Reproducibility in Artificial Photosynthesis: A Case Study on SnO_2/Cu Photocatalysts

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Resumo/Abstract

RESUMO - Este estudo examina sistematicamente como as rotas de síntese e as condições de armazenamento afetam a confiabilidade dos dados de desempenho fotocatalítico de catalisadores SnO_2/Cu. Demonstramos que a especiação do cobre, a estabilidade das nanopartículas e a atividade na redução de CO_2 (CO_2RR) são significativamente influenciadas pela presença de etanol adsorvido — um subproduto frequentemente negligenciado nos métodos de síntese por química branda. Este etanol persiste na superfície dos catalisadores mesmo após processos de secagem ou tratamentos térmicos, alterando propriedades físico-químicas e impactando diretamente o comportamento fotocatalítico. Durante um período de armazenamento de duas semanas, o etanol permaneceu detectável, especialmente em catalisadores com alta carga de cobre, indicando fortes interações entre o etanol e os sítios de cobre. As análises pós-reação revelaram transições dinâmicas das fases do cobre: Cu^0 oxidou-se gradualmente a CuO durante o armazenamento em ambiente aberto, enquanto CuO foi reduzido a Cu_2O sob condições de CO_2RR — provavelmente associado à oxidação do etanol durante a exposição à luz. Também observamos lixiviação de cobre, redução fotoinduzida e reprecipitação sobre o SnO_2 em meio aquoso, sugerindo uma possível rota fotocatalítica in situ para a síntese de semicondutores de ampla banda proibida à base de Cu. Essas transformações indicam a presença de um ciclo redox ativo do Cu na superfície. Além disso, os resultados destacam o duplo papel do etanol como contaminante residual e como doador de elétrons reativo, ressaltando a importância de se considerar adsorvatos oriundos da síntese para garantir avaliações reprodutíveis e precisas de sistemas fotocatalíticos.

Palavras-chave: Redução de CO2; Cobre; Etanol; Fotocatálise; Estabilidade.

ABSTRACT - This study systematically examines how synthesis routes and storage conditions affect the reliability of photocatalytic performance data for SnO_2/Cu catalysts. We show that copper speciation, nanoparticle stability, and CO_2 reduction (CO_2RR) activity are significantly influenced by adsorbed ethanol—an often-overlooked byproduct of soft-chemistry synthesis. This ethanol persists on catalyst surfaces despite drying or thermal treatments, altering physicochemical properties and directly impacting photocatalytic behavior. Over two weeks of storage, ethanol remained detectable, especially in catalysts with high copper loading, indicating strong interactions between ethanol and copper sites. Post-reaction analyses revealed dynamic copper phase transitions: Cu^0 gradually oxidized to CuO in ambient storage, while CuO was reduced to Cu_2O under CO_2RR conditions—likely linked to ethanol oxidation during light exposure. We also observed copper leaching, light-induced reduction, and redeposition on SnO_2 in aqueous media, suggesting a possible in-situ photocatalytic route for synthesizing Cu-based wide band gap semiconductors. These transformations indicate the presence of a surface-active Cu redox cycle. Moreover, the results highlight ethanol's dual role as both a residual surface contaminant and a reactive electron donor, highlighting the importance of accounting for synthesis-derived adsorbates to achieve reproducible and accurate assessments of photocatalytic systems.

Keywords: CO2 reduction; Copper; Ethanol; Photocatalysis; Stability.

Intro

One of the main challenges of humankind is the mitigation of the anthropogenic CO_2. Since this stable molecule needs high energy input for its conversion, catalytic routes are required to decrease the thermodynamic energy barrier to convert CO_2 into products. However, the lack of reproducibility in the recent literature on Cu-based photocatalysts leads to doubtful conclusions about CO_2 conversion. Reliable results are as crucial as high-efficiency materials. Hence, it is important to consider that most soft-chemical synthesis pathways can result in residual hydrates and adsorbates, which may hinder or overestimate photocatalytic outcomes. In the latter case, these residues can act as sacrificial agents, providing electrons for the reduction reaction. It is important to highlight that, even in the event of contamination, these are still photocatalytic

processes but driven by the oxidation of these extraneous species (instead of water oxidation).

