Metal-Seeded SnO_2 Nanowires Synthesized by Coupled Vapor Deposition for CO_2 Electroreduction

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Resumo/Abstract

RESUMO - Este trabalho investiga a síntese e o desempenho catalítico de nanofios de SnO_2 semeados com metais para a redução eletroquímica de CO_2. As nanoestruturas de SnO_2 foram obtidas por deposição química em fase vapor (CVD) sobre substratos de papel de carbono, utilizando Au, Ag e Cu como metais sementes. As análises estruturais e morfológicas confirmaram a formação da fase cassiterita dos nanofios, com variações no comprimento em função do metal utilizado. Os testes eletroquímicos foram realizados utilizando eletrólitos de $KHCO_3$ e Na_2SO_4 em diferentes densidades de corrente. As amostras crescidas com ouro apresentaram atividade limitada, com eficiências faradaícas na faixa de 20–30% para a formação de formato em baixas correntes. Por outro lado, os nanofios crescidos com cobre demonstraram desempenho catalítico superior, atingindo eficiências de até 58% a –32 mA cm^{-2}, atribuídas às interações favoráveis entre Cu e SnO_2. As amostras crescidas com prata apresentaram desempenho comparável com ouro, com perdas significativas na seletividade para formato nas menores e maiores correntes testadas. Os resultados destacam o desempenho superior dos nanofios de SnO_2 crescidos com cobre, reforçando a relevância do cobre como promotor eficiente e economicamente viável em sistemas de redução de CO_2.

Palavras-chave: CVD, SnO_2, nanofios, CO_2RR, Cobre.

ABSTRACT - This work investigates the synthesis and catalytic performance of metal-seeded SnO_2 nanowires for the electrochemical reduction of CO_2. SnO_2 nanostructures were grown via chemical vapor deposition (CVD) on carbon paper substrates using Au, Ag, and Cu as seeding metals. Structural and morphological analyses confirmed the formation of cassiteritephase nanowires, with variations in wire length depending on the metal seed. Electrochemical tests were conducted using $KHCO_3$ and Na_2SO_4 electrolytes across a range of current densities. Gold-seeded samples exhibited limited activity, with Faradaic efficiencies toward formate in the range of 20–30% at low currents. Copper-seeded nanowires, on the other hand, demonstrated enhanced catalytic behavior, achieving Faradaic efficiencies up to 58% at –32 mA cm^{-2}, attributed to favorable Cu–SnO_2 interactions. Silver-seeded samples showed a comparable performance with gold, but with significant losses in formate selectivity at both the lowest and highest currents tested. These findings highlight the superior performance of Cu-seeded SnO_2 nanowires, reinforcing copper's relevance as a cost-effective and efficient promoter in CO_2 reduction systems.

Keywords: CVD, SnO2, nanowires, CO_2RR, Copper.

Intro

CO_2 emission and accumulation from anthropogenic sources are directly associated with climate change, urging the need for efficient catalytic processes to restore this inorganic molecule back to its natural cycle. The selective electrochemical CO_2 reduction reaction (CO_2RR) is among the most promising strategies to generate value-added chemicals and fuels from a non-fossil and renewable source. Formic acid and formate are important products to achieve, as both are considered good energy carriers or even H_2 suppliers in some reactions (1). In this context, Sn-based catalysts are highly efficient for the selective formation of these products, despite the disadvantages of overpotential and mass-transfer challenges faced in the electrocatalytic process.

SnO_2 nanowires employed in CO_2RR have been explored in a few studies, with the grain boundaries of their porous structure being identified as responsible for outperforming bare SnO_2 nanoparticles, particularly with outstanding selectivity towards formate (2,3). However, when synthesized via hydrothermal procedures, an additional step is required to disperse the powdered material onto working electrodes, which may compromise the material's stability and reproducibility in catalysis. Therefore, the chemical vapor deposition (CVD) method appears highly suitable for the seed-assisted growth of SnO_2 nanowires on porous substrates.

These nanowires are typically grown via the vapor–liquid–solid (VLS) mechanism, wherein a metallic source droplet—formed under specific pressure and temperature conditions—is supersaturated by a volatile phase of the precursor. This interaction induces nucleation of a new solid phase, which grows away from the substrate, typically featuring a characteristic metal tip at the end of each wire (4).

In this context, various metals can be employed as "seeds" to modify the catalyst's electronic properties (5) and act as co-catalysts to enhance catalytic activity. Hence, this ongoing work investigates the chemistry of SnO_2 nanowire (NW) formation and their properties as catalysts to overcome the energy barriers associated with the conversion of stable CO_2 molecules

Experimental

Catalysts Synthesis

The materials were deposited on Carbon Paper (CP) substrates by the thermal Coupled Vapor Deposition (CVD) method. This procedure consists of custom-made quartz and borosilicate glassware apparatus connected to a Leybold turbo molecular pump vacuum. A thermocouple is connected to a graphite holder where the substrate is glued on with Ag paste. The heating occurs inductively by a high frequency generator coil around a quartz tube.

