



Lanthanides-based graphene catalysts for high performance hydrogen evolution and oxygen reduction



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ABSTRACT

The design of efficient electrocatalysts for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) has received enormous consideration due to their effectiveness in modern renewable energy technologies such as fuel cells, electrolyzers, and metal–air batteries. Herein, we present a facile method to fabricate lanthanides (L = La, Eu, Yb)-doped graphene materials as catalyst for the HER and ORR that show desirable electrocatalytic activities as well as long-term stability. The Eu-graphene hybrid has showed unbeatable HER performance such as small values of onset potential (81 mV), overpotential (160 mV), and Tafel slope (52 mV dec⁻¹), along with a high exchange current density (7.55×10^{-6} A cm⁻²). The L-graphenes also exhibit superior electrocatalytic activity for ORR, including small Tafel slopes (96, 66, and 105 mV dec⁻¹ for La-Gr, Eu-Gr, and Yb-Gr, respectively), positive onset potential (~0.83–0.92 V), high electron transfer numbers (~3.84–4.03), and excellent enduring strength, analogous to those of viable Pt/C catalysts. The excellent electrocatalytic performance is attributed to the synergistic effect of abundant edges and doping sites, high electrical conductivity, large active surface areas and fast charge transfer; which renders lanthanide-based graphene hybrids as potentially great candidate for energy conversion systems.

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1. INTRODUCTION

With rising concerns about worldwide energy crisis and global warming, there are intense efforts to search renewable and green energy sources as alternatives to fossil fuels [1–3]. Water splitting and regenerative fuel cells are highly effective, eco-friendly energy conversion and storage systems, consisted of two core reactions; HER and ORR, which are enormously relied on the catalytic performance of electrode. These are of significant importance in the transformation of electricity (or sun light) to chemical energy (for HER), and the conversion of the chemical energy to electricity (for ORR) [4]. As a result, regenerative fuel cells are expected to provide a sustainable energy density, by combining an electrolyzer and a fuel cell in a dual-mode operation system [5]. Even though the best HER and ORR electrocatalytic performances were reported from the noble metal catalysts, such as Pt, Pd and their alloys, their unaffordable price, scarcity, and meager durability hamper their widespread applications [6,7]. Thus, it is desirable but challenging to design/prepare competent non-precious (Pt-free) corrosion-resistant and highly active electrocatalysts for both HER and ORR.

Presently, non-precious transition metal based oxides, sulfides and nitrides prepared in the form of nickel foam, particle agglomerates and thin films are an exciting family of catalysts for HER or ORR [8–13], however, their catalytic performance in acidic/alkaline solutions is deteriorating by lack of control over size, pitiable electronic conductivity and structure of organic-inorganic hybrid. Thus, development of alternate highly efficient catalysts with long-term constancy is urgently required. In this respect, graphene, a sp²-bonded carbon network in a honeycomb lattice is a promising candidate for electrochemical reactions owing to its interesting structural (large surface area), electrical and mechanical properties. Elevated chemical strength of graphene promises steady electrode performance and high durability, but in contrast, shows meager catalytic activity for HER and ORR. Various chemical modifications such as co-catalysts (C₃N₄/graphene and WN/graphene) [14,15], doping, and preparation of nanostructures can be applied to significantly improve catalytic performance by creating abundant active sites. Among these, atomic doping with various additives is recognized as a promising way to realize new functions in materials to reduce overpotentials. Heteroatom doping in graphene lattice stimulates change in the asymmetry spin density and local charge density of the neighboring carbons (C) as a result of the electronegativity difference

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among the doped heteroatoms and C, reveals creation of plentiful active sites for catalysis. Meanwhile, quantum mechanical calculations predict the carbonaceous materials doped with heteroatoms (such as non-metals (N, S, P, B) [16,17] and metals (Pt, Fe, Al) [18,19]) have better oxygen electrocatalysis. Based on these predictions, numerous co-doped (B/N, N/S, N/P, S/Se, S/O) [20–22] carbon materials also studied and confirm synergistic effects can improve HER or ORR catalytic activity. However, their performance is still inadequate compared to transition metal catalysts (such as MoS₂, WS₂ etc. [23,24]) because of either small surface area or accessible active sites. Can lanthanides with graphene to form a hybrid functions as even more effective catalyst? Since, lanthanides combined with graphene boosts π bonding in the framework that sustains their electron donor–acceptor properties, and thus enhances their catalytic activity for specific electrochemical reactions.

Inspired by these features, we speculate that lanthanide-doped graphene could offer additional liberty for multifunctional electrocatalytic performance. Even so, no any successful belongings have been reported in this field. For the first time, we present a facile and scalable in-situ synthesis of lanthanide (La, Eu, Yb) assimilated graphene frameworks as novel catalysts for hydrogen evolution and oxygen reduction reactions by ion-adsorption and a subsequent thermal exfoliation process. These hybrids have many intriguing properties favorable for catalysis, such as highly exposed catalytic centers, high electrical conductivity, and strong mechanical flexibility. Electrochemical studies show that the obtained L-graphene exhibits superior HER catalytic activity with low onset overpotential (160 mV), large current densities and excellent durability comparable to commercial Pt/C in acidic medium. The Eu-graphene hybrid confirms outstanding ORR catalytic activity with a positive onset potential, an electron transfer number of 4.03 and stability superior to commercial Pt/C in alkaline (0.1 M KOH) environments. The fabulous electrocatalytic performance signifies that these catalysts have immense prospective to be employed in regenerative fuel cells and other technological areas.