Therefore, herein, we propose a detailed study of SnO_2/Cu photocatalyst activity for CO_2RR under different storage conditions and its evolution through time as a model to understand the indirect effects that can impact the photocatalytic results. The copper oxidation states were tracked by a variety of techniques, enabling the investigation of redox transitions and leaching in water. Moreover, the catalytic discrepancies were deeply discussed and supported the copper redox reversibility and its possible interaction with the synthesis adsorbates.

Experimental

The detailed synthesis procedure and characterization techniques can be found in the published paper. (1)

Results and Discussion

Our investigation into SnO_2/Cu photocatalysts for CO_2 reduction revealed several critical insights regarding performance, stability, and reproducibility. Firstly, we observed that ethanol residuals originating from the synthesis protocol persist over extended periods—even after calcination and low-temperature drying—particularly in samples with higher copper content. These adsorbed ethanol species were stable up to two weeks at -18 °C and influence the photocatalytic activity by acting as supplementary electron donors, thus confounding interpretations of CO_2 conversion rates.

Concurrently, real-time monitoring of the catalyst structure indicates dynamic phase transformations within the copper component under both storage and reaction conditions. In the absence of light (uncontrolled storage), metallic Cu^0 gradually oxidizes to CuO. However, during photocatalytic CO_2 reduction, copper undergoes reduction to Cu_2O—a process facilitated by ethanol oxidation under illumination as depicted in **Figure 1**. This redox cycling suggests an active role for copper in electron management during catalysis.

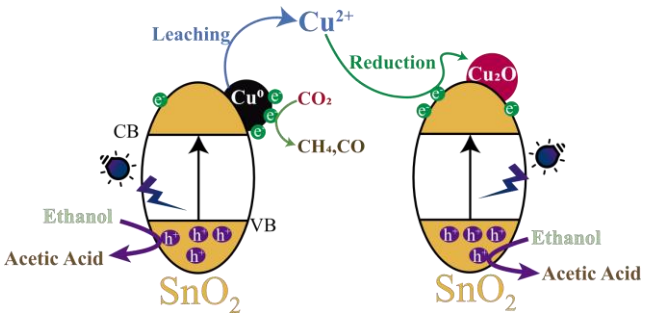

Figure 1. Mechanism proposed of the Cu2O reprecipitation over SnO2 during the CO2RR.

Furthermore, trace copper leaching and subsequent deposition on SnO_2 in aqueous media under light exposure imply a potential light-driven pathway for generating Cu-based semiconductor interfaces in situ. This finding supports the concept of active Cu redox cycling on SnO_2 surfaces, with implications for catalyst rejuvenation and lifetime.

Conclusions

Moreover, these findings highlight the critical importance of accounting for residual synthesis species and the dynamic nature of the catalyst's structural evolution when evaluating photocatalytic CO_2 reduction systems. The persistence of ethanol adsorbates over extended periods, even after cleaning and storage, introduces an unintended and often overlooked source of electrons that can substantially affect the apparent catalytic performance. Simultaneously, the copper phase demonstrates considerable structural flexibility, undergoing reversible transformations depending on the storage conditions and reaction environment. These redox-driven changes, strongly influenced by the presence of ethanol and light exposure, can significantly alter the catalyst's reactivity and stability. Therefore, it becomes evident that ensuring reproducibility in artificial photosynthesis research requires more than reporting CO_2 conversion rates. It necessitates rigorous post-synthesis treatment, meticulous control and documentation of storage parameters, and careful monitoring of the catalyst's physicochemical state prior to each experiment. Establishing such practices is essential to produce reliable, comparable data that can meaningfully advance the field of photocatalytic CO_2 reduction.

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Reference

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