RESEARCH ARTICLE

Multi-chambered, carbon-coated Ni_{0.4}Fe_{2.6}O_{4} nanoparticle superlattice microspheres for boosting water oxidation reaction

Mingzhong Li\(^1\) | Yuwei Deng\(^1\) | Guanhong Wu\(^1\) | Shuqing Xue\(^2\) | Yancui Yan\(^2\) | Zihan Liu\(^1\) | Jinxiang Zou\(^1\) | Dong Yang\(^2\) \* | Angang Dong\(^1\)

1 Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai, China
2 State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, Shanghai, China

Abstract

Developing active and robust non-noble-metal-based electrocatalysts for the oxygen evolution reaction (OER) is of vital practical significance for accelerating the kinetics of water splitting. Here, a novel double emulsion template method is proposed to design and prepare hierarchically multichambered, carbon-coated Ni_{0.4}Fe_{2.6}O_{4} nanoparticle superlattice microspheres (M-NFO@C-NSMs) for the highly efficient oxygen evolution. The high-temperature calcination under inert gas enables an improved electrochemical property by rationally transforming the long-chain organic capping ligands into partially graphitized uniform carbon coatings. More importantly, benefiting from the unique hierarchical superstructure with macro-/meso-/microporosities and three-dimensional continuous conductive carbon frameworks, M-NFO@C-NSMs exhibit comprehensively enhanced OER activity in a dilute alkaline electrolyte as compared to their solid counterparts and most spinel-based electrocatalysts reported to date. Notably, the collective property of supraparticles endowed M-NFO@C-NSMs with superior long-term cyclic stability. This work sheds light on the sophisticated design of functionalized supraparticles for efficient water splitting.

KEYWORDS

carbon coating, OER, porous electrocatalyst, self-assembly, supraparticle

1 INTRODUCTION

Over the past decade, the exploration of new-style clean renewable energy is extremely imminent owing to the emergence of energy crises and environmental pollution threats.\(^{[1–2]}\) Hydrogen (H\(_2\)) is deemed to be an attractive alternative energy carrier to conventional fossil fuels. From a clean and sustainable perspective, water splitting is an effective and environmentally friendly process to generate H\(_2\) and oxygen (O\(_2\)) in high purity by the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) occurring on the cathode and anode, respectively.\(^{[3–6]}\) However, the overall energy efficiency is limited by the sluggish kinetics and high overpotential of the OER due to its complex four proton-coupled electron transfer process.\(^{[5–10]}\) Up to now, iridium dioxide (IrO\(_2\)) and ruthenium dioxide (RuO\(_2\)) are regarded as the state-of-the-art electrocatalysts for the OER, but their large-scale use is hampered by the scarcity and high cost of noble metals, making this energy production system less profitable on the practical application.\(^{[11,12]}\)

Consequently, it is of critical importance to develop earth-abundant, cost-effective, and efficient non-noble-metal-based OER catalysts, which can promote the electrocatalytic performance at a reduced overpotential.

Recently, transition metal oxides (TMOs) have been widely studied as one of the most compelling OER electrocatalysts in alkaline solutions owing to their low cost, abundant source, and unique electronic structure.\(^{[6,13–16]}\) In particular, nickel ferrite (NiFe\(_2\)O\(_4\)), which belongs to the mixed-metal spinel oxides, displays superior electrocatalytic activities because of the electron hopping between different valence states of Ni\(^{2+}\) and Fe\(^{3+}\), which can provide necessary surface redox-active centers for oxygen adsorption and activation.\(^{[17–19]}\) However, its semiconductor nature with intrinsic low electrical conductivity seriously limits the rapid electron transfer, resulting in the underutilization of active sites.\(^{[20]}\) In addition, the large volume variation of NiFe\(_2\)O\(_4\) during the electrocatalytic process usually leads to...
inferior structure stability.\cite{17,21,22} Despite a variety of methods have been employed to solve the aforementioned problems, such as doping hetero-elements,\cite{23} introducing oxygen vacancies,\cite{24} designing unique nanostructures, and forming composites with conductive materials,\cite{25–29} further efforts are still required to explore alternative NiFe$_2$O$_4$-based electrocatalysts with high activity and durability.

On the other hand, self-assembled superlattices of nanoparticles (NPs) have been extensively applied in catalysis,\cite{30–32} sensors,\cite{33} and drug delivery\cite{34} by virtue of their collective and/or synergetic properties relative to the isolated NPs.\cite{35} In this regard, considerable attention has been paid to construct sophisticated functionalized NP superlattices with different sizes, morphologies, and compositions.\cite{36–39} Among them, porous supraparticles are recognized as particularly promising candidates for electrocatalysis because of the higher diffusion efficiency, larger surface areas, and more exposed active sites.\cite{40–42} Unfortunately, there are still several fatal deficiencies that hinder their practical applications. First, the colloidal NPs, which serve as the building blocks of supraparticles, typically suffer from poor electrical conductivity due to the capping of long-chain organic ligands.\cite{43} Second, the neighboring NPs are prone to deformation and aggregation under long-term recycling redox reaction.\cite{44} Finally, the majority of existing porous supraparticles exhibit single and narrow pore size distribution, which impedes the electrolyte infiltration and mass transport.\cite{44} Accordingly, rational design and engineering of hierarchically porous NiFe$_2$O$_4$ NP supraparticles with ameliorating conductivity and stability are expected to render greater opportunities for boosting OER performance.

