

Sustainable ammonia synthesis using graphene/MnFe₂O₄-based gas-diffusion electrodes via photo-, electro-, and photo-electro-catalytic routes

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Significance and Relevance

In this work, dinitrogen (N₂) molecule was converted to ammonia (NH₃) by electro-catalytic (EC), photo-catalytic (PC) and photo-electro-catalytic (PEC) approaches, using novel gas-diffusion electrodes (GDEs) based on MnFe₂O₄ or graphene (GH)-MnFe₂O₄ semiconductors supported on gas diffusion layers (GDLs). Catalytic tests were performed in an optimized (photo-)reactor operating at room temperature and atmospheric pressure. The GH-MnFe₂O₄/GDL electrode achieved an outstanding NH₃ yield of 7.3 ppm h⁻¹ and Faradaic efficiency of 90% at -0.2 V vs. RHE in PEC systems, demonstrating significant potential as an alternative to the energy-intensive Haber-Bosch process for nitrogen reduction under ambient conditions.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization, Fundamental advances in understanding catalysis. Oral preferred or Short Oral / Poster

Introduction and Motivations

Large-scale ammonia production relies predominantly on the Haber-Bosh process, which operates under severe conditions (400-600 °C and 20-40 MPa)¹. In contrast, emerging technologies such as photocatalytic (PC), electrocatalytic (EC), and photoelectrocatalytic (PEC) methods offer promising pathways for more sustainable and decentralized NH₃ production². The efficiency of these processes depends critically on factors like the electronic structure, material composition, semiconductor morphology, and the separation efficiency of photoinduced charge carriers. Spinel ferrites (MFe₂O₄ where M = Fe, Co, Ni, Mg, Mn, Cu, Zn) have garnered attention due to their unique optical properties –narrowed band gaps and enhanced visible light absorption– attributed to the d-d transitions influenced by oxygen ligand arrangements around Fe ions. Furthermore, substrate porosity plays a crucial role in facilitating N₂ reduction to NH₃.

Materials and Methods

Graphene (GH)-manganese ferrite (MnFe₂O₄) was synthesized by dissolving MnCl₂·6H₂O and FeCl₃·6H₂O salts in 100 mL of water enriched with Natural Organic Matter (NOM). The pH was adjusted to 0.5 using a 5 M HCl aqueous solution, followed by the addition of graphite. The mixture was basified to a pH of 10.5, dried at 100 °C for 48 h, washed with deionized water, and redried at 60 °C for 72 h. MnFe₂O₄ catalyst was synthesized using the same methodology without graphite dispersion. The catalysts were deposited on GDLs via drop-coating method. For this, 10 mg of powder, 500 μ L of isopropanol and 500 μ L of water were mixed and sonicated for 1 h. The resulting ink was uniformly deposited on the GDL surface (loading: 1 mg cm⁻²) and then dried at room temperature. Commercial GDL substrates with different porosity were used to study the influence of diffusion phenomena on catalytic reactivity.

Nitrogen reduction tests were performed at ambient conditions in a custom three-electrode flow electrochemical cell equipped with a quartz window³. Ammonia was quantified by ion chromatography (IC) and UV-Vis spectrophotometry⁴.



Results and Discussion

Figure 1a compares the PEC performance of MnFe₂O₄/GDL and GH-MnFe₂O₄/GDL electrodes under applied potentials ranging from -0.2 V to -0.6 V vs. RHE. For the MnFe₂O₄/GDL electrode, NH₃ production increases with applied potential, reaching a maximum of around 3 ppm at -0.4 V. The Faradaic Efficiency (FE) is higher at low voltage, and then decreases significantly with the applied potential, dropping from 36% at -0.2 V to 0.11% at -0.6 V. In contrast, the GH-MnFe₂O₄/GDL electrode, incorporating graphene into its structure, exhibits superior performance. At -0.2 V, it achieves an NH₃ concentration of 7.3 ppm, with an outstanding FE of 90% at -0.2 V. As illustrated in Figure 1b, the NH₃ formation rates are quite different across the three reduction processes, i.e. PC, EC, and PEC. The highest performance is observed with the GH-MnFe₂O₄/GDL when this electrode is used as photoelectrode in a PEC apparatus. This higher efficiency was due to the adsorption capacity of the N₂ molecule on semiconductors containing empty or half-filled *d* orbitals, such as the manganese ions present in the GH-MnFe₂O₄ structure.



Figure 1 a) Production of NH_3 for $MnFe_2O_4/GDL$ and $GH-MnFe_2O_4/GDL$ electrodes a) at different applied potentials and b) with different catalytic approaches (photo-catalytic -PC, electro-catalytic -EC, and photo-electro-catalytic -PEC).

The influence of substrate porosity was also investigated by testing different GDLs with varying pore size to enhance diffusion properties and overcome the issue of low N_2 solubility in aqueous media. Results demonstrate that substrate porosity plays a critical role NH_3 production, with higher porosity leading to increased NH_3 production rate.

References

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