

A Supramolecular Coordination Polymer Derived Electrocatalyst for Oxygen Evolution Reaction

Chi Zhang,^a Chen Zhang,^b Yunchao Xie,^a Xiaoqing He,^c Tommi White,^{c, d} Derek Demaree,^e Mark H. Griep,^e Jerry L Atwood^{*b} and Jian Lin^{*a}

- a. Department of Mechanical & Aerospace Engineering, University of Missouri, Columbia, Missouri 65211, United States. E-mail: linjian@missouri.edu
- b. Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States. E-mail: Atwoodj@missouri.edu
- c. Electron Microscopy Core Facility, University of Missouri, Columbia, MO 65211, United States
- d. Department of Biochemistry, University of Missouri, Columbia, MO 65211, United States
- e. U.S. Army Research Laboratory, 4600 Deer Creek Loop, Aberdeen Proving Groun, Maryland 21005, United States

An iron oxide decorated nickel iron alloy nanoparticle/porous graphene hybrid exhibits high electrocatalytic activity and excellent durability toward oxygen evolution reaction (OER). It displays a LOW overpotential of 274 mV at 10 mA/cm², and low Tafel slope of 37 mV/dec, showing a superior performance to the state-of-the-art RuO₂ OER electrocatalysts.

Scanning electron microscopy (SEM) was performed to characterize the morphology and structure. Fig. 1b shows that the nanoparticles are well dispersed on the surface of the LIG sheets. The corresponding elemental mapping confirms the existence of the C, O, Fe, and Ni elements and their uniform dispersion. High-resolution TEM (HRTEM) was further performed to investigate the nanostructures in more details. The HRTEM image (Fig. 1d) reveals well-resolved lattice fringes with interplanar distances of 0.205 nm, 0.290 nm and 0.364 nm, of Fe₃O₄ and (002) plane of graphene, respectively. Meanwhile, it is interesting to see that FeNi₃ NPs are surrounded by few-layer graphene which might be formed due to the quick carbonization of the SCP-3-Ni.

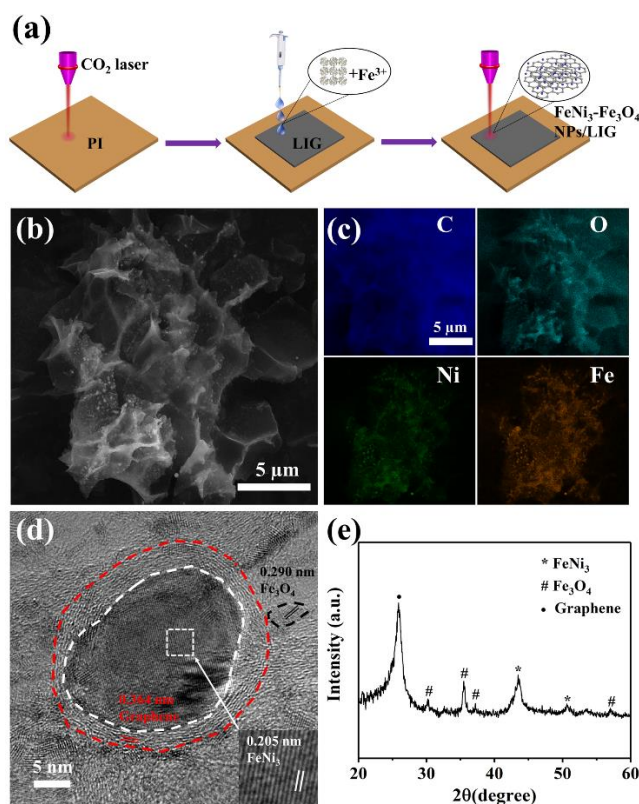


Fig. 1 (a) Schematic of fabrication process of FeNi₃-Fe₃O₄ NPs/LIG nanocatalysts. (b) SEM images of FeNi₃-Fe₃O₄ NPs/LIG. (c) The corresponding elemental mapping of C, O, Ni and Fe. (d) HRTEM images of FeNi₃-Fe₃O₄ NPs/LIG. (e) XRD pattern of the FeNi₃-Fe₃O₄ NPs/LIG