Herein, hierarchically multichambered, carbon-coated Ni$_{0.4}$Fe$_{2.6}$O$_4$ NP superlattice microspheres (M-NFO@C-NSMs) were prepared through the droplet-based template method using Ni$_{0.4}$Fe$_{2.6}$O$_4$ NPs as the basic units; the native organic ligands tethered to the NP surface were carbonized in situ to obtain uniform carbon coatings by calcination. The unique hierarchical superstructure with macro-/meso-/microporosities can not only offer a substantial increase in the number of accessible external active sites but can also facilitate the rapid mass transport and evolved O$_2$ release. Additionally, the close-packed carbon shells derived from the native surface-capping ligands form a 3D continuous electron transfer network, enabling all the encapsulated Ni$_{0.4}$Fe$_{2.6}$O$_4$ NPs to be electrochemically active and stable. As a proof of concept, compared with their solid counterparts (S-NFO@C-NSMs) and commercial IrO$_2$ catalysts, M-NFO@C-NSMs manifest superior electrocatalytic activity with a comparably low overpotential of 316 mV at a current density of 10 mA cm$^{-2}$ and outstanding long-term cyclic stability toward OER in an alkaline electrolyte.

2 | RESULTS AND DISCUSSION

As illustrated in Figure 1, a self-assembly technique based on an emulsification process was employed to fabricate two kinds of carbon-coated Ni$_{0.4}$Fe$_{2.6}$O$_4$ NP superlattice microspheres (NFO@C-NSMs). Briefly, a hexane dispersion of 6 nm OA, OAm-capped Ni$_{0.4}$Fe$_{2.6}$O$_4$ NPs (Figure S1b) was first mixed with an aqueous solution of DTAB under homogeneous stirring. In the resulting mixture, the hydrophobic Ni$_{0.4}$Fe$_{2.6}$O$_4$ NPs were confined within the oil (hexane) droplets stabilized by surfactants to form an oil-in-water emulsion system. The subsequent evaporation of hexane drove NPs to pack densely within the emulsion droplets, yielding solid Ni$_{0.4}$Fe$_{2.6}$O$_4$ superlattice microspheres. Interestingly, when the ratio of water to hexane quadrupled while fixing other parameters, the obtained Ni$_{0.4}$Fe$_{2.6}$O$_4$ superlattice microspheres would undergo a solid-to-porous structural transformation. It is speculated that the formation of porous supraparticles is ascribed to the evolution of water-in-oil-in-water (W/O/W) double emulsions in the case of high water-to-oil ratios. Note that the composition of the aqueous phase in the emulsion system was increased, a number of tiny water droplets were thus introduced into the oil phase droplets during the vigorous stirring process. Due to the action of surfactants, the water droplets were relatively stable to avoid evident aggregation, thereby obtaining a hierarchical double emulsion system of oil-in-water and water-in-oil.

