Incorporating Nitrogen-Doped Graphene Quantum Dots and Ni$_3$S$_2$ Nanosheets: A Synergistic Electrocatalyst with Highly Enhanced Activity for Overall Water Splitting

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A noble-metal-free electrocatalyst is fabricated via in situ formation of nanocomposite of nitrogen-doped graphene quantum dots (NGQDs) and Ni$_3$S$_2$ nanosheets on the Ni foam (Ni$_3$S$_2$-NGQDs/NF). The resultant Ni$_3$S$_2$-NGQDs/NF can serve as an active, binder-free, and self-supported catalytic electrode for direct water splitting, which delivers a current density of 10 mA cm$^{-2}$ at an overpotential of 216 mV for oxygen evolution reaction and 218 mV for hydrogen evolution reaction in alkaline media. This bifunctional electrocatalyst enables the construction of an alkali electrolyzer with a low cell voltage of 1.58 V versus reversible hydrogen electrode (RHE) at 10 mA cm$^{-2}$. The experimental results and theoretical calculations demonstrate that the synergistic effects of the constructed active interfaces are the key factor for excellent performance. The nanocomposite of NGQDs and Ni$_3$S$_2$ nanosheets can be promising water splitting electrocatalyst for large-scale hydrogen generation or other energy storage and conversion applications.

1. Introduction

Electrolysis of water to molecular hydrogen is widely accepted as one of promising approaches for sustainable energy supplies.[1] However, the overall water splitting reaction is quite difficult to motivate due to the high overpotential of its two half reactions: oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).[3] In this regard, electrocatalysts are needed to activate the overall water splitting reaction, which always involve the Ir or Ru oxides for OER and Pt-based materials for HER.[3] Nevertheless, the prohibitive cost, low abundance, and poor stability of these materials limit their extensive commercial usage.

Hence, intense efforts have been devoted to the development of high performance, inexpensive, and earth-abundant substitutes for the noble-metal-based electrocatalysts.[4] Recently, carbon nanomaterials, such as carbon nanotubes and graphene layers, have been integrated with transition metal-based nanocrystals (M$_x$N$_y$, M = Ni, Co, Fe, etc., N = O, S, C, P, etc.) as a new kind of functional OER and HER electrocatalysts with rapidly escalating attention.[5–7] In nature, graphene quantum dots (GQDs), the graphene sheets with lateral dimensions less than 100 nm in single, double, and a few layers (3–10 layers),[8] not only inherit excellent properties from graphene but also can be expected some new phenomena associated with its quantum confinement and edge effects.[9,10] Moreover, doping carbon nanomaterials with heteroatoms, such as nitrogen, phosphorus, boron, sulfur, into the carbon frameworks can effectively modulate the electronic characteristics, surface and local chemical features, which subsequently promotes the catalytic performance.[11,12]
To this end, various attempts have been dedicated to developing highly efficient hybrid of carbon dots or heteroatom-doping graphene with transition metal-based nanocrystals for OER or HER, such as carbon nanodots/CoO4 nanoclusters,[13] carbon quantum dot/NiFe layered double-hydroxide,[14] Fe2P/nitrogen-doped graphene,[15] and N-doped Co9S8/graphene.[5] As a promising electrocatalyst for water splitting, Ni3S2 nanomaterials recently have received numerous attention due to its intrinsic metallic behavior, rich abundance, and environmentally friendly.[16–18] Nevertheless, sole Ni3S2 nanostructures are still poorer than conventional noble metals in the catalytic activity. Some reports have proved that coupling Ni3S2 with other active species can efficiently improve their catalytic ability, such as MoS2/Ni3S2,[19] MoOx/Ni3S2,[20] and vanadium-doped Ni3S2.[21] Therefore, the smart coupling engineering of heteroatom-doping graphene quantum dots with Ni3S2 can be an effective route to tune their activity for overall water splitting.

