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Heteroatom (N, O, and S)-Based Biomolecule-Functionalized Graphene Oxide: A Bifunctional Electrocatalyst for Enhancing Hydrazine Oxidation and Oxygen Reduction Reactions

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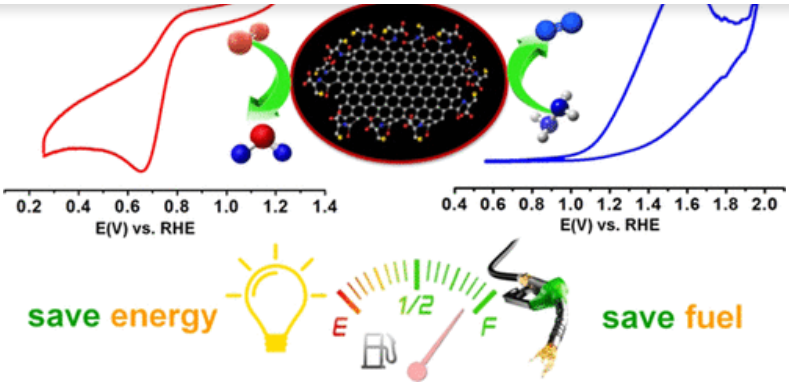
SUBJECTS: Electrical properties, Electrocatalysts, Functionalization, Redox reactions, Stability

Abstract



In this work, a new method is developed to synthesize an L-cysteine-based graphene oxide (L-Cy-rGO) electrocatalyst by a chemical synthesis approach. The electrocatalytic studies of L-Cy-rGO for the oxygen reduction reaction (ORR) and hydrazine oxidation reaction (HOR) have been demonstrated, as important fuel-cell oxidation and reduction reactions confirm its bifunctional nature. The electrochemical ORR performance of L-Cy-rGO is significantly improved with an onset potential of 0.77 V vs reversible hydrogen electrode (RHE) and a current density of −2.32 mA/cm^2 in O_2-saturated 0.5 M KOH electrolytes. The electrochemical impedance spectroscopy (EIS) and chronoamperometric (i–t) measurements of the electrocatalyst are also carried out toward determining the feasibility of electron transfer and current/potential stability at the interface. The L-Cy-rGO electrocatalyst shows excellent activity toward ORR in alkaline medium. Furthermore, L-Cy-rGO shows better electrocatalytic activity toward HOR at an onset potential of 1.01 V vs RHE and the maximum current density of 65 mA/cm^2 at a potential of 1.59 V vs RHE at 35 μM hydrazine hydrate in 0.5 M KOH. The electrochemical studies show that the L-Cy-rGO exhibits the highest electrocatalytic activity toward hydrazine oxidation. Moreover, the L-cysteine-functionalized graphene oxide supporting material plays an excellent role that could be from their synergistic catalytic effect. The L-Cy-rGO electrocatalyst shows excellent electrochemical ORR and HOR performances due to the presence of S- and N-heteroatom-containing surface of GO that enhances the electrocatalytic activity and electron transfer capabilities toward the ORR. Morphological studies based on high-resolution transmission electron microscopy (HRTEM) confirm that the size of L-Cy-rGO is ∼10 nm. X-ray photoelectron spectroscopy (XPS) analysis confirms the surface functionalization of GO by L-cysteine (L-Cy-rGO) from the binding energies of C–S, C–N, C–O, and C–C signals. Based on these findings, we find that the metal-free amino acid-functionalized carbon-based electrocatalyst shows excellent electrochemical ORR and HOR performances and demonstrate its key role toward enhancement in activities.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c04298.

- Synthesis of graphene oxide from graphite and some characterization and electrochemical results related to the electrocatalyst: SEM and TEM of GO; XPS of Cy-rGO; BET of GO; CV and EIS of GO and L-Cy-rGO in KOH; CV and (*i*–*t*) of Pt/C and L-Cy-rGO in KOH; EIS and equivalent circuit of L-Cy-rGO in KOH; CV of L-Cy-rGO comparing Pt and a graphite rod as counter electrodes; CV of GCE, GO, and L-Cy-rGO with NH_2NH_2; CV curves of GCE, GO, and L-Cy-rGO with NH_2NH_2; and tables for calculated EFs for ORR and HOR (PDF)

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Supporting	Mentioning	Contrasting

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