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Preview

Electrocatalysis over Graphene-Defect-Coordinated Transition-Metal Single-Atom Catalysts

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The family of single-atom catalysts dispersed in defective graphene matrices are now of increasing interest for a wide range of reactions given their tunable coordination environments and electronic structures. In this issue of *Chem*, Yao and co-workers demonstrate atomic Ni@graphene catalysts for water splitting via different active motifs.

Transition-metal single-atom catalysts (SACs) are well known for their superb specific activity arising from the maximum atom efficiency, as well as their low-coordinated nature for the investigation of surface chemistry. Because a single atom typically represents a large surface free energy, metal oxide supports that have strong interactions with single atom species are generally used to better anchor and/or disperse SACs from aggregation. So far, these SACs have been widely reported in CO preferential oxidation,[1] aldehyde hydrogenation,[2] methane partial oxidation,[3] and so on.

Despite these continuous efforts with metal-oxide-supported SACs, defective graphene matrices have recently been of particular interest as SAC hosts in electrocatalysis because of their large surface area, high electron conductivity, chemical stability, and abundance of defect configurations with or without alien metalloid dopants (B, N, P, S, etc.) for potential metal-support coordination. Take the Fe–N–C SAC for example: it is widely studied as the alternative oxygen reduction reaction (ORR) catalyst in place of Pt, and the latest aberration-corrected scanning transmission electron microscopy (STEM) technique directly visualized and identified Fe-N_4 species embedded in graphene layers as the active center.[4] Similar Co–N_x–C[5] and Ni–N_4–C[6] sites have also been demonstrated to effectively catalyze electrochemical hydrogen evolution reaction (HER) and CO_2 reduction reaction (CO_2RR), respectively. Extended X-ray absorption fine structure (EXAFS) and microscopic analyses assigned direct metal–N rather than metal–C bonding as the predominant chemical environment within these SACs. In a recent *Chem* paper,[7] our group reported single Ni atomic sites embedded in graphene vacancies as highly active and selective electrocatalysts for CO_2-to-CO conversion. Three-dimensional atomic probe tomography of over ~10,000 individual Ni single atoms clearly revealed that direct Ni–C coordination predominates within the graphene shell structure. Further density functional theory (DFT) calculations showed that the atomic Ni trapped in a graphene single vacancy (SV) and/or double vacancy (DV) (see Figure 1A) is responsible for weakening CO adsorption on Ni sites (leading to a more facile desorption and evolution) and suppressing HER side reactions.

Given the wide variety of graphene defects,[8] more diverse metal–C moieties are expected to be employed in different catalytic applications. In this issue of *Chem*, Yao and co-workers first employed an impregnation method with acid leaching to prepare defective-graphene-supported Ni SACs with Ni loading up to 1.24%.[9] By calculating the formation energy, the authors identified several stable Ni–C coordination structures, including those trapped in graphene DVs (5775 defects [D5775] and perfect hexagons, as shown in Figure 1A), which were further reinforced by high-angle annular dark field (HAADF)-STEM imaging (Figures 1B–1D, Ni@DV) plus X-ray adsorption spectroscopic characterization and fitting analysis.

Electrochemical measurements demonstrated that the present Ni SAC exhibits superb full water-splitting performance (η_{HER} = 70 mV and η_{OER} = 270 mV, where OER is the oxygen evolution reaction) at a current density of 10 mA/cm^2, analogous or even superior to that of benchmark Pt/C and IrO_2 catalysts. Although both the earlier work[7] and the current report[9] on Ni@SV and Ni@DV suggest suppressed HER activity over these two Ni–C sites, the presence of Ni@D5775 (ca. 44 atom % by linear combination fitting of Ni near-edge structure) favors thermodynamic H_2 evolution close to that on the Pt surface. Meanwhile, Ni@DV sites (ca. 36 atom % content) exhibit an optimized binding strength for *O and *OOH active intermediates, thus boosting the overall OER activity. Last but not least, Ni SACs maintain good catalytic and structural stability even after long-term operation in an acidic solution of 0.5 M H_2SO_4, suggesting a strong interaction between Ni and its neighboring C atoms, which is quite similar to the well-studied stabilizing effect of metal-metal oxide.

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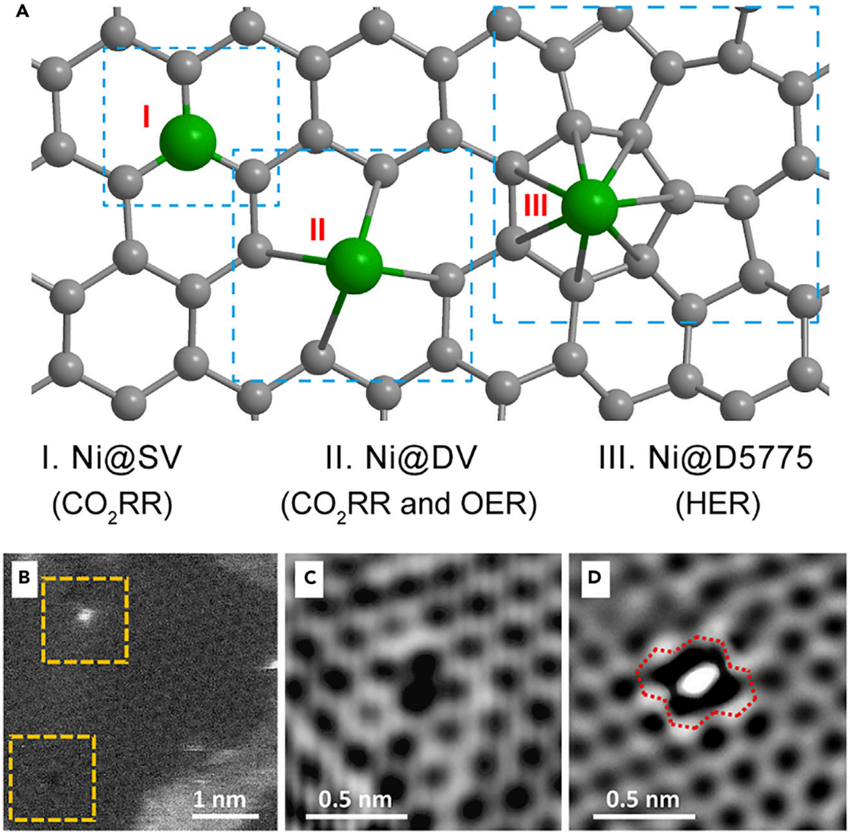

Figure 1. Demonstration of Transition-Metal Single Atoms Embedded in Graphene Defects

(A) Schematic of Ni atoms (green balls) coordinated in single-vacancy (SV), double-vacancy (DV), and 5775 (D5775) carbon (gray balls) defects. Ni@SV and Ni@DV are selective for CO_2RR over HER in neutral pH,[7] and the latter is also active for OER in alkaline media.[9] Ni@D5775 is identified as the active site for HER in acidic electrolyte.[9]

(B) Corresponding HAADF-STEM characterization of graphene defects with or without a trapped Ni atom (bright white dot) in Ni@DV.

(C) Zoomed-in view of lower-left box in (B).

(D) Zoomed-in view of upper-left box in (B).

This is a vivid demonstration that the electronic structure of atomic Ni can be fine-tuned by bonding to diverse types of graphene defects through different target reactions. In fact, more two-dimensional materials beyond graphene can be employed as the proper host matrix for incorporating transition-metal single atoms, giving rise to an important platform for both fundamental mechanism studies in catalysis and a variety of applications in industry and the renewable energy field.

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