In order to compensate the potential loss caused by the external resistance and accurately reflect the intrinsic catalytic activity of the electrocatalyst, an *i*R correction was employed. All the reference electrodes reported here were calibrated with respect to the reversible hydrogen electrode (RHE). The detailed calibration method is shown in ESI. As comparison, glassy carbon, RuO₂ and LIG were also studied. Fig. 2a shows the anode polarization curves recorded at 2 mV/s. As expected, RuO₂ displays good OER activity with an onset overpotential of 270 mV, whereas the bare glassy carbon and LIG shows no catalytic activity. It is very interesting to see that FeNi₃-Fe₃O₄ NPs/LIG show better performance than the benchmark RuO₂. It only needs an overpotential of 274 mV to achieve 10 mA/cm². However, when the FeNi₃-Fe₃O₄ NPs/LIG is reduced at 300 °C under 5% H₂/95% Ar flow, the reduced sample (FeNi₃-Fe₃O₄ NPs/LIG-R) exhibits an increase overpotential of 323 mV. The superior OER activity of FeNi₃-Fe₃O₄ NPs/LIG to the reduced sample could be attributed to the modification of electronic properties of FeNi₃ caused by the Fe₃O₄. Similar effect has also been reported in other work. Reduction process diminishes such positive effect.

The Tafel slopes derived from the corresponding polarization curves are shown in Fig. 2b to get more insight into the reaction mechanism. These Tafel slopes are fitted according to the following equation $\eta = b \log j + a$, where *j* is the current density and *b* is the Tafel slope. The Tafel slope of RuO₂ is 75 mV/dec, while FeNi₃-Fe₃O₄ NPs/LIG has a Tafel slope of 37 mV/dec which is smaller than that of FeNi₃-Fe₃O₄ NPs/LIG-R (41 mV/dec), suggesting the its fast reaction kinetics. Stability of FeNi₃-Fe₃O₄ NPs/LIG was assessed by the continuous cyclic voltammetry scanning. Fig. 2c shows anode polarization curves at the first cycle and after 1000 cycles. The almost overlapped curves imply the excellent stability of FeNi₃-Fe₃O₄/LIG. Chronopotentiometric measurements at a fixed current density of 10 mA/cm² were also conducted. As shown in Fig. 2d, FeNi₃-Fe₃O₄ NPs/LIG maintains its high catalytic activity with only a slight increase of overpotential of 9 mV after 18 hour testing, which could be attributed to the formation and desorption of the copious O₂ bubbles on the catalyst surface.

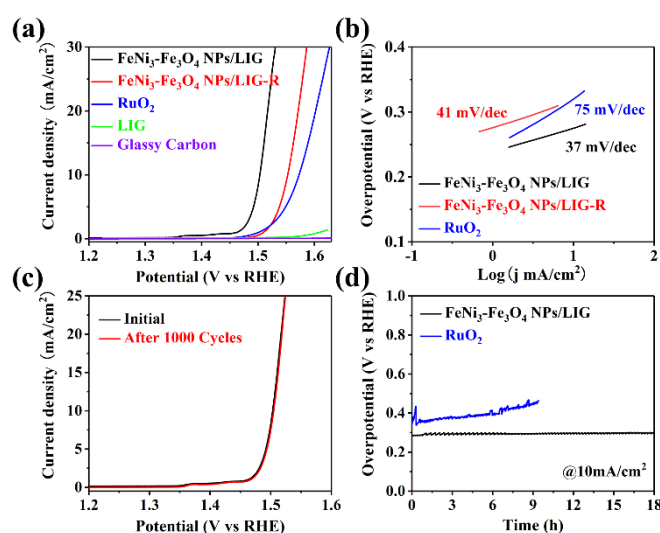


Fig. 2 (a) LSV curves of FeNi₃-Fe₃O₄ NPs/LIG (black), FeNi₃-Fe₃O₄ NPs/LIG-R (red), RuO₂ (blue), LIG (green) and a bare GC electrode (purple) in O₂-saturated 1.0 M KOH at 2 mV/s. (b) Corresponding Tafel plots of LSV curves shown in (a). (c) Polarization curves of the FeNi₃-Fe₃O₄ NPs/LIG before and after 1000 cycles of CV scans. (d) Chronopotentiometry plot of the OER process operated with the FeNi₃-Fe₃O₄ NPs/LIG at a constant current density of 10 mA/cm².