Herein, we design a nanocomposite by coupling of the nitrogen-doped graphene quantum dots (NGQDs) with Ni3S2 nanosheets on the surface of the Ni foam (Ni3S2-NGQDs/NF). Microwave synthetic technique was applied to prepare the nitrogen-doped graphene oxide quantum dots (NGQDs) with a biomass, watermelon fleshes, as both the C and N sources, followed by a hydrothermal treatment with NF in thiourea aqueous for the formation of Ni3S2-NGQDs/NF. As expected, the ingenious incorporation of NGQDs with Ni3S2 nanosheets induces an excellent catalytic activity and stability for OER, HER, and the overall water splitting reaction, which is comparable to the state-of-the-art nonprecious-metal-based water splitting catalysts in alkaline media.

2. Results and Discussion

Figure 1A illustrates the synthetic process of NGOQDs, including the hydrothermal treatment of watermelon fleshes, the pyrolysis of carbon aerogels under N2 atmosphere and the microwave treatment of carbon powders. After separation and dialysis, 300 mL deep brown NGOQDs aqueous with the concentration of 1800 mg L−1 could be obtained at one time with a high yield of 54% (Figure S1A, Supporting Information). The NGOQDs can emit bright greenish-yellow fluorescence when irradiated under 365 nm ultraviolet visible (UV) light (Figure S1B,C, Supporting Information). The quantum yield is measured to be 14% by using fluorescein in 0.1 m NaOH as the reference. The UV spectrum of NGOQDs aqueous shows a typical absorption peak at 225 nm from π−−π* transitions of aromatic sp2 domain (Figure S2A, Supporting Information).[8] Meanwhile, the photoluminescence (PL) spectra of NGOQDs aqueous with different excitation wavelengths are shown in Figure S2A (Supporting Information). The emission peak slightly shifts to longer wavelength with red shift of the excitation wavelength and displays a maximum emission wavelength at 510 nm, in accordance with their trait of greenish-yellow fluorescence.[22]

The atomic force microscopy (AFM) image shows that the average topographic height of the NGOQDs is 1.0 nm.
(Figure 1B), unraveling that most of the NGOQDs are single layer or bilayer.[23] The NGOQDs are uniformly dispersed with an average lateral size of 4.6 nm as shown in the transmission electron microscopy (TEM) image (Figure 1C and its inset). Besides, two sets of lattice fringes can be observed in the high-resolution TEM (HRTEM) image (Figure 1D), displaying interplanar distances of 0.24 and 0.21 nm in accordance with the (1120) and (100) planes of graphite, respectively.[8,24] Meanwhile, different from the raw carbon powders with an evident peak at 26° (Figure S3A, Supporting Information), the X-ray diffraction (XRD) pattern of the NGOQDs gives a broad peak located at 11° (Figure S2B, Supporting Information) matched well with the (001) diffraction of graphite,[25] which is close to the exfoliated graphene oxide.[26,27]

The X-ray photoelectron spectrum (XPS) of the NGOQDs shows that the NGOQDs mainly consist of C, N, and O elements with the atomic concentration ratio of 64.05, 5.53, and 30.43 at%, respectively (Figure 1E), along with the mass ratio of C (62.50 wt%) and N (12.38 wt%) as examined from the elemental analysis. Four peaks can be observed in the C 1s deconvoluted high-resolution XPS spectrum (Figure 1F). They are originating from the C in the C 1s deconvoluted high-resolution XPS spectrum from the elemental analysis. Four peaks can be observed in the C 1s deconvoluted high-resolution XPS spectrum (Figure 1F). They are originating from the C=C (283.8 eV), C=O/C=N (284.6 eV), C=O/C=N (285.7 eV), O=C=O (287.5 eV), respectively, in good agreement with the Fourier transform infrared spectroscopy (FT-IR) spectrum result (Figure S2C, Supporting Information).[8,28,29] These oxygen-contained groups would be formed by the strong acidification process for there are less oxygen-contained groups in the raw carbon powders as revealed from the FT-IR spectrum (Figure S3B, Supporting Information). The N 1s high-resolution XPS spectrum comprises peaks corresponding to chemisorbed-like (405.1 eV), quaternary-like (400.6 eV), and pyridinic-like (398.8 eV) nitrogen atoms (Figure 1G).[8] The N in NGOQDs arises from the rich amino acid, protein or nitrogen atoms (Figure 1G). [8] The NGOQDs have been fabricated in gram-scale by using the sulfidization hydrothermal process.[16]