When hexane was continuously volatilized, the NPs were densely packed and the space occupied by the small water droplets still existed to afford hierarchically multichambered Ni$_{0.4}$Fe$_{2.6}$O$_4$ superlattice microspheres. At last, both types of Ni$_{0.4}$Fe$_{2.6}$O$_4$ superlattice microspheres were calcined at 500°C under N$_2$ to carbonize the organic ligands, yielding NFO@C-NSMs while retaining the structural integrity. Detailed structural and textural features of NFO@C-NSMs were examined using various characterization techniques. Low-magnification SEM and TEM images of S-NFO@C-NSMs are shown in Figure 2A and Figure S2D, respectively. The TEM images in Figure 2B and Figure S2D demonstrate that each solid superlattice microsphere is composed of numerous closely packed Ni$_{0.4}$Fe$_{2.6}$O$_4$ NPs, which is...
confirmed by HRSEM (Figure S2A and B). It can be observed the diameter of S-NFO@C-NSMs ranges from 200 to 1400 nm with a statistical average diameter of \( \sim 700 \text{ nm} \) (Figure S3A). As for M-NFO@C-NSMs, the SEM images in Figure 2C and D and Figure S4A show a relatively regular spherical morphology with multiple pores on the surface in the main view. Their diameter ranges from 400 to 1800 nm with a statistical average diameter of \( \sim 1000 \text{ nm} \) (Figure S3B), which is slightly larger than the solid ones, presumably ascribing to the involved tiny water droplets. The cross-sectional HRSEM image in Figure 2E, and Figure S4B and C shows the continuous hierarchically multichambered architecture with interconnected pores and holes of diverse sizes throughout the single sphere, while the shell is constructed by multilayer, close-packed NPs. The corresponding 3D schematic illustration for the main view and the cross-section of M-NFO@C-NSMs are inserted in Figure 2C and E, respectively, to reveal their structural features more visually. The TEM image of M-NFO@C-NSMs in Figure 2F and Figure S4D clearly shows the contrast differences in alternating domains, confirming the presence of diverse hierarchical porosities as well. Note that owing to the inhomogeneous distribution of stirring force in the double emulsion system, the size of the wrapped water droplets is unevenly distributed, such that the porous structure formed during assembly is continuous but disordered with different cavity diameters ranging from 100 to 1000 nm. SAXS was conducted to obtain additional assessment of the regularity of NFO@C-NSMs. As indicated by SAXS patterns (Figure 3A), both types of NFO@C-NSMs are long-range ordered superlattices with a typical face-centered cubic (FCC) symmetry. It is noteworthy that the pores and holes of the M-NFO@C-NSMs slightly deteriorate the overall structural ordering, as evidenced by the smeared diffraction peaks. X-ray diffraction (XRD) patterns of both solid and multichambered NP microspheres in Figure 3B exhibit
Figure 3 (A) SAXS patterns, (B) XRD patterns, (C) TGA curves, and (D) nitrogen adsorption–desorption isotherms of solid and multi-chambered NFO@C-NSMs.

A series of diffraction peaks that can be well indexed to cubic spinel-type nickel ferrite (JCPDS No. 87–2335), suggesting that the carbonization process of organic ligands did not convert the crystalline phase of Ni$_{0.4}$Fe$_{2.6}$O$_4$ NPs. Precise molar ratio of Fe and Ni was determined by ICP-AES to be 5.57. Therefore, the exact molecular formula of the as-prepared nickel ferrite was calculated to be Ni$_{0.4}$Fe$_{2.6}$O$_4$.

TGA carried out in air was employed to investigate the mass fraction of the amorphous carbon shell coated on Ni$_{0.4}$Fe$_{2.6}$O$_4$ NPs. As shown in Figure 3C, the carbon content of the solid and multichambered NP microspheres is similar (~5 wt%). The specific surface areas were determined by nitrogen adsorption–desorption measurements. Both NFO@C-NSMs exhibit type IV isotherms with H$_4$ type hysteresis loops at high $P/P_0$ (>0.9) region (Figure 3D), indicative of the co-existence of mesopores and micropores,[45] which are probably attributed to the interstitial space between neighboring NPs and amorphous carbon shells, respectively. According to the Brunauer–Emmett–Teller (BET) method, the specific surface area of multichambered NP microspheres is 43 m$^2$ g$^{-1}$, much higher than that (16 m$^2$ g$^{-1}$) of their solid counterparts. In addition, Figure S5 shows that M-NFO@C-NSMs exhibit narrower pore size distribution with much higher pore volume compared with S-NFO@C-NSMs (0.05 vs. 0.01 cm$^3$ g$^{-1}$). The unique interconnected hierarchically porous superstructure of M-NFO@C-NSMs can not only provide abundant exposed active sites but can also enhance the electrolyte diffusion and O$_2$ bubbles release.

Raman spectroscopy was employed to further investigate the chemical composition of M-NFO@C-NSMs. As expected, the Raman signal of Ni$_{0.4}$Fe$_{2.6}$O$_4$ can be detected in the low wavenumber region (Figure 4A). The peaks of Raman shift at 220 and 480 cm$^{-1}$ represent the $T_{2g}$ vibrational mode, while the peak at 284 cm$^{-1}$ represents the $E_g$ vibrational mode and the peak at 682 cm$^{-1}$ represents the $A_{1g}$ vibrational mode, in good agreement with previously reported crystalline nickel ferrite.[46] With respect to the high wavenumber region (Figure 4B), the D-band peak at 1331 cm$^{-1}$ (the defect-induced mode), and the G-band peak at 1578 cm$^{-1}$ (the graphitic mode) demonstrate the presence of carbon shells with a low graphitization degree ($I_D/I_G = 1.86$).[47] Partially graphitized carbon shells not only possess quite good conductivity for electron transfer, but the oxygen-containing functional groups on the surface can also increase the hydrophilicity and wettability in the electrolyte, both of which are conducive to accelerating the reaction kinetics of electrocatalysis. To gain more insights into the elemental composition and oxidation state, X-ray photoelectron spectroscopy (XPS) measurements were performed. The full XPS survey spectrum demonstrates the presence of Ni, Fe, C, and O elements (Figure 4C). The relatively high intensity of C is attributed to the amorphous carbon shells. High-resolution XPS spectrum of Ni 2p (Figure 4D) shows two dominant peaks located at 856.2 eV (Ni 2p$_{3/2}$) and 873.8 eV (Ni 2p$_{1/2}$) with two shakeup satellite peaks at 861.9 and 880.3 eV, respectively. The fitted Fe 2p spectrum (Figure 4E) exhibits two characteristic peaks at 711.2 eV (Fe 2p$_{3/2}$) and 724.9 eV (Fe 2p$_{1/2}$), and the deconvolution of overlapped peaks determines the $Fe^{3+}/Fe^{2+}$ ratio as 2:1, indicating the co-existence of rich metal valence states.[26] Concerning the fitted O 1s spectrum (Figure 4F), there are three peaks denoted as $O_A$ (530.3 eV), $O_B$ (531.6 eV), and $O_C$ (532.5 eV), which are ascribed to metal-oxygen bonds, chemically absorbed oxygen.
species at surface defect sites, and the physically adsorbed water, respectively.\[^{17}\]\] Interestingly, the quite high peak area ratio of \(\text{O}_2\) denotes the existence of large amounts of surface oxygen vacancies perhaps caused by the calcination treatment under inert gas, which can lower the charge transfer resistance,\[^{18}\] thus benefiting the electrochemical activity.

