Development of Ultrathin Bi-based Electrocatalysts for the Conversion of CO_2 to Formic Acid.

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ABSTRACT

The electrocatalytic reduction of CO_2 to formic acid, powered by renewable energy sources, represents a promising approach to mitigate the climate changes and satisfy energy demand. The development of electrocatalyst with high activity, selectivity and stability is the main challenge in this field. In this investigation, ultrathin two-dimensional Bi metalenes with a high exposure of the active sites were developed via inert atmosphere synthesis. The characterization of the bismuthene samples demonstrated that increasing the synthesis temperature simultaneously optimizes morphology, crystallinity, and chemical purity. From this perspective, SEM and TEM images reveal ultrathin, hexagonal sheets with minimal overlap; HRTEM confirms regular lattice fringes consistent with β-Bi planes and indicative of high atomic order; while XRD exhibits sharp peaks without secondary phases and a high degree of crystallinity. Furthermore, FTIR confirms the absence of Bi–O bonds, attesting to metallic purity, and Raman spectroscopy records shifts to longer wavelengths and narrowing of the E_g and A_{1g} bands with increasing temperature, signaling sheet thinning and defect reduction. This convergence of evidence underscores the critical role of thermal control in obtaining homogeneous, highly crystalline BiNSs. Finally, the electrochemical CO_2 reduction performance was evaluated, the Bi-150 °C sample exhibited a current density of ~130 mA·cm^{-2} and a faradaic efficiency of 68.15% at −1.0 V vs. RHE, performance attributed to the synergy between specific crystal facets and an increased density of active sites and future work will investigate Sb and SnO_2 in flow cells.

Palavras-chave: CO_2 Electroreduction, Catalysis, Metallenes, 2D Materials

Introduction

The intensification of fossil fuel use has led to a significant increase in carbon dioxide (CO_2) emissions, resulting in its accumulation in the atmosphere and causing environmental imbalances such as global warming and extreme climate events [1]. In response to this challenge, the electrochemical reduction of CO_2 (CO_2RR) has emerged as a promising route for converting carbon into fuels and value-added chemicals, contributing not only to emission mitigation but also to the advancement of clean energy technologies [2]. Among the various catalytic materials investigated for CO_2RR, bismuth (Bi)-based materials have stood out due to their high selectivity toward formic acid production, low toxicity, and natural abundance in the Earth's crust[3]. Currently, the engineering of ultrathin two-dimensional (2D) nanomaterials, such as Bi metallenes, offers new perspectives for improving catalytic activity, owing to their large surface area, abundance of exposed active sites, and tunable electronic properties [4]. In this work, we synthesized and characterized ultrathin 2D bismuth metallenes to understand how their structural and physicochemical properties influence performance in CO_2 electroreduction. The catalytic activity and selectivity of Bi metallenes were evaluated in aqueous media, with a focus on the correlation between structure and electrocatalytic performance.

Experimental

Synthesis of Bismuth Nanoparticles (BiNSs).

Bismuth nanoparticles were synthesized by dissolving $Bi(NO_3)_3 \cdot 5H_2O$ in 2-ethoxyethanol, followed by sonication and vigorous stirring under argon at 100 °C in a glycerol bath. A $NaBH_4$ aqueous solution was added dropwise as reducing agent. The resulting black precipitate was filtered, washed, and dried at 60 °C. The procedure was repeated at 120 °C and 150 °C, and the samples were labeled Bi-100, Bi-120, and Bi-150.

Characterization

The bismuth (Bi) samples were initially characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to evaluate their morphology. The crystalline structure was investigated using X-ray diffraction (XRD), while infrared spectroscopy (FTIR) and Raman spectroscopy were employed to analyze the chemical bonds and to verify the presence of possible surface oxides. After characterization, the materials were applied as cathodes in a flow electrochemical cell for the CO_2 reduction reaction (CO_2RR), using 1.0 M KOH as the electrolyte. Gaseous products were analyzed by gas chromatography with a thermal conductivity detector (GC-TCD), and liquid products were identified and quantified by high-performance liquid chromatography (HPLC).