The substrate reactivity was controlled by distinct sputtering loads (Quorum, Q150T ES) of Au, Ag and Cu, aiming to make a seeded growth of the SnO_2 nanowires. The CVD system was operated at high vacuum ($10^{-5} – 10^{-6}$ mbar) with deposition temperature of 750 °C. $Sn(O^tBu)_4$ was previously synthesized (6) and used as metal precursor. The sublimation temperature was controlled by a thermostatic bath under 27°C during the 1.5 h deposition. After the synthesis, the materials were sprayed with a Nafion 2% solution in methanol by spray coating in a hot plate.

Characterization

The catalysts were characterized by a thin film X-ray diffraction (XRD, STOE-STADI MP, Mo-source) to investigate the phases of the obtained depositions. Optical images to evaluate the nanowires morphologies and length were obtained by an optical microscope (Nikon Eclipse LV 150) and the Scanning Electron Microscopy (Zeiss Sigma 300 VP RISE) confirmed its formation.

Catalysis

The electrochemical CO_2 reduction reactions (CO_2RR) were performed in a three-electrode H-type cell configuration, consisting of a platinum counter electrode, a saturated Ag/AgCl reference electrode, and a working electrode to which the carbon paper substrate was attached. Potassium bicarbonate ($KHCO_3$) and sodium sulfate (Na_2SO_4) were employed as electrolytes. All electrochemical measurements were carried out using a potentiostat/galvanostat (VersaSTAT 4A, Princeton Applied Research).

The liquid-phase products were quantified by nuclear magnetic resonance (NMR) spectroscopy using a Bruker Neo 400 MHz instrument. Deuterium oxide (D_2O) was used as the solvent, with dimethyl sulfoxide (DMSO) as the internal standard. The Faradaic Efficiency was calculated using the following equation:

$$(n * F * mol_{formate} \, / \, I * t) * 100\%$$

where n is the number of electrons required to produce one mole of formate from CO_2 (n = 2), F is the Faraday constant (96485 C mol^{-1}), I the current (A) and t the time (s).

Results

Obtained CVD depositions

The CVD deposition was confirmed by the X-ray diffraction patterns of the samples (**Figure 1**), confirming the formation of the cassiterite phase of SnO_2 (JCPDS #411445), superimposed on the characteristic peaks of the carbon paper (CP) substrate. Notably, variations in the amount of sputtered gold did not lead to noticeable changes in the diffraction peaks.

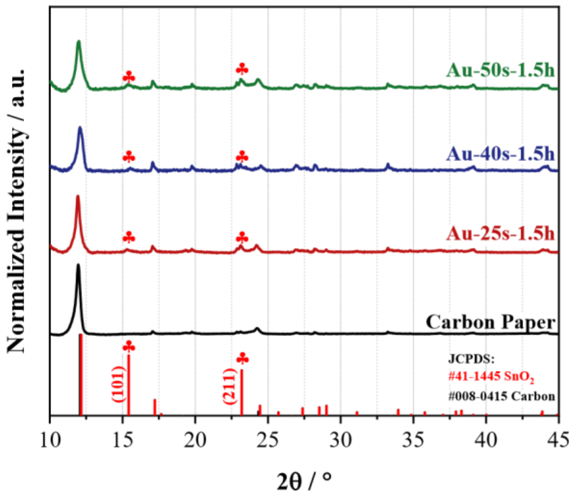

Figure 1. XRD patterns of SnO2 nanowires grown by different amounts of sputtered Au on Carbon Paper

Consistent with previous studies (7,8), scanning electron microscopy (SEM) revealed the successful growth of SnO_2 nanowires. These nanowires appear uniformly distributed across the entire surface of the CP fibers, as illustrated in **Figure 2A**. The main morphological difference among the samples lies in the size of the Au tips at the ends of the nanowires, which becomes evident when comparing the magnified images corresponding to sputtering durations of 40 s and 25 s (**Figure 2C-D**).