The OER activities of the as-prepared catalysts were investigated in 0.1 M KOH by linear scan voltammetry (LSV) methods after IR correction. The performance of Ni\(_{0.4}\)Fe\(_{2.6}\)O\(_4\)/C composites and commercial IrO\(_2\) was tested under the same conditions for comparison. The polarization curves in Figure 5A indicate that M-NFO@C-NSMs exhibit a substantially high OER catalytic activity with the lowest onset potential. Specifically, M-NFO@C-NSMs afford a current density (\(j\)) of 10 mA cm\(^{-2}\) at an overpotential (\(\eta\)) of only 316 mV (Figure 5B), which is significantly lower than that of S-NFO@C-NSMs (\(\eta\) = 352 mV), Ni\(_{0.4}\)Fe\(_{2.6}\)O\(_4\)/C composite (\(\eta\) = 372 mV), and commercial IrO\(_2\) (\(\eta\) = 390 mV). In addition, the mass activity of M-NFO@C-NSMs at \(\eta\) = 320 mV also remains superior to those of other reference samples (Figure S6 and Figure 5B). As shown in Figure 5C, M-NFO@C-NSMs have a Tafel slope of 51 mV dec\(^{-1}\), which is much smaller than that of S-NFO@C-NSMs (64 mV dec\(^{-1}\)), Ni\(_{0.4}\)Fe\(_{2.6}\)O\(_4\)/C composite (88 mV dec\(^{-1}\)), and commercial IrO\(_2\) (95 mV dec\(^{-1}\)), indicating their more favorable catalytic kinetics for OER. It should be noted that the outstanding catalytic activity of M-NFO@C-NSMs was obtained using a common glassy carbon (GC) electrode in a dilute electrolyte of 0.1 M KOH rather than nickel foam, copper foil, or carbon cloth electrodes with large supportive areas and high nonfaradaic background currents in a concentrated electrolyte of 1 M KOH. Even so, the catalytic performance of M-NFO@C-NSMs is still superior to that of most previously reported TMOs-based OER catalysts under alkaline conditions (Table S1).

Annauresic impedance spectroscopy (EIS) was performed to deeply understand the electrode reaction kinetics during the catalytic process. Generally, the semicircle in the Nyquist plots corresponds to the charge-transfer resistance (\(R_{ct}\)) at the electrode/electrolyte interface.\[^{17}\] As illustrated in Figure 5D, M-NFO@C-NSMs exhibit the lowest \(R_{ct}\) among all catalysts evaluated, indicating that the hierarchically multichambered superstructure along with the partially graphitized carbon shells could effectively expedite the charge-transfer kinetics between active sites and reactants. The obtained results are in accordance with the corresponding OER polarization curves and Tafel slopes. As shown in Figure S7 and Table S2, the electrochemically active surface area (ECSA) was calculated through the measurement of electrochemical double layer capacitance (\(C_{dl}\)) in the non-Faradaic regions. The \(C_{dl}\) of M-NFO@C-NSMs is almost twice higher than that of S-NFO@C-NSMs. The larger ECSA implies better exposure and enhanced utilization of active sites, thereby accounting for the improved catalytic activity. The LSV curves of both NFO@C-NSMs were normalized based on the ECSA to explore their intrinsic activity (Figure 5E and Table S2). As expected, the ECSA-normalized current density of M-NFO@C-NSMs becomes only slightly higher as compared with their solid counterparts. Therefore, the enhanced OER activity of M-NFO@C-NSMs can be mainly attributed to the increased specific active surface area with precisely controlled nano- and microscale architectures, revealing the quantitative structure–activity relationship of accessible active sites and practical electrocatalytic performance.

