Communication

Structural and electronic optimization of graphene encapsulating binary metal for highly efficient water oxidation

Yunchuan Tu,a,b,c,1 Pengju Ren,d,e,1 Dehui Deng,a,b,x Xinhe Bao,a,b,x

A R T I C L E   I N F O

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A B S T R A C T

Encapsulating non-precious metals within graphene layers represents a promising strategy to substitute precious metal catalyst towards the oxygen evolution reaction (OER). The surface electronic structure of graphene can significantly affect the OER performance, which depends on the types of encapsulated metal and their proportion but it still lacks efficient methods to modulate them. Herein, we report a universal strategy to encapsulate FeNi binary metal nanoalloy within ultrathin graphene layers, which can efficiently optimize the electronic properties and the OER activity on the graphene surface via modulating Fe/Ni ratio. The optimized catalyst with Fe/Ni of 1 shows a low overpotential of 280 mV at the current density of 10 mA cm$^{-2}$. Both the catalytic activity and durability of the catalyst are better than the commercial IrO$_2$. Theoretical calculations indicate that the adsorption strength of each intermediate on graphene can be optimally balanced by modulating the metal proportion of the encapsulated FeNi, leading to an enhanced OER activity with reduced overpotential on the graphene surface.

1. Introduction

Water splitting, as a promising strategy of scalable conversion of renewable electric power to storable hydrogen fuel, has sparked intense research interest in the demand of sustainable-energy conversion technology and production of clean energy carrier in the future [1]. Water oxidation, i.e. the oxygen evolution reaction (OER) plays a key role in overall water electrolysis process due to its intrinsically sluggish kinetics, which leads to a high anodic overpotential and reduced energy efficiency [2,3]. At present, precious metals oxides such as iridium dioxide (IrO$_2$) and ruthenium dioxide (RuO$_2$) are regarded as active electrocatalysts to enhance the reaction rate, while the high cost and scarcity greatly hamper their large-scale practical application.

Recently, 3d transition metals (TMs) and their derivatives, including oxides [4–6] and (oxy)hydroxides [7–12] have been broadly considered as promising alternatives to precious metals because of their relative abundance, low cost and considerable catalytic activity. However, 3d TMs suffer from unfavorable stability under strongly alkaline and highly oxidative operation conditions. To address this problem, our previous studies proposed a novel strategy to encapsulate 3d TMs into graphene layers, which can prevent the inner metallic cores from oxidation and simultaneously trigger the catalytic activity of the inert carbon surface due to the electron transfer from the encapsulated metal cores [13,14]. Up to now, considerable research interest has focused on this strategy for various catalytic reactions, such as water electrolysis [15–18], oxygen reduction reaction (ORR) [13,19] as well as metal-air batteries [20,21]. Previous studies indicated that the surface electronic structure of graphene can significantly affect the OER performance [18], which may depend on the types of encapsulated metals and their proportion. However, to date, it still lacks efficient methods to tune the encapsulated metals and their proportion, leading to that the correlation between the encapsulated metal proportion and the OER activity has not been investigated.

To this end, we report a facile and universal synthetic strategy to encapsulate FeNi alloy within ultrathin graphene layers (denoted as FeNi@Gr). By controlling the annealing temperature and the metal...
proportion of the encapsulated FeNi, the electronic structure of the graphene surface can be effectively optimized, which balances the adsorption strength of each intermediate on graphene surface. The optimum catalyst annealed at 900 °C with a Fe/Ni ratio of around 1 (FeNi@Gr-900, the metal content is about 39 wt%), Table S2) exhibited remarkably enhanced OER catalytic activity and durability in comparison with commercial IrO2 catalyst.