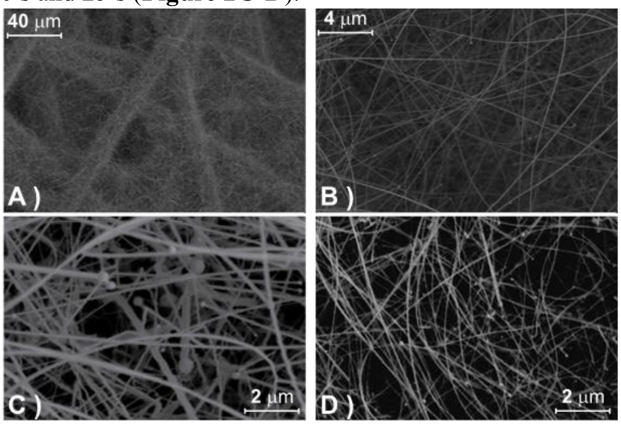

Figure 2. SEM images of (A-C) SnO2 nanowires grown by 40 s sputtered Au at distinct magnifications, and (D) the 25 s sputtered Au sample.

On the other hand, compared with the Au-seeded SnO_2 NWs, Cu- and Ag-seeded materials were obtained after several experiments to find the optimum sputtering rate and promote nanowire formation (results not shown). However, these structures exhibited shorter lengths, as roughly observed by optical microscopy at the same zoom level (1000x, **Figure 3).** This phenomenon can possibly be related to the CVD synthesis conditions, which were optimized for the Au-seeded SnO_2 nanowires. According to the VLS mechanism, the metal droplet must be formed and react with the volatile phase of $Sn(OtBu)_4$ to produce SnO_2 (4). Therefore, the solubility differences among the metal species and precursors under these conditions may influence the growth rate.

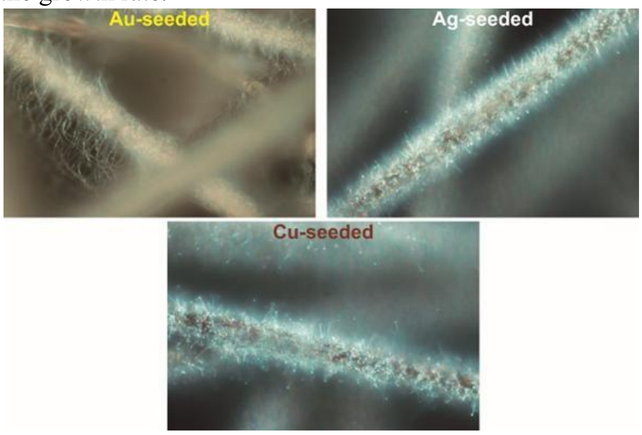

Figure 3. Optical microscope images with a 1000x magnification of metal-seeded SnO_2 nanowires on Carbon Paper substrate.

The XRD of these materials (**Figure 4**) evidence that the relative peak intensity is higher in Ag-seeded samples, even though the length of the nanowires were smaller. Further characterization is still required to rationalize these differences; however, these catalysts were more clearly compared based on their catalytic performance.

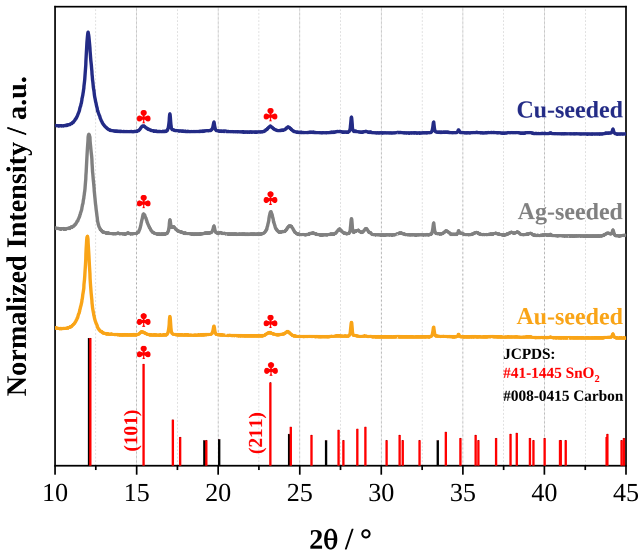

Figure 4. XRD patterns of SnO2 nanowires grown by Au, Ag and Cu on Carbon Paper

CO_2 reduction reaction

The Au-seeded materials showed low Faradaic efficiency towards formate in reactions conducted at 4 mA cm^{-2} for 1 hour, achieving values in the range of 20–30% across a variety of experiments using $KHCO_3$ as the electrolyte under similar current density conditions (**Figure 5,** right y-axis). The choice of these materials for the 1-hour catalytic reaction was mainly intended to track the effect of gold based on a well-established synthesis procedure. The formate yield after 1 hour of reaction showed similar results (**Figure 5,** left y-axis), indicating that varying Au loadings do not significantly affect the selectivity toward formate at those conditions.