Long-term durability is another significant metric for OER electrocatalysts besides activity. In this regard,
the chronoamperometric measurements were recorded at different constant overpotentials, which drove each of catalysts to generate a same initial current density of 10 mA cm$^{-2}$. As shown in Figure 5F, the $j$ value of Ni$_{0.4}$Fe$_{2.6}$O$_4$/C composite reduced rapidly to about zero, presumably owing to the observed severe agglomeration of NPs during the cyclic electrocatalysis (Figure 6A and Figure S8). In contrast, for both M- and S-NFO@C-NSMs, the $j$ value remained relatively stable over 30,000 s with a small degradation, suggesting the self-assembled superlattice structure of NPs.
is particularly beneficial for enhancing the durability of electrocatalysts. The SEM images after the durability test in Figure 6B–D demonstrate the overall spherical morphology of both S- and M-NFO@C-NSMs was well preserved without cracking except for the smoother surface probably caused by the numerous cyclic redox reactions. The HRSEM images in Figure S9 reveal that the majority of close-packed Ni0.4Fe2.6O4 NPs retain their size and shape. In addition, the XRD pattern of M-NFO@C-NSMs after cycling demonstrates that the crystalline structure of Ni0.4Fe2.6O4 NPs was largely maintained with negligible deterioration of the peak intensity (Figure S10). To sum up, the overall ex situ characterization results of M-NFO@C-NSMs before and after long-term durability testing corroborate their robust structural stability at meso-, nano- and atomic scales.

The favored electrochemical durability of both S- and M-NFO@C-NSMs presumably originates from the enhanced interface stability of supraparticles as a consequence of collective interactions arising from the carbon-coated, close-packed NP superlattices relative to the isolated NPs loaded on carbon substrate, as schematically illustrated in Figure 7. Furthermore, the 3D continuous carbon network, constructed from the interconnected carbon shells on individual Ni0.4Fe2.6O4 NPs, can efficiently alleviate the migration and aggregation of NPs during the repeated electrocatalytic process. Taken together, all of the aforementioned results reasonably validate the excellent activity and stability of M-NFO@C-NSMs for electrocatalytic water oxidation.

Based on the above discussions, the superior electrocatalytic OER performance of M-NFO@C-NSMs can be attributed to their unique structure features. First, the hierarchically multichambered architecture with highly abundant macro-, meso-, and microporosities is favorable for exposing abundant accessible active sites as well as for facilitating electrolyte diffusion and evolved O2 bubbles release. In addition, the interconnected carbon shells can not only increase the electrical conductivity to expedite the reaction kinetics but can also play a protective and supporting role in preventing the loss of active sites caused by structural collapse during cyclic electrolysis process. Finally, the collective property of NP superlattice catalysts can simultaneously promote the electrocatalytic activity and long-term durability compared with the conventional isolated NP catalysts.

3 | CONCLUSION

In summary, multichambered, carbon-coated Ni0.4Fe2.6O4 NP superlattices have been successfully designed and synthesized by an emulsion-based assembly process. The unique hierarchically multichambered architecture endows M-NFO@C-NSMs with large specific area and enhanced accessibility of active sites, thus favoring the diffusion of electrolytes and the release of evolved O2. In addition, the 3D continuous conductive framework formed by the close-packed carbon shells enables all the encapsulated NPs to be electrochemically active and stable. Thanks to the optimized chemical composition and structural advantages, M-NFO@C-NSMs exhibit superior electrocatalytic OER activity compared with most TMO-based electrocatalysts reported previously. By delicately tuning the architecture and composition, this novel strategy is anticipated to be applicable for fabricating a broad range of hierarchically porous supraparticles for versatile potential applications such as catalysis, bio-imaging, energy storage, and water treatment.

4 | EXPERIMENTAL SECTION

4.1 | Materials

Oleic acid (OA, 90%), oleylamine (OAm, 90%), dodecyltrimethylammonium bromide (DTAB, 98%) potassium hydroxide (KOH, 99.99%), and benzyl ether were purchased from Sigma-Aldrich. Iron acetylacetonate [Fe(acac)3] and nickel acetylacetonate [Ni(acac)2] were purchased from Aladdin. Anhydrous ethanol and hexane were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were used as received without further purification.

