Wang *et al*., 2020).

molecule (R), oxidising it: h^++R→O. The oxidised form O is reduced back to R by the electrons that re-enter the cell from the external circuit, as in Figure 8. Much of the work on regenerative cells has focused on electron-doped (*n*-type) II/VI or III/V semiconductors using electrolytes based on sulphide/polysulphide, vanadium (II)/vanadium (III) or I^2/I^- redox couples. Conversion efficiencies of up to 19.6% have been reported for multijunction regenerative cells

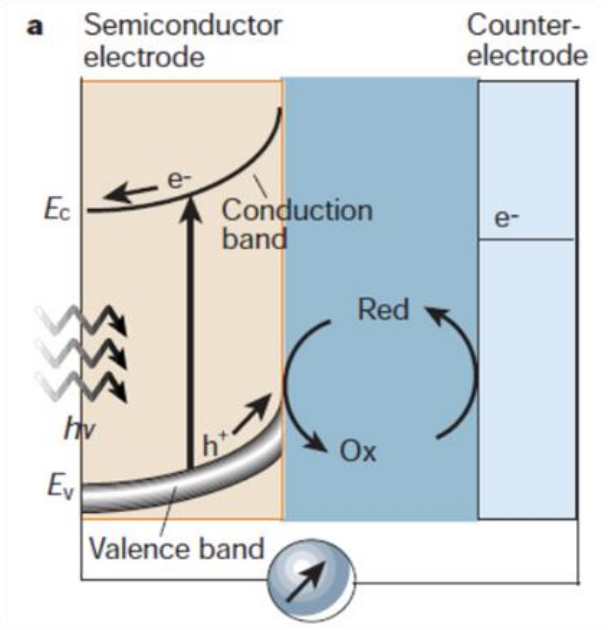

Figure 8. A regenerative PEC cell producing electric current from sunlight (Grätzel, 2001).

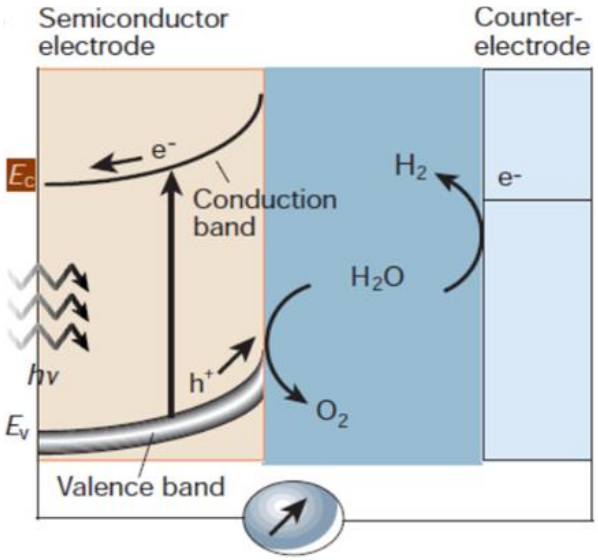

Figure 9. Photocatalytic PEC cell that produce chemical fuel (hydrogen) through water splitting (Grätzel, 2001).

(Hagfeldt and Gratzel, 2000).

Photocatalytic PEC solar cell

Photoelectrochemical cells function on a related concept to regenerative PEC cells but involve two distinct redox processes: one that interacts with photogenerated holes at the surface of the semiconductor electrode, and another that engages with electrons at the counter-electrode. In the illustrated case in Figure 9, water molecules are oxidised to oxygen at the semiconductor photoanode, while hydrogen is produced by reduction at the cathode (Lu *et al*., 2024). This results in the solar-driven splitting of water. Titanium dioxide has been the most commonly used semiconductor in these investigations, largely due to its pioneering application by Fujishima and Honda in the photolysis of water. Unfortunately, because of its large band gap (3–3.2 eV), TiO_2 absorbs only the ultraviolet part of the solar emission and so has low conversion efficiencies. Numerous attempts to shift the spectral response of TiO_2 into the visible, or to develop alternative oxides affording water cleavage by visible light, have so far failed (Hagfeldt and Gratzel, 2000).

Single-photoelectrode PEC cells

Numerous photoanode PEC cells have been reported in the literature, employing n-type metal oxide semiconductors such as TiO_2, Fe_2O_3, WO_3, $BiVO_4$, and ZnO, which are capable of driving oxidation reactions under illumination due to their stability under anodic conditions. While p-type semiconductors include Cu_2O, Si, and GaP, among others, which are capable of driving reduction reactions.

Single-photoelectrode PEC cells employ one light-absorbing semiconductor electrode, such as cuprous oxide (Cu_2O), coupled with a non-photoactive counter electrode, commonly Pt or carbon. When illuminated, Cu_2O absorbs visible light and generates electron–hole pairs, which are separated by the built-in electric field at the Cu_2O–electrolyte interface. Cu_2O is rarely used as a photoanode PEC cell due to recombination and overpotential from the surface defect. However, this challenge was solved by surface modification as shown in the work of Kafi *et al*. (2020), where a PEC cell containing 0.1 M sodium acetate aqueous solution with a platinum plate as the counter electrode and Ag/AgCl reference electrode was used for the PEC characterisation of the Cu_2O film electrodes. As a result of the surface modification by ammonium sulphide vapour treatment, n-Cu_2O films improve the PEC water splitting by 12-fold. Surface-modified n-Cu_2O films were able to produce a solar-to-hydrogen conversion efficiency of 1.47 % at the bias potential of 0.553 V vs RHE.

