

pubs.acs.org/JPCC

## Boosting CO<sub>2</sub> Activation and Reduction by Engineering the Electronic Structure of Graphitic Carbon Nitride through Transition Metal-Free Single-Atom Functionalization

Published as part of The Journal of Physical Chemistry virtual special issue "Early-Career and Emerging Researchers in Physical Chemistry Volume 2".

Syed Fozia, Afshana Hassan, Showkat Ahmad Reshi, Priti Singh, Gulzar A. Bhat, Mudit Dixit,\* and Manzoor Ahmad Dar\*



ABSTRACT: In recent years, electrochemical reduction of CO<sub>2</sub> to high-value chemicals and fuels using carbon-based two-dimensional materials has emerged as a promising alternative for reducing the atmospheric CO<sub>2</sub> levels and addressing global energy challenges. However, rationally tuning the electronic structure of these materials for optimizing their catalytic performance remains a great challenge. Herein, using first-principles simulations, we investigate the electronic and catalytic properties of the single atom (SA)-functionalized graphitic carbon nitride (g-C2N) monolayer for CO<sub>2</sub> activation and reduction. Our results reveal that SA substitution leads to effective activation and capture of



CO2. In-depth electronic structure analysis based on the crystal orbital Hamilton population (COHP) and integrated density of states unraveled the atomic-level details of the interaction of CO<sub>2</sub> with the SA-substituted monolayers. Furthermore, the simulated reaction pathways demonstrate that the Al-SAC is highly proficient for CO2 conversion to HCOOH, whereas the B-SAC reduces  $CO_2$  to  $CH_3OH$  with a record-low limiting potential of -0.45 V. In addition, the Al- and B-SACs effectively suppress the competitive hydrogen evolution reaction (HER), making CO2 reduction highly selective on these catalysts. Furthermore, the small CH<sub>1</sub>OH desorption energy of 0.73 eV on the B-SAC makes it a suitable candidate for CO<sub>2</sub> reduction to methanol. Thus, our findings not only provide theoretical guidance for accelerating the design of new and promising catalysts for CO<sub>2</sub> reduction but also elucidate the structure-activity correlations.

## 1. INTRODUCTION

Continuous use of fossil fuels and rapid industrial growth have led to record-high CO2 emissions during the past decade. The increased concentration of CO2 in the atmosphere has caused an average increase in global temperature by 0.80 °C during the past few decades, leading to global warming and other serious environmental problems.1 Thus, attempts have been made on international platforms such as the Paris agreement to reduce CO<sub>2</sub> emissions either by reducing the dependence on fossil fuels through the development of alternative energy sources<sup>2-4</sup> or by utilizing and converting CO<sub>2</sub> to value-added products.5-8 However, utilization and conversion of CO2 are a challenging task due to the centrosymmetric nature, high ionization potential, low electron affinity, and strong bonds of the CO<sub>2</sub> molecule.<sup>9-12</sup> Various approaches differentiated on the basis of the source of energy required for activating the inert CO2 molecule such as radiation,13 thermal,14 photoand electrocatalytic methods<sup>16</sup> have been well catalytic, tested for converting CO2 to different value-added products.

Out of the different methods, electrocatalytic conversion of CO2 has received great attention due to two main advantages: first, water can be used as a proton source and second, it can be carried at room temperature.<sup>17</sup> The electrocatalytic reduction of CO2 suffers from the disadvantage of a competitive hydrogen evolution reduction (HER).18,19 Thus, efficient electrocatalysts which not only promote CO2 reduction but also possess the ability to suppress the HER need to be designed. Traditionally, noble metal-based electrocatalysts of Cu, 20-22 Ag, 23-25 and Au<sup>26-28</sup> have been employed for the CO2 reduction reaction (CO2RR). Although much progress

Received: January 17, 2023 Revised: April 26, 2023 Published: May 10, 2023



ACS Publications