4.2 | Synthesis of Ni0.4Fe2.6O4 NPs

Monodisperse Ni0.4Fe2.6O4 NPs stabilized by OA and OAm were prepared by a seed-mediated growth method according to literature. In a typical synthesis of 4 nm Ni0.4Fe2.6O4 seeds, 11.3 g of Fe(acac)3, 4.1 g of Ni(acac)2, 15 g of OA, and 55 g of OAm were dissolved in 50 mL of benzyl ether in a 200-mL three-neck flask. The solution was heated at 200°C under N2 for 1.5 h and was further heated at 295°C under N2 atmosphere for 1 h. After cooling down to room temperature, anhydrous ethanol was added to precipitate Ni0.4Fe2.6O4 NPs. The precipitated Ni0.4Fe2.6O4 NPs collected by centrifugation were redispersed in hexane to form a stable colloidal solution with a concentration of ~40 mg mL−1. In a typical procedure to synthesize 6 nm Ni0.4Fe2.6O4 NPs, 5.6 g of Fe(acac)3, 2 g of Ni(acac)2, 7.5 g of OA, and 23 g of OAm were dissolved in 80 mL of benzyl ether in a 200-mL three-neck flask. A total of 20 mL of the solution of Ni0.4Fe2.6O4 seeds in hexane was injected into the solution at 110°C. After reaction at 110°C under N2 for 10 min, the solution was heated to 200°C for 1 h and was further heated at 295°C for 40 min. After the solution was cooled down to room
4.3 Fabrication of carbon-coated Ni0.4Fe2.6O4 NP superlattice microspheres

Ni0.4Fe2.6O4 NP superlattice microspheres were fabricated by an emulsion-based assembly method. In brief, a hexane dispersion of Ni0.4Fe2.6O4 NPs (10 mL) was added to an aqueous solution of DTAB (20 mg mL\(^{-1}\), 100 mL). The resulting mixture was subjected to homogenization with a homogenizer (6000 rpm) for 10 min, producing an oil-in-water (O/W) emulsion system. Under continuous mechanical stirring (500 rpm), the emulsion was then heated to 40\(^{\circ}\)C under N\(_2\) for 2 h, during which the evaporation of hexane led to solid microspheres composed of close-packed Ni0.4Fe2.6O4 NPs. The resultant Ni0.4Fe2.6O4 NP superlattice microspheres suspended in water could be readily collected by a magnet. Hierarchically multichambered Ni0.4Fe2.6O4 NP superlattice microspheres were fabricated by a similar procedure, except that the ratio of water to hexane was increased fourfold. To carbonize the surface-coating OA ligands, both solid and multichambered Ni0.4Fe2.6O4 NP microspheres were calcined at 500\(^{\circ}\)C under N\(_2\) atmosphere for 2 h, resulting in carbon-coated Ni0.4Fe2.6O4 NP superlattice microspheres while retaining the NPs ordering.

4.4 Synthesis of Ni0.4Fe2.6O4/C composite

To elucidate the advantages of Ni0.4Fe2.6O4 NP microspheres, Ni0.4Fe2.6O4/C composite was synthesized via loading Ni0.4Fe2.6O4 NPs on Ketjen carbon (C) based on the literature method.\(^{[46]}\) The specific procedure is as follows: 40 mg of Ni0.4Fe2.6O4 NPs and 10 mg of Ketjen carbon were dispersed in the mixed solution of hexane and acetone (V/V = 1:1) and sonicated for 1 h. After centrifugation, the precipitated NPs-C powders were calcined at 500\(^{\circ}\)C under N\(_2\) atmosphere for 2 h to obtain the Ni0.4Fe2.6O4/C composite.

4.5 Characterization

Scanning electron microscopy (SEM) and high-resolution SEM (HRSEM) images were obtained using a Zeiss Ultra-55 microscope operated at 5 kV. Energy dispersive X-ray spectroscopy (EDS) and elemental mapping were carried out on the equipped Oxford X-Max 50 detector. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images were obtained on a Tecnai G2 F20 S-TWIN microscope operated at 200 kV. Small-angle X-ray scattering (SAXS) was tested on a Xenocs Xeuss 2.0 SAXS system using Cu-K\(_z\) radiation (50 kV, 35 mA). Inductively coupled plasma and atomic emission spectroscopy (ICP-AES) was employed to determine the ration of Ni and Fe on a Thermo-Fisher iCap 7400 spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 TGA analyzer. XRD was conducted on a Bruker D8 X-ray diffractometer. Nitrogen adsorption–desorption isotherms were tested on a Quantachrome Autosorb-IQ instrument. Raman spectra were recorded at room temperature with an Xplora Raman system. XPS was carried out on an SSI S-Probe XPS spectrometer equipped with a monochromatic Al-K\(_z\) source (1486.6 eV).