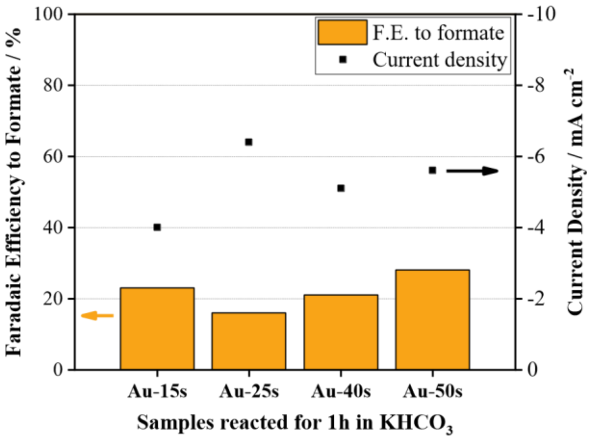

Figure 5. Catalytic screening of Au-seeded SnO_2 nanowires with similar current densities for 1 hour.

Since the quantity of the sputtered metal did not affect the results at low currents, the main objective was redirected towards obtaining nanowires composed of distinct metals that exhibit similar electronic properties and belong to the same group of the periodic table. Although the amount of these metals may vary in the formation of nanowires, it is possible that this variation will not alter the catalytic performance, as observed with gold.

Under these circumstances, Na_2SO_4 was chosen as a new electrolyte to boost the performance of SnO_2 towards formate, as it is known to promote superior activity (9). The catalysts were tested under different fixed currents to observe the yield evolution toward formate in Na_2SO_4. The Au-15 s sample was chosen to allow comparison with the other metal-seeded SnO_2 catalysts, and the results toward formate showed interesting current-dependent Faradaic efficiencies (**Figure 6**). Higher currents favored CO_2RR in Na_2SO_4 up to –32 mA cm^{-2}, reaching formate values of up to 58% for the Cu-seeded samples.

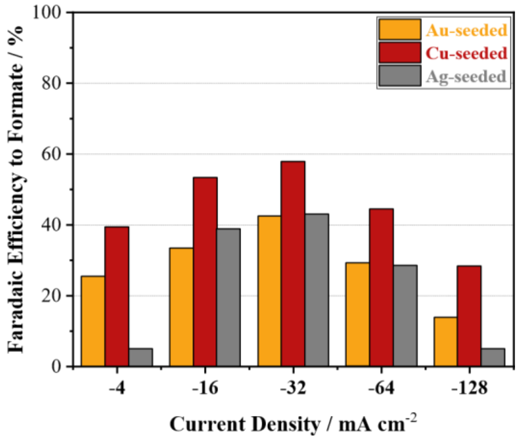

Figure 6. Current screening CO_2RR of metal-seeded SnO_2 nanowires

Understanding its activity across a wide range of current densities is an interesting starting point for further evaluating its stability. As shown in **Figure 6**, both Au and Ag displayed similar activities, though inferior to copper, suggesting enhanced Cu–SnO_2 interactions during CO_2RR. This interaction can suppress the Hydrogen evolution reaction (HER) as studied by Ye *et. al.* (10). However, at higher current densities, the selectivity may have shifted toward H_2 production for all materials.

Preliminary gas-phase analysis showed no formation of any C_1^+ products; only H_2 was detected, although it has not yet been quantified for a complete Faradaic efficiency profile.

Interestingly, although silver shares many properties with gold (5), the Ag-seeded materials exhibited similar catalytic results only at intermediate current densities; at both the lowest and highest currents tested, the selectivity toward formate dropped significantly, for reasons that remain unclear and may involve complex surface or electronic effects. A higher crystallinity of this sample was observed by XRD (**Figure 4**), which may have decreased the surface area of active catalytic sites towards formate, but further investigation is required to understand how the same material is comparable to gold at higher currents.

On the other hand, the Cu-seeded materials show significantly higher relevance. Copper is highly available and is considerably cheaper than these noble metals. Therefore, studying the interactions between SnO_2 and Cu, as well as their stability, is important for understanding how these materials perform in CO_2RR. Further work exploring the electronic properties, surface interactions, reproducibility, and the specific role copper plays in shaping the reaction pathway could offer key insights into improving their efficiency and stability. These studies will help deepen our understanding of copper-based catalysts and guide future developments in CO_2RR.

Conclusions

This study investigated metal-seeded SnO_2 nanowires for CO_2 reduction, focusing on gold (Au), silver (Ag), and copper (Cu). Gold showed limited activity at low currents, with a low Faradaic efficiency toward formate. Copper, however, exhibited significantly better performance, with enhanced Cu–SnO_2 interactions leading to higher formate production at moderate currents. Interestingly, while silver displayed similar catalytic activity to gold at intermediate currents, its selectivity toward formate dropped significantly at both the lowest and highest currents, suggesting complex surface or electronic effects that warrant further exploration. Among the three, copper emerges as the most promising candidate for continued investigation due to its superior performance and practical advantages.

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