Results and Discussion

The combined analyses of SEM, XRD, Raman, and TEM/HRTEM of the bismuth samples synthesized at different temperatures indicate that increasing the temperature promotes higher crystallinity, particle growth, and structural organization. SEM images (Figure 1) reveal a spongy and porous morphology with denser agglomerations at higher temperatures, indicating progressive sintering. XRD diffractograms (Figure 2A) confirm the formation of the rhombohedral Bi phase (JCPDS 96-231-0890), with more intense and sharper peaks as the temperature increases, evidencing greater crystalline order. Raman spectroscopy (Figure 2B) shows characteristic vibrational modes of Bi (Eg, A1g, and 2Eg), with increasing intensities and sharper definition in Bi-150, suggesting lower structural disorder. Complementarily, TEM and HRTEM images (Figure 3) reveal lamellar structures and interconnected nanorods, with well-defined interatomic planes in monocrystalline regions, corroborating the high crystallinity and structural coherence observed in the other analyses. These results are consistent with the reports of Wang et al. (2016), reinforcing the crucial role of temperature in the structural quality of the synthesized bismuth. These structural factors directly influenced the electrocatalytic performance, as Bi-150 showed the highest efficiency, with a current density of ~130 mA-cm^{-2} (Figure 4A) and a faradaic efficiency of 68.15% for HCOOH at -1.0 V vs. RHE, (Figure 4B) a result attributed to its high crystallinity and greater exposure of active facets. In contrast, Bi-100, with a more disordered structure, favored the formation of H_2. These data highlight the importance of structural control in optimizing electrocatalytic performance.

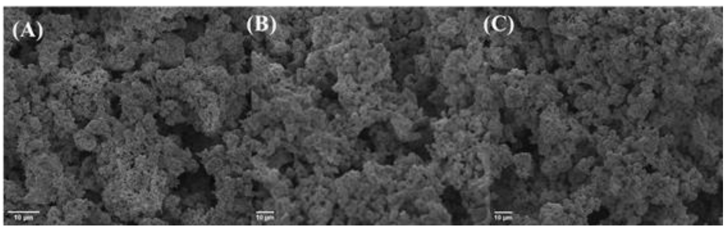

Figure 1. SEM image of the Bi sample synthesized at 60°C, 100°C and 150°C.

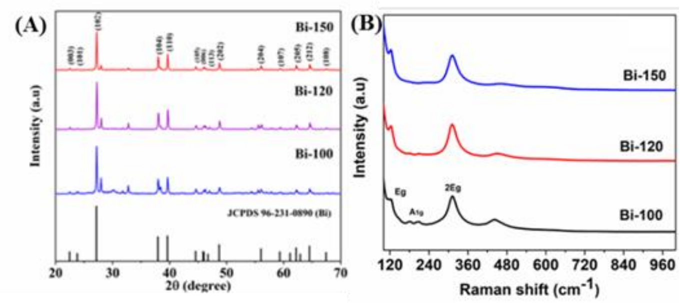

Figure 2. X-ray diffraction (A) Raman spectrum (B)

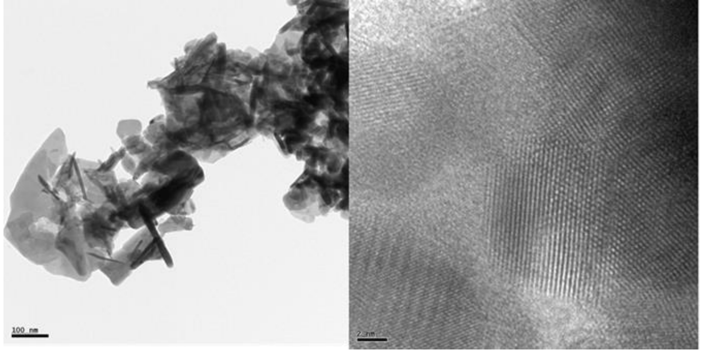

Figure 3. TEM and HRTEM image

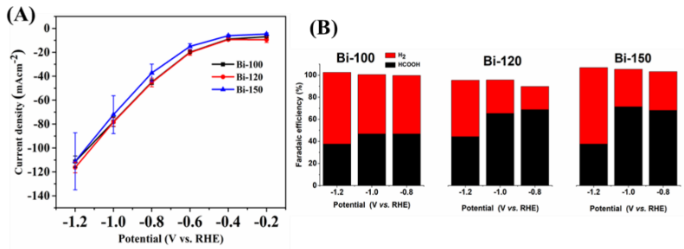

Figure 5. (A) Polarization curves, (B) Faradaic efficiency for BiNSs.

Conclusions

The results indicate a strong dependence between the synthesis/treatment conditions and the structural properties of BiNSs

Faradaic efficiency is influenced by both the applied potential and the electrode material.

Bi-150 showed high electrocatalytic performance in the reduction of CO_2, with a current density of ~130 mA-cm^{-2} and a faradaic efficiency of 68.15% for the production of HCOOH at -1.0 V vs. RHE.

Acknowledgments

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