4.6 Electrochemical measurements

The OER performance was measured using a typical three-electrode system in 0.1 M KOH electrolytes on an electrochemical workstation (Autolab 204 N). A graphite rod was used as the counter electrode and a commercial saturated calomel electrode (SCE) acted as the reference electrode. All potentials reported in this work were converted into potentials against the reversible hydrogen electrode (RHE) using the following equation: \(E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \, \text{pH} + 0.241 \, \text{V}\). To prepare the working electrode for OER, 1 mg of catalyst, 0.25 mg of Ketjen carbon and 6 \(\mu\)L of Nafion solution (5 wt\%) were dispersed in 250 \(\mu\)L of ethanol ultrasonically until a homogeneous ink was formed. Then 6 \(\mu\)L of the catalyst ink was pipetted onto GC electrodes (loading amount of 0.34 cm\(^2\)) and dried naturally. For comparison, a working electrode composed of commercial IrO\(_2\) catalyst was prepared in the same way. Cyclic voltammetry (CV) was performed at a scan rate of 50 mV/s from 0.2 to 0.8 V and recorded for 20 cycles when oxygen-evolving currents were stable. LSV was recorded at 5 mV s\(^{-1}\) to obtain the polarization curves, corrected for the iR compensation, and the overpotential (\(\eta\)) was calculated by \(\eta = E_{\text{RHE}} - 1.23 \, \text{V}\). EIS measurements were carried out at a overpotential of 320 mV via performing an applied voltage with the amplitude of 5 mV in a frequency range from 10\(^{5}\) to 1 Hz. Tafel slopes \((b)\) were obtained via fitting the linear regions of Tafel plots based on the Tafel equation \((\eta = b \times \log j + a)\), where \(j\) is the current density. Chronoanperometry technique was used to determine the long-term cyclic stability of electrocatalysts at current density = 10 mA cm\(^{-2}\). The electrochemical double-layer capacitance \((C_{dl})\) was determined via measuring the CV curves in the potential range of 1.1–1.2 V with scan rates from 2 to 10 mV s\(^{-1}\).

ACKNOWLEDGMENTS

The authors acknowledge the financial support from NSFC (22025501, 21872038, 21733003, and 51773042) and MOST (2020YFB1505803 and 2017YFA0207303).

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Dong Yang https://orcid.org/0000-0002-9677-8778