As a p-type semiconductor, Cu_2O typically functions as a photocathode, where photogenerated electrons migrate to the surface and participate in reduction reactions (e.g., hydrogen evolution), while holes are transported through the external circuit to the counter electrode to drive the complementary oxidation reaction. Owing to its suitable band gap, strong visible-light absorption, and earth abundance, Cu_2O is widely investigated in single-photoelectrode PEC configurations for solar fuel and electricity generation (Chen *et al*., 2024). Just like in the work of Choi *et al*. (2024) Cu_2O with NiMo as a catalyst was

employed as a photocathode for photocatalytic water splitting. Here, the catalyst was there to improve the efficiency and stability of the Cu_2O photocathode. Under simulated 1-sun illumination, the optimised NiMo catalyst achieved 93% of the performance of conventional Pt catalysts and maintained stable hydrogen production for over 20 hours. Heo *et al*. also presented a work on a Cu_2O photocathode PEC cell, whose surface was modified by graphene oxide (GO). The optimally deposited GO−Cu_2O photocathode exhibited a photocurrent density of −0.39 to −1.20 mA/cm^2, which was three times that of a photocathode composed of pristine Cu_2O. The surface decoration of Cu_2O with GO reduced charge recombination and improved the PEC water splitting performance.

Dual-photoelectrode PEC Cells (Tandem)

Dual-photoelectrode photoelectrochemical (PEC) cells, also called tandem PEC cells, are advanced PEC systems in which both electrodes are photoactive—that is, a photoanode and a photocathode simultaneously absorb light and generate charge carriers to drive chemical reactions, most commonly water splitting. Which we are going to see subsequently from previous literature.

Chen *et al*. (2023) developed an unprecedented standalone tandem cell that consisted of dual Cu_2O, which yielded a strong photovoltage, which contributed to carrying out unassisted photoelectrochemical water splitting using energy exclusively from the sun. Further deposition of the n–type TiO_x overlayer on p–type Cu_2O engineered into a wire–like nanostructure formed the core–shell p–n heterojunction that provided additional photovoltage to accelerate the hydrogen evolution reaction, and the circumvention of the severe charge accumulation at the Schottky Cu/n–Cu_2O back contact that well relaxed the associated kinetic overpotentials. The synergistic effect renders the solar–to–hydrogen efficiency of the tandem n–TiO_x/p–Cu_2O//n–Cu_2O device amounted to 0.32%, which is among the highest performance reported to date for the Cu_2O–based tandem PEC//PEC cells in the literature.

A self-driven tandem cell for overall water splitting composed of a p-Cu_2O photocathode modified with a thin Cu_2S layer connected to a n-ZnO/CdS nanowire photoanode is demonstrated in the work of Bai and Zhang (2017). By calculating the absorbed photon flux, it is proven that the two photoelectrodes are well-spectral-matched in the wavelength range of 300–800 nm. Compared with the bare Cu_2O photocathode, the Cu_2S modified Cu_2O counterpart has a higher photocurrent and a more anodic turn-on voltage due to the improved light absorption and the reduced charge transfer resistance. An apparent photocurrent was observed for the tandem cell at zero bias, corresponding to a photoconversion efficiency of 0.38%. Their results indicated that the tandem PEC cells based on connected semiconductor electrodes made from earth-abundant elements have promising application potential in overall solar water splitting.

Yin *et al.* (2019) designed an integrated solar water splitting tandem cell without external bias using a FeOOH modified TiO_2/$BiVO_4$ as a photoanode and p-Cu_2O as a photocathode in their study. An apparent photocurrent (0.37 mA/cm^2 at an operating voltage of +0.36 VRHE) for the tandem cell without applied bias was measured, which corresponds to a photoconversion efficiency of 0.46%. Besides, the photocurrent of FeOOH modified TiO_2/$BiVO_4$–Cu_2O is much higher than the operating point given by pure $BiVO_4$ and Cu_2O photocathode (~0.07 mA/cm^2 at +0.42 VRHE). These led to the establishment of FeOOH modified TiO_2/$BiVO_4$–Cu_2O two-electrode system whose current density-voltage curves were taken under AM 1.5G illumination. The unassisted photocurrent density is 0.12 mA/cm^{-2}, and the corresponding amounts of hydrogen and oxygen evolved by the tandem PEC cell without bias were reported to be 2.36 μmol/cm^2 and 1.09 μmol/cm^2 after testing for 2.5h. This aspect provided a fundamental challenge to establish an unbiased and stabilised photoelectrochemical (PEC) solar water splitting tandem cell with higher solar-to-hydrogen efficiency.