2. Experimental Section

2.1. Materials preparation

Typically, Fe(NO3)3·9H2O, Ni(NO3)2·6H2O (the sum of the moles of metal nitrates is 3.6 mmol) and dicyandiamide (1.2 g, 14.3 mmol) were filled into the channels of SBA-15 (1.0 g) by an impregnation method with 100 mL methanol solution, the critical mole ratio of dicyandiamide to total metal nitrates is about 4.1. After the above solution drying at room temperature under magnetic stirring, the powder was then placed in a quartz boat and heated at 900 °C in a tube furnace for 3 h in Ar atmosphere with a heating rate of 3 °C min\(^{-1}\) to produce a black powder. After cooling to room temperature, the samples were treated in 5% HF aqueous solution for 6 h, followed by washing in distilled water and ethanol, and then drying at 80 °C for 12 h. The resulting sample was labeled as FeNiNi@Gr. Since completely encapsulating Fe by carbon shells is likely more difficult than Ni, large amount of Fe can be corrosive after the acid leaching [22]. We did not receive any Fe@Gr catalyst through changing the different ratios of Fe precursor and dicyandiamide to obtain some insights into the synthesis annealing temperature-structure-electrocatalytic activity relationships, four additional samples were prepared by heating the same precursor in Ar atmosphere at 600, 700, 800 or 1000 °C for 3 h, respectively. For comparison, an additional FeNi@Gr sample was prepared in the same way except using the silica sphere (70 nm in diameter) instead of SBA-15 as the silica template.

2.2. Materials characterization

X-ray diffraction (XRD) was performed on a Rigaku Ultima IV diffractometer with Cu Kα radiation at a voltage of 40 kV and a current of 30 mA. Scanning electron microscopy (SEM) was carried out on Hitachi S5500 operated at 30 kV. High resolution transmission electron microscopy (HRTEM) was conducted on a FEI Tecnai F20 microscope operated at an accelerating voltage of 200 kV. Raman spectroscopy was conducted on a Renishaw instrument with a 532 nm excitation laser. X-ray absorption near-edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) were measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) recorded in a transmission mode. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB Xi spectroscopy using Al Kα X-rays as the excitation source with a voltage of 15 kV and power of 150 W. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out in IRIS Intrepid II XSP (Thermo ELECTRON). The composition of CHN were determined by Vario EL III instrument (Elementar Analysen Sytem GmbH, Germany).

2.3. Electrochemical measurement

The electrocatalytic properties were conducted on a three-electrode system using an electrochemical workstation (Parstat MC). Pt wire and Hg/HgO (1 M KOH solution) were used as the counter electrode and reference electrode, respectively. To prepare the working electrode, the catalyst (5 mg) was dispersed in ethanol (2 mL) containing 50 μL Nafion solution (5 wt%, Du Pont) under ultrasonic until a homogeneous ink was formed. Then, 25 μL of this ink was transferred dropwise onto a glassy carbon electrode (GCE) with 5 mm diameter and dried under room temperature. This gave the final catalyst loading of ~0.32 mg cm\(^{-2}\) on GCE. To evaluate the OER activities, linear sweep voltammetry (LSV) of different catalysts were conducted on rotating disk electrode (RDE) measurements in O\(_2\)-saturated 1 M KOH electrolyte at 25 °C with a scan rate of 5 mV s\(^{-1}\) under 1600 rpm. An accelerated degradation measurement was employed to evaluate the durability of FeNi@Gr-900 on GCE. Before recording the OER polarization curve in this accelerated degradation test, the catalyst firstly ran for 1000 cyclic voltammetry (CV) cycles between −0.35 and 0.65 V (vs. Hg/HgO) at 100 mV s\(^{-1}\). The long-term stability performance was measured by using chronopotentiometric measurement at a constant current density of 10 mA cm\(^{-2}\). The electrochemical impedance spectroscopy (EIS) tests were performed at 1.55 V vs. RHE in a frequency range from 100 kHz to 0.1 Hz with a 5 mV amplitude. All the final potentials have been calibrated with respect to a reversible hydrogen electrode (RHE).

2.4. Theoretical calculations

Vienna Ab-initio Simulation Package (VASP) [23–26] was used for all calculations with Perdew-Burke-Ernzerhof (PBE) functional [27] for the exchange-correlation term and the projector augmented wave method [28,29]. The cutoff energies for all calculations were set to 400 eV. The models of metal particles encapsulated into graphene layer (Fe\(_{x}\)Ni\(_{55-x}\)@Gr) consist of C\(_{240}\) encapsulating 55 atomic metal clusters, where x and 55-x are the number of iron and nickel, respectively. The element distributions of FeNi nanoparticles were chosen fully random for all of the structures according to its alloy nature. All structures were fully relaxed to the ground state and spin-polarization was considered in all calculations. The convergences of energy and force were set to 1 × 10\(^{-4}\) eV and 0.05 eV Å\(^{-1}\), respectively. The free energies of the intermediates HO* and O* were obtained by \(ΔG = ΔE + TΔS + eU\), where \(ΔE\) is the binding energy of adsorption species HO* and O*, \(ΔS\) and \(U\) are the zero point energy changes, entropy changes and applied potentials, respectively. 298.15 K was chosen as the temperature according to the experimental condition. The free energy of HOO* was obtained by the relation \(ΔG\text{(HOO*)} = ΔG\text{(HO*)} + 3.2\text{eV}\) according to our previous work [18].