2. EXPERIMENTAL METHODS

2.1. Synthesis of La, Eu, and Yb-doped graphene (L-graphene) hybrids

Graphene oxide was synthesized by improving Hummers method [25]. Briefly, graphite powder, and KMnO₄ were mixed in concentrated H₂SO₄ under vital agitation in an ice bath. Then reaction mixture was transferred to a 40 °C oil bath and vigorously stirred for about 30 min. Afterward, 150 mL of water was added and the solution was stirred for another 15 min at 95 °C. An additional 500 mL of water was added and followed by the slow addition of 15 mL of H₂O₂ (30%). The mixture was filtered and sequentially washed with dilute HCl, deionized water, ethanol, acetone and polyether. Finally, the prepared graphene oxide powder was pyrolyzed at 900 °C for 3 h under N₂ atmosphere that yielded graphene for further use.

The synthesized pristine graphene (200 mg) was dispersed in deionized water (100 mL) by sonication for 30 min. L-graphene hybrids were synthesized by the accumulation of 50 mL of aqueous solution containing 10 wt.% Ln ions (in the forms of an acidified aqueous solution of lanthanum nitrate, europium nitrate and ytterbium nitrate, respectively). The prepared reaction solution was stirred for 4 h and left for 12 h, during which the graphene absorbed the Ln ions from the solution. Then, it was filtered by suction and repetitively cleaned three times with deionized water before being dried in a rotary evaporator proceeding to further use. The respective suspensions were then thermally exfoliated at 1000 °C for 1 h under N₂ atmosphere and allowed to cool to room temperature. Thermal exfoliation process was carried out as

follows. First, the precursor was positioned in a porous quartz glass capsule attached to a magnetic manipulator in a vacuum-tight quartz reactor under a controlled atmosphere. This system could offer a temperature gradient of over 1000 °C min⁻¹. Then, the sample was flushed repeatedly with pure nitrogen, then inserted into a preheated reactor in N₂ atmosphere to produce doped graphene hybrids. We have maintained N₂ gas flow (1 liter per min) to ensure the elimination of reaction byproducts. Differently doped L-graphene hybrids were prepared using this facile and scalable method. Finally, these hybrids were investigated to evaluate their electrocatalytic performance.

2.2. Materials characterization

FE-SEM images and EDS maps of the samples were examined by means of field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800II, 3 kV). The transmission electron microscope (TEM) measurements were made using a JEOL JEM-2100F, 200 kV instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Scienta, Scienta R3000 model in an ultrahigh vacuum of 10⁻⁹ mbar. BET analysis for surface area and pore size distribution was executed using the Micromeritics, ASAP 2020 surface and porosity analyzer. Raman spectra were acquired using a RM 1000 spectrometer (Renishaw, UK).

2.3. Electrochemical measurements

2.3.1. Hydrogen Evolution Reaction (HER)

L-graphene hybrids were examined for their HER analysis using a standard three-electrode setup in N₂-purged 0.5 M H₂SO₄ solution. Firstly, glassy carbon (GC) electrodes (3 mm diameter, CH Instrument Inc.) were refined with 0.05 and 0.3 μ m alumina slurry (CH Instrument Inc.), and then cleaned with deionized water and ethanol before drying under a gentle nitrogen stream. L-graphene hybrids (1 mg/ml) were ultrasonically dispersed in deionized water having 5 wt.% Nafion (0.1 ml). After that, 20 μ L of the consequential slurry was casted onto the refined GC surface and gently dried at room temperature, in order to get a working electrode. The Pt wire and Ag/AgCl were utilized as counter and reference electrodes, respectively. All potentials were referenced to that of a reversible hydrogen electrode (RHE) as 0.205 + 0.059 \times pHV. Electrochemical impedance spectroscopy (EIS) measurements were carried in the range of 0.1 Hz to 2 MHz frequency at a 0.2 V bias potential. The electrolyte was purged for 30 min by N₂ flow before the experiment to remove dissolved oxygen.

2.3.2. Oxygen Reduction Reaction (ORR)

The electrochemical activity toward ORR for the L-graphene hybrids was investigated using cyclic voltammetry (CV) and linear sweep voltammograms (LSVs) in N₂ and O₂-saturated 0.1 M KOH electrolyte. The scan rate 10 mV/s was fixed for all measurements. The catalyst ink was prepared by using 1 mg dispersion of L-graphene catalyst in 160 μ L of ethanol, 30 μ L of DI water and 10 μ L of Nafion solution for 30 min in order to acquire homogeneous suspension. 1.5 μ L resulted slurry was casted onto glassy carbon rotating disk electrode (working electrode, 3 mm in diameter) and desiccated at room temperature. A Pt wire and Ag/AgCl was used as the counter and reference electrodes, respectively. All potentials were referenced to the RHE scale.

The electron transfer number concerned in the ORR process was calculated using the Koutecky–Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

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