This review has examined the key material properties that make Cu_2O a viable candidate for photoelectrochemical solar cell applications. Various deposition and synthesis techniques reported in the literature were discussed, highlighting their influence on the structural, optical, and electrical characteristics of Cu_2O. In addition, different types and configurations of PEC solar cells were reviewed to provide a broader understanding of device operation and design. Collectively, these insights underscore both the potential of Cu_2O for PEC applications and the importance of optimised material processing and device engineering to achieve improved performance.

Table 1 summarises the deposition methods, PEC performance (photocurrent, efficiency, stability), and photoelectrode configurations from some literature. The reviewed studies demonstrate that surface engineering, buffer layer optimisation, and tandem photoelectrode configurations significantly enhance PEC water splitting performance. Graphene oxide decoration and sulphide surface treatment improved photocurrent density by reducing charge recombination and enhancing charge transfer. Dual buffer layers in Cu_2O photocathodes improved photovoltage through better band alignment. Tandem systems such as Cu_2O/Cu_2S–ZnO/CdS and FeOOH/TiO_2/$BiVO_4$–Cu_2O enabled self-driven water splitting under zero external bias. Among the reviewed works, the highest reported stability was achieved using the hybrid polyethyleneimine/TiO_2 protective layer, which maintained performance for over 400 h. Overall, the studies confirm that interface engineering and tandem integration remain effective strategies for improving PEC efficiency, photovoltage, charge separation, and opera-

Table 1. Summary of the deposition methods, PEC performance and photoelectrode configurations of some literature.

S/N	Author	Deposition / Fabrication Method	Photoelectrode Configuration	PEC Performance	Stability / Key Observation
1	Bae *et al*., 2025	Atomic Layer Deposition (ALD) of hybrid polyethyleneimine/TiO_2 protective layer	Polyethyleneimine/TiO_2 modified $BiVO_4$ and $Fe2O_3$ photoanodes	Improved hole transfer and enhanced optoelectronic performance for solar water oxidation	Excellent photostability over 400 h due to corrosion-resistant hybrid TiO_2 layer
2	Heo *et al*., 2023	Electrodeposition of graphene oxide (GO) onto Cu_2O photocathode	GO–Cu_2O/FTO photocathode	Photocurrent improved from −0.40 to −1.20 mA cm^{-2} at 0 V vs RHE; ~3× enhancement	GO reduced charge recombination and charge transfer resistance; stability still limited
3	Cheng *et al*., 2023	Fabrication of dual buffer layers (Ga_2O_3/ZnGeOx) with TiO2 protection	Cu_2O/Ga_2O_3/ZnGeOx/TiO_2 photocathode	Photovoltage increased to 1.07 V; onset potential improved by 0.16 V	Dual buffer layers improved band alignment and reduced interfacial barriers
4	Kafi *et al*., 2020	Electrodeposition followed by ammonium sulphide vapour surface modification	Surface-modified n-Cu_2O thin film electrode	12-fold PEC enhancement; STH efficiency of 1.47% at 0.553 V vs RHE	Surface modification reduced Fermi level pinning and surface recombination
5	Bai and Zhang, 2017	Cu_2S coating on Cu_2O and ZnO/CdS nanowire fabrication	Tandem Cu_2O/Cu_2S photocathode coupled with ZnO/CdS photoanode	Zero-bias photocurrent achieved; photoconversion efficiency of 0.38%	Cu_2S improved light absorption and reduced charge transfer resistance
6	Yin *et al*., 2019	FeOOH modification and TiO_2 coating on BiVO4 photoanode	FeOOH/TiO_2/$BiVO_4$ photoanode coupled with Cu2O photocathode	Tandem photocurrent of 0.37 mA cm^{-2}; unassisted photocurrent 0.12 mA cm^{-2}; efficiency of 0.46%	Improved charge separation and 5.3× higher photocurrent than bare $BiVO_4$/Cu_2O system

tional stability of Cu_2O-based photoelectrochemical systems.

CONCLUSION AND FUTURE PERSPECTIVES

The future success of Cu_2O in PEC solar cell applications will depend not on isolated material improvements, but on holistic optimisation of defects, interfaces, stability, and device architecture. With continued advances in surface passivation, tandem integration, and scalable fabrication, Cu_2O remains a strong candidate for cost-effective and sustainable solar fuel generation.

Despite these advantages, several fundamental challenges continue to limit the performance and stability of Cu_2O photoelectrodes. These include short minority-carrier diffusion lengths, high defect densities, and susceptibility to photocorrosion in aqueous environments.

Future research should focus on strategies aimed at improving charge carrier transport and enhancing material stability. Approaches such as surface passivation, protective oxide layers, catalyst integration, and hetero-junction engineering have shown significant promise in improving PEC performance.

In addition, the development of tandem PEC architectures incorporating Cu_2O with complementary semiconductors may enable efficient solar-to-hydrogen conversion without external bias. Continued progress in materials engineering, device design, and scalable fabrication techniques will be essential for realising the full potential of Cu_2O-based PEC solar fuel technologies.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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