

Photoelectrochemical and Structural Analysis of Electrodeposited CeO₂ Photoanodes

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Introduction

The growing demand for renewable energy solutions has led to the development of various photoelectrochemical systems that can harness solar energy for applications such as water splitting and energy conversion. Among the key components of these systems, photoanodes play a critical role in facilitating the photocatalytic processes that drive reactions like water oxidation. Metal oxide semiconductors, particularly Cerium Oxide (CeO₂), have gained attention as promising materials for PEC photoanodes due to their unique electronic and chemical properties, such as high oxygen evolution reaction activity, stability, and the ability to undergo reversible redox processes. CeO₂ is a wide bandgap material, which can be tuned for photoelectrochemical applications, offering not only good charge transport properties but also excellent surface chemistry for electron and hole generation. The combination of these characteristics makes CeO₂ an ideal candidate for use as a photoanode material in solar-driven PEC systems. The electrodeposition technique, which involves the deposition of CeO₂ films onto conductive substrates, offers an effective and cost-efficient method for preparing these photoanodes. By manipulating parameters such as deposition time, temperature, and electrolyte composition, the structure and performance of CeO₂ photoanodes can be fine-tuned for optimal PEC performance. This research explores the photoelectrochemical behavior and structural characteristics of electrodeposited CeO₂ photoanodes, aiming to provide insights into how the deposition process influences their efficiency and stability in PEC applications.

Description

Electrodeposition of CeO₂ thin films involves the application of an electric current to a solution containing cerium salts, which leads to the reduction of cerium ions onto a substrate, forming a thin oxide film. This method is widely used because it is simple, low-cost, and capable of producing uniform coatings with controlled thickness. The structure of the electrodeposited CeO₂ films is influenced by various factors, such as the composition of the electrolyte, the deposition potential, and the temperature during the deposition process. By adjusting these parameters, researchers can manipulate the crystallinity, morphology, and surface area of the CeO₂ films, which, in turn, affect their performance as photoanodes. For instance, higher deposition potentials tend to promote the formation of CeO₂ films with larger crystallites, which can improve charge transport but may reduce the surface area available for photocatalytic reactions. On the other hand, lower deposition potentials often yield more amorphous films, which may enhance the surface area but reduce the electrical

conductivity of the films. These structural changes are closely related to the photoelectrochemical performance of the CeO₂ photoanodes. A key factor in their performance is the ability of the material to efficiently separate and transport charge carriers generated under illumination. In CeO₂, the oxygen vacancy defects and Ce³⁺/Ce⁴⁺ redox couples contribute significantly to charge transfer processes, which influence the overall PEC activity.

The photoelectrochemical properties of CeO₂ photoanodes are primarily determined by their ability to drive the oxygen evolution reaction, a key step in solar-driven water splitting. Under illumination, the CeO₂ photoanode generates electron-hole pairs, with the photogenerated holes driving the oxidation of water to oxygen at the surface of the material. The efficiency of this process depends on several factors, including the electronic properties of the CeO₂ film, the concentration of oxygen vacancies, and the surface characteristics. The band gap of CeO₂, typically around 3.1 eV, makes it capable of absorbing UV light, though the material's ability to harness visible light is limited. Recent studies have shown that modifying the CeO₂ films, for example, by doping with metal ions or by controlling the size and distribution of oxygen vacancies, can extend the light absorption range into the visible spectrum, thus improving the overall PEC performance. Furthermore, the structural properties of the electrodeposited films play a significant role in their photoelectrochemical behavior. The morphology, surface roughness, and crystallinity of the CeO₂ films affect the density of active sites for the oxygen evolution reaction, as well as the charge transport pathways. Films with a higher surface area, for example, are likely to exhibit enhanced OER activity because they provide more active sites for the reaction. Similarly, well-aligned crystalline structures can facilitate better charge transport, reducing the recombination of charge carriers and improving the overall efficiency of the photoanode.

A critical aspect of photoelectrochemical performance is the stability of the photoanode material under operational conditions. For practical applications in solar energy conversion, a photoanode must not only be efficient but also durable under prolonged exposure to electrochemical conditions. The stability of CeO₂ photoanodes is influenced by factors such as the rate of surface degradation, the formation of undesirable surface states, and the susceptibility to corrosion or phase transformation. In the case of CeO₂, its ability to undergo reversible Ce³⁺/Ce⁴⁺ redox cycling is beneficial for its long-term stability, as it allows the material to recover from surface oxidation during PEC operation. However, high rates of water oxidation can lead to the formation of surface defects, which can negatively impact the material's performance. This challenge can be mitigated by optimizing the electrodeposition conditions to create films with a more robust structure, which can better withstand the electrochemical environment. Additionally, post-deposition treatments, such as annealing, can improve the crystallinity and stability of the films, enhancing their photoelectrochemical performance over time [1-5].

Conclusion

In conclusion, electrodeposited CeO₂ photoanodes exhibit promising photoelectrochemical and structural properties that make them suitable for use in solar-driven water splitting and other PEC applications. The electrodeposition method provides an efficient way to prepare CeO₂ films

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with tunable structural characteristics, which can be optimized for improved PEC performance. Key factors such as the morphology, crystallinity, and surface area of the films influence their ability to support efficient charge transfer and oxygen evolution reactions. Furthermore, the ability of CeO₂ to undergo reversible redox reactions contributes to its long-term stability under operational conditions, making it a promising candidate for sustainable energy applications. While there is significant progress in understanding the photoelectrochemical behavior of CeO₂ photoanodes, further research is needed to refine the electrodeposition process and improve the material's performance, particularly in enhancing its visible light absorption and reducing charge carrier recombination. With continued advancements in material design and deposition techniques, CeO₂-based photoanodes have the potential to play a crucial role in the development of efficient and cost-effective renewable energy systems.

Acknowledgment

None.

Conflict of Interest

None.

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