3. Results and discussion

The FeNi@Gr was synthesized by a facile thermal treatment in Ar atmosphere by using Fe\(_3\)\(^{1+}\), Ni\(_2\)\(^{2+}\), dicyandiamide as precursors, and the ordered mesoporous silica (SBA-15) as the template (see the materials preparation section for details). The nanostructures of graphitic carbon are closely related to the used metal salts and carbon/nitrogen precursors [30,31]. For instance, Fe, Co and Ni are able to catalyze the graphitization of dicyandiamide to form porous nanocarbon containing abundant active sites [22]. In the annealing process, dicyandiamide would be firstly decomposed to CN\(_x\) intermediates around 500 °C [32]. With the temperature increasing, these CN\(_x\) intermediates were further transformed to graphitic carbon shells around FeNi species with the catalytic carbon deposition of FeNi nanoallot, which finally led to the in situ formation of graphene shells encapsulating FeNi nanoparticles (Fig. 1a). This method can readily modulate the Fe/Ni ratio according to the feed ratio.

Scanning electron microscopy (SEM; Fig. S1) and transmission electron microscopy (TEM; Fig. 1b) images show that the sample which annealed at 900 °C (FeNi@Gr-900) consisted of uniform nanoparticles densely spreading over the carbon skeleton. Due to the confinement of the SBA-15 channels, the size distribution of the metal nanoparticles (NPs) is controlled of 4–6 nm (see the statistical analysis of metal NPs in Fig. 1b, inset). Further high resolution (HR) TEM image (Fig. 1c) indicates that the metal nanoparticles are completely encapsulated by few-layer graphene shells with the layer spacing of around 3.4 Å. In addition, the metal NPs exhibit a d-spacing of 2.1 Å, corresponding to the (111) plane of the FeNi alloy (Fig. 1d). As the statistical analysis
shown in Fig. 1f, the layer number of graphene shells encapsulating the FeNi NPs are only 1–4 layers, and most of them (> 80%) consist of no more than two layers. Likewise, the FeNi@Gr samples annealed at different temperatures show a similar morphology as analyzed by TEM (Fig. S2). In contrast, a control experiment was carried out by using an equivalent mass of silica sphere (70 nm in diameter) instead of SBA-15, the metal NPs size of this as-prepared sample is in the range of 15–20 nm, or even larger, as shown in Fig. S3h. This result further confirms that the smaller size of metal NPs within graphene layers is due to the confinement of the SBA-15 channels during the preparation process.

Synchrotron-based X-ray absorption near-edge structure (XANES) analysis and X-ray photoelectron spectroscopy (XPS) were performed to investigate the electronic properties of FeNi@Gr-900. As shown in Figs. 1g and 1h, the near-edge absorption energy of the Fe K-edge and Ni K-edge of FeNi@Gr-900 is similar with that of the reference Fe and Ni foil, respectively. The extended X-ray absorption fine structure (EXAFS) spectra only present the Fe-Fe or Ni-Ni peak at about 2.2 Å (without phase correction), indicating that Fe and Ni maintain metallic state in FeNi@Gr, which is consistent with the XPS analysis (Fig. 1i). The Ni 2p spectrum can be fitted into Ni0 2p1/2 at 870.1 eV and 2p3/2 at 852.9 eV, with the satellite peak locating at 859.1 eV. Similarly, the Fe0 2p1/2 and 2p3/2 peak located at 720.3 eV and 707.0 eV, respectively. The peak located at 712.0 eV can be attributed to the L3M23M45 Auger peak of Ni. In addition, the N 1s XPS (Fig. S4d) and element analysis (Table S1) indicate that there are a few of N atoms (around 3.4 at%) doped into the carbon matrix.

