

Electrochemical conversion of CO₂ (CO₂RR) powered by intermittent renewable energy sources has emerged as an economically viable route to the conversion of CO₂ into usable chemicals and fuels. Recent studies have shown that nitrogen-doped graphene-based (sp² rich) nanostructured materials and nitrogen-doped diamond materials (sp³ rich) show excellent performance towards electrochemical CO₂ reduction. However, there are no studies that probe hybrid carbon materials between diamond and graphitic extremes for CO₂RR. Therefore, in this work, carbon films were synthesized by microwave-assisted chemical vapor deposition by varying sp³ and sp² carbon contents while maintaining the same nitrogen content. Our results confirm that the host structure of nitrogen dopants is extremely crucial for the catalytic activity and enhanced CO₂RR performance in sp²-rich electrode over the sp³-rich electrode. In the nitrogen-doped sp³-rich electrode, the Faradaic efficiency (FE) of CO generation is limited to 20% and the hydrogen evolution reaction was dominant. However, in the nitrogen-doped sp²-rich electrode, shows CO FE up to 81%, with excellent activity and selectivity at -1.10 V vs. RHE. Detailed micro and the nanostructure of each catalyst were evaluated by scanning electron microscope and transmission electron microscope techniques, respectively. X-ray photoelectron spectroscopic measurements were used to characterize the nitrogen content, nitrogen configuration and sp²/sp³ ratio of each catalyst. Furthermore, The important role of the host structure and the potential catalytic sites were evaluated by density functional theory (DFT) calculations. Thus, this study closes the structure-property relation gap between the nitrogen-doped sp³ rich and sp²-rich materials for electrochemical CO₂ reduction.