REFERENCES

1. A. Hepbasli, Renew. Sust. Energy Rev. 2008, 12, 593.
2. N. Kittner, F. Lill, D.M. Kammen, Nat. Energy 2017, 2, 17125.
3. J. Song, C. Wei, Z. Huang, C. Liu, L. Zeng, X. Wang, Z.J. Xu, Chem. Soc. Rev. 2020, 49, 2196.
4. R. Gao, D. Yan, Adv. Energy Mater. 2019, 10, 1900954.
5. F. Song, L. Bai, A. Moyiadiou, S. Lee, C. Hu, L. Liardet, X. Hu, J. Am. Chem. Soc. 2018, 140, 7748.
6. I. Roger, M.A. Shipman, M.D. Symes, Nat. Rev. Chem. 2017, 1.
7. H. Chen, X. Liang, Y. Liu, X. Ai, T. Asefa, X. Zou, Adv. Mater. 32, 2020, 2002435.
8. B.S. Yeo, A.T. Bell, J. Am. Chem. Soc. 2011, 133, 5587.
9. Z.P. Wu, X.F. Lu, S.Q. Zang, X.W.D. Lou, Adv. Funct. Mater. 2020, 30, 1910274.
10. W. Zhang, D. Li, L. Zhang, X. Shie, D. Yang, J. Energy Chem. 2019, 39, 39.
11. T. Audichon, T.W. Napporn, C. Canaff, C. Morais, C. Comminges, K.B. Kokoh, J. Phys. Chem. C 2016, 120, 2562.
12. Y. Lee, J. Santivich, K.J. May, E.E. Perry, Y. Shao-Horn, J. Phys. Chem. Lett. 2012, 3, 399.
13. Z. Li, X. Yu, U. Paik, J. Power Sources 2016, 310, 41.
14. J. Bao, X. Zhang, B. Fan, J. Zhang, M. Zhou, W. Yang, X. Hu, H. Wang, B. Pan, Y. Xie, Angew. Chem. 2015, 54, 7399.
15. C.F. Du, X. Sun, H. Yu, W. Fang, Y. Jing, Y. Wang, S. Li, X. Liu, Q. Yan, InfoMat. 2020, 2, 950.
16. B. Wang, C. Tang, H. Wang, X. Chen, R. Cao, Q. Zhang, J. Energy Chem. 2019, 38, 8.
17. G. Liu, K. Wang, X. Gao, D. He, J. Li, Electrochim. Acta 2016, 211, 871.
18. M. Li, Y. Xiong, X. Liu, X. Bo, Y. Zhang, C. Han, L. Guo, Nanoscale 2015, 7, 8920.
19. H. Chen, J. Yan, H. Wu, Y. Zhang, S.F. Liu, J. Power Sources 2016, 324, 499.
20. J. Liu, D. Zhu, T. Ling, A. Vasileff, S. Qiao, NanoEnergy 2017, 40, 264.
21. C. Mahala, M.D. Sharma, M. Basu, Electrochim. Acta 2018, 273, 462.
22. A. Martínez-Lázaro, A. Rico-Zavala, F.I. Espinosa-Lagunes, J. Torres-González, L. Álvarez-Contreras, M.P. Gurrero, L.G. Arriaga, J. Ledesma-García, E. Ortiz-Ortega, J. Power Sources 2019, 412, 505.
23. M. Fei, H. Shi, J. Zhao, N. Kang, W. He, H. Li, F. Yang, ChemCatChem 2018, 10, 5174.
24. Y. Huang, W. Yang, Y. Yu, S. Hao, J. Electroanal. Chem. 2019, 840, 409.
25. D. Das, S. Santra, K.K. Nanda, ACS Appl. Mater. Interfaces 2018, 10, 35025.
26. J. Huang, J. Han, R. Wang, Y. Zhang, X. Wang, X. Zhang, Z. Zhang, Y. Zhang, B. Song, S. Jin, ACS Energy Lett. 2018, 3, 1698.
27. G. Guo, L. Ji, X. Shen, B. Wang, H. Li, J. Hu, D. Yang, A. Dong, J. Mater. Chem. A 2016, 4, 16128.
28. J. Liu, H. Yuan, Z. Wang, J. Li, M. Yang, L. Cao, G. Liu, D. Qian, Z. Lu, Chem. Commun. 2019, 55, 10860.
29. X. Lu, L. Gu, J. Wang, J. Wu, P. Liao, G. Li, Adv. Mater. 2017, 29, 1604437.
30. C. Zhang, B. Wang, X. Shen, J. Liu, X. Kong, S.S.C. Chuang, D. Yang, A. Dong, Z. Peng, Nano Energy 2016, 30, 503.
31. L. Yao, B. Wang, Y. Yang, X. Chen, J. Hu, D. Yang, A. Dong, Chem. Commun. 2019, 55, 1229.
32. T. Li, B. Xue, B. Wang, G. Guo, D. Han, Y. Yan, A. Dong, J. Am. Chem. Soc. 2017, 139, 12133.
33. M. Kobayashi, J. Ueno, M. Enami, S. Katsuta, A. Ichiba, K. Ogura, K. Onomitsu, Y. Horikoshi, J. Cryst. Growth 2005, 278, 273.
34. C. Sun, J.S.H. Lee, M. Zhang, Adv. Drug Delivery Rev. 2008, 60, 1252.
35. K. Hou, J. Han, Z. Tang, ACS Mater. Lett. 2019, 2, 95.
36. M.A. Boles, M. Engel, D.V. Talapin, Chem. Rev. 2016, 116, 11220.
37. S. Wintzheimer, T. Granath, M. Oppmann, T. Kister, T. Thai, T. Kraus, N. Vogel, K. Mandel, ACS Nano 2018, 12, 5093.
38. Y. Yan, G. Guo, T. Li, D. Han, J. Zheng, J. Hu, D. Yang, A. Dong, Electrochim. Acta 2017, 246, 43.
39. D. Han, G. Guo, Y. Yan, T. Li, B. Wang, A. Dong, Energy Storage Mater. 2018, 10, 32.
40. W. Liu, M. Kappi, H. Butt, ACS Nano 2019, 13, 13949.
41. L. Yao, Y. Peng, Y. Zhang, ACS Appl. Energ. Mater. 2020, 3, 4139.
42. J. Qi, W. Zhang, R. Xiang, K. Liu, H.Y. Wang, M. Chen, Y. Han, R. Cao, Adv. Sci. 2015, 2, 1500199.
43. Y. Jiao, D. Han, Y. Ding, X. Zhang, G. Guo, J. Hu, D. Yang, A. Dong, Nat. Commun. 2015, 6, 6420.
44. X. Yu, G. Chen, Y. Wang, J. Liu, K. Pei, Y. Zhao, W. You, L. Wang, J. Zhang, L. Xing, J. Ding, G. Ding, M. Wang, R. Che, Nano Res. 2020, 13, 437.
45. M. Li, G. Wu, Z. Liu, X. Yi, X. Xia, J. Ning, D. Yang, A. Dong, J. Hazard. Mater. 2020, 397, 122766.
46. P. Sivakumar, R. Ramesh, A. Ramanand, S. Ponnusamy, C. Muthamizhchelvan, Mater. Res. Bull. 2011, 46, 2204.
47. D. Han, Y. Jiao, W. Han, G. Wu, T. Li, D. Yang, A. Dong, Carbon 2018, 140, 265.
48. H. Zhu, S. Zhang, Y. Huang, L. Wu, S. Sun, Nano Lett. 2013, 13, 2947.

**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

---

**How to cite this article:** Li M, Deng Y, Wu G, et al. Multi-chambered, carbon-coated NiO4Fe2.6O4 nanoparticle superlattice microspheres for boosting water oxidation reaction. Aggregate. 2021;2:e17. https://doi.org/10.1002/agt2.117