A typical three-electrode electrochemical cell with a rotating disk electrode (RDE) configuration was adopted to evaluate the OER performance of the FeNi@Gr catalysts. Firstly, we investigated the OER polarization curves of FeNi@Gr catalysts prepared at different annealing temperatures (their detail structural information see the XRD analysis in Fig. S5) in comparison with the commercial IrO2 (Fig. 2a). The trend of the overpotential at different current density, i.e. 10, 50 and 150 mA cm-2, respectively, we found that the trend of
the overpotential of these samples is $900 < \text{IrO}_2 < 1000 \approx 800 < 700 < 600$ (Fig. 2b). It indicates that the FeNi@Gr-900 sample has the highest OER activity. The superior OER activity may originate from the ultrathin graphene shells greatly promoting the electron transfer from the encapsulated FeNi cores to the graphene surface, which increases the electron density of the graphene surface and thereby triggers the OER activity on the inert graphene surface [17,18,34]. In contrast, it is difficult to form ideal graphene shells at lower temperature ($\leq 800 ^\circ C$), therefore the encapsulated FeNi NPs are readily oxidized during OER process. While the size of FeNi NPs will increase significantly at higher temperature ($\geq 1000 ^\circ C$), as confirmed by the statistical distribution of particle size (Fig. S2) and XRD analysis (Fig. S5). In both cases, the OER activity will decrease. In addition, the sample prepared using silica sphere as the template shows a very inferior OER activity (Fig. S8), in which the size of the encapsulated metal NPs is in a range of 15–20 nm and the layer number of the graphene shells is far more than 5 layers. These results indicate that the well-defined ultrathin graphene shells encapsulating smaller FeNi NPs will promote the OER activity.

The stability test was conducted with catalysts loading on both the glassy carbon electrode (GCE) and the carbon fiber paper (CFP). An accelerated degradation measurement was employed to evaluate the durability of FeNi@Gr-900 on GCE. The polarization curve of FeNi@Gr-900 after 1000 cycles decayed slightly, while the IrO$_2$ catalyst declined rapidly under the same condition (Fig. S2). As shown in the electrochemical measurement section for details). Moreover, a galvanostatic measurement at a constant current density of 10 mA cm$^{-2}$ was carried out to evaluate the stability of FeNi@Gr-900 on CFP with the same catalyst loading (0.32 mg cm$^{-2}$). The potential maintains very stable around 1.5 V without rising over 24 h. Both the graphene shells and the encapsulated FeNi nanoparticles were well maintained after the OER durability measurements, as confirmed by HRTEM images (Fig. S9).

In order to investigate the effect of Fe/Ni ratio of these FeNi-based catalysts ($\text{Fe}_x\text{Ni}_{1-x}\text{Gr}$) on OER activity, four samples with different Fe/Ni ratios had been prepared at the optimized temperature of 900 $^\circ C$. The Fe/Ni atomic ratio were controlled according to the ratio of feed precursors, and the Fe and Ni contents in these samples were also confirmed by inductively coupled plasma atomic emission spectroscopy analysis (Table S2). From the XRD (Fig. S5) and TEM (Fig. S3) analysis, metal NPs with similar size distribution can be completely encapsulated within ultrathin graphene shells in all these samples. Firstly, the OER activities were evaluated by linear sweep voltammograms (Fig. 3a). Two parameters were used as a function of Fe content of $\text{Fe}_x\text{Ni}_{1-x}\text{Gr}$ samples for the OER activity [35,36]. One is the current density at a constant overpotential of 300 mV and the other is the overpotential at a current density of 10 mA cm$^{-2}$ (Fig. 3c). Both of them indicate that the sample with a Fe/Ni ratio of 1 possesses the best OER activity among the different Fe/Ni ratios. Fig. 3c reveals the minimum overpotential of 280 mV at 10 mA cm$^{-2}$ and the maximum current density of 19 mA cm$^{-2}$ at 300 mV for the sample with a Fe/Ni ratio of 1, the current density of which is even 10 times than that of the pure Ni sample. In addition, the Tafel slopes of these $\text{Fe}_x\text{Ni}_{1-x}\text{Gr}$ samples are all around 70 mV dec$^{-1}$, suggesting that these samples possess a similar OER kinetics (Fig. 3b). In contrast, without the Fe, the Tafel slope of the Ni@Gr increases to around 135 mV dec$^{-1}$, indicating the lower OER...
kinetics than that of the Fe containing sample. Furthermore, electrochemical impedance spectra (EIS) of the catalysts measured at a constant potential of 1.55 V (vs. RHE) (Fig. 3d and Table S3) shows that the FeNi@Gr sample possesses the lowest Rct value comparing with the other samples, further confirming its superior OER catalytic activity. These results indicate that coexistence of Fe and Ni within graphene shells with a Fe/Ni ratio of 1 can synergistically enhance its OER activity.

Density functional theory (DFT) calculations were carried out to provide further insight into the influence of various metal proportions of FexNi1-x@Gr towards the OER. As shown in Fig. 4b and Table S4, replacing Fe by Ni can increase the free energy of all reaction intermediates of OER, which means that the adsorption of HO*, HOO* and O* on graphene becomes weaker. According to the Bader charge analysis in Fig. 4b, the charge which transfers from metal cluster to graphene layer is linearly increased with the Fe content increasing. This result indicates that the interaction strength between iron and carbon is larger than the one between nickel and carbon, i.e. compared to nickel, iron has a more significant activation effect on carbon. However, the calculated overpotential shows reversed volcano shape with Fe content increasing in FexNi1-x alloy (Fig. 4c), which coincides with our experimental result well. This is because the OER process involves multiple elementary steps, and the overpotential not just depends on the adsorption strength of a certain intermediate but the balance of each intermediate. To better explain this point, we investigate the free energy profiles of the OER process over various Fe/Ni ratios at an equilibrium potential (U = 1.23 V) (Fig. 4a). Due to the too strong binding of O* on Fe@Gr, which could block the active sites, the overpotential exhibits much higher. On the contrary, the adsorption of HO* is too weak on Ni@Gr. The overpotential can be tuned to the minimum by modulating the metal proportion of FeNi alloy, and the optimal Fe/Ni ratio appears at around 1 (Fig. 4c), agreeing with the experiment results (Fig. 3c). Note that the qualitative result, i.e. the well correlation between theoretical and experimental study, aims to predict a general trend due to the simplified catalyst structure and theory used.

4. Conclusions

In summary, we developed a universal strategy to encapsulate uniform FeNi nanoalloy within ultrathin graphene layers. By controlling the annealing temperature and metal proportion of the encapsulated FeNi binary metal, the optimized catalyst annealed at 900 °C with a Fe/Ni ratio of around 1 exhibits superior OER activity and durability comparing with IrO2 catalyst. DFT calculations indicate that the balance of the adsorption strength of each intermediate on graphene surface can be efficiently optimized by modulating the metal proportion of the encapsulated FeNi, leading to an enhanced OER catalytic activity with reduced overpotential on the graphene surface. These findings could pave a way towards the rational design and development of cost-effective and highly active non-precious metal electrocatalysts for advanced energy conversion devices.

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Appendix A. Supporting information
Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.07.062.

References
Yunchuan Tu received his B. S. degree in Applied Chemistry from Sichuan University in 2012. He is currently a Ph. D. candidate under the supervision of Prof. Xinhe Bao and Dehui Deng at Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS). His research is focused on novel non-precious metal catalysts for electro-chemical energy-related catalysis, such as water electrolysis and metal-air batteries.

Pengju Ren received his B. S. in Henan Normal University in 2008 and Ph. D. in Physical Chemistry from DICP, CAS in 2015. He subsequently joined Institute of Coal Chemistry, CAS as postdoctoral research associate and then joined Synfuels China Co. Ltd. since 2018. His research focuses on understanding the mechanism of catalytic processes and designing novel catalysts for energy and environment applications using computational approaches.

Dehui Deng received his B. S. in Light Industry Engineering and B. S. in National Economy Management from Sichuan University in 2007 and Ph. D. in Physical Chemistry from DICP, CAS in 2012. He subsequently joined State Key Laboratory of Catalysis, DICP as an Associate Professor, and became a Full Professor in 2017. Since January 2015, he served as an iChEM Research fellow at Xiamen University. He also served as a visiting scholar in Stanford University between 2015 and 2016. His research interests include development of non-precious metal catalysts and fundamental research in heterogeneous catalysis and electro-catalysis.

Xinhe Bao received his Ph. D. in Physical Chemistry from Fudan University in 1987. He held an Alexander von Humboldt Research Fellow position at the Fritz-Haber Institute, Berlin, between 1989 and 1995. Following that, he joined DICP as a full Professor. He became a member of the CAS in 2009. His research interests are nano- and interfacial catalysis, focusing on the fundamental understanding of heterogeneous catalysis, including the development of new catalysts and novel catalytic processes related to energy conversion and storage.