After hydrothermal deposition, the NF turns brown and some rough species are in situ grown on it (Figure 3A inset), as is compared to the original NF (Figure S4A, Supporting Information). The scanning electron microscopy (SEM) and TEM were first used to observe the morphology and crystalline structure of Ni$_3$S$_2$-NGQDs/NF. The 3D open pore microstructure of NF is still retained (Figure 3A inset), which can facilitate the mass transport of the reactants and gaseous products (O$_2$ and H$_2$).[32] The coated Ni$_3$S$_2$-NGQDs on NF are the interlaced free-standing nanosheets with 20 nm in thickness, forming plentiful secondary pore canals with greatly enlarged working surface area (Figure 3A,B). The morphology of the Ni$_3$S$_2$ keeps the nanosheets feature when the NF was directly treated by the sulfidization process with thiourea (Figure S4B, Supporting Information).[16]

The TEM image (Figure 3C) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images (Figure S5A,B, Supporting Information) show that the NGOQDs are homogeneously attached on the surface of the Ni$_3$S$_2$ nanosheets. The interplanar distances of 0.24 and 0.21 nm observed in the HRTEM image conform to the (1120) and (100) crystallographic planes of graphitic carbon (Figure 3D). [8,24] Meanwhile, the FT-IR spectra of Ni$_3$S$_2$-NGQDs/NF and NGOQDs/NF in Figure 4A (curve a, c) both show the characteristic peaks of O–H stretching vibration (3444 cm$^{-1}$), C=O stretching vibration (1645 cm$^{-1}$), C–N/C–O stretching vibrations (1381/1088 cm$^{-1}$) and the Ni–O stretching vibration (590 cm$^{-1}$).[28,33] While almost without any typical peaks can be observed for Ni$_3$S$_2$/NF (Figure 4A, curve b), revealing the formation of hybrid between Ni$_3$S$_2$ and NGOQDs. Moreover, the solid-state PL and Raman spectra of Ni$_3$S$_2$-NGQDs/NF in Figure S6A,B (Supporting Information) all present the prominent signals from NGOQDs.
These results evidence that the NGQDs were tightly incorporated with the Ni$_3$S$_2$ nanosheets.[14,18]

The XRD pattern of Ni$_3$S$_2$-NGQDs/NF was further used to analyze the crystalline structure (Figure 4B). The diffraction peaks at 21.7°, 31.1°, 37.7°, 49.7°, and 55.2° are corresponding to the (101), (110), (003), (113), and (122) of Ni$_3$S$_2$ hexagonal phase crystal (JCPDS no. 44-1418).[16] close to the Ni$_3$S$_2$ nanorods of previous literature.[18] Moreover, the NGQDs are formed by the reduction of NGOQDs in the hydrothermal deposition process as indicated from the diffraction peak at 26° for the (002) plane of graphite (JCPDS no. 41-1487).[34,35] The other three typical diffraction peaks associating to the (111), (200), and (220) of Ni metal (JCPDS no. 70-0989) are derived from the NF and NiO.[1] The XRD results further confirm that the Ni$_3$S$_2$-NGQDs/NF is a mixture of three phases: Ni$_3$S$_2$, NGQDs, and NF.

The existence of Ni, S, C, N, and O elements in Ni$_3$S$_2$-NGQDs/NF was revealed by HAADF-STEM energy-dispersive X-ray (HAADF-STEM-EDX) mapping images (Figure S5C–G, Supporting Information), EDX (Figure S7A, Supporting Information), and XPS spectra (Figure S7B, Supporting Information). Besides, these elements are uniformly dispersed throughout the nanosheets with the atomic concentration ratio of Ni/C to be 1/1. The Ni 2p XPS spectrum (Figure 4C) shows that the Ni exists in the forms of metal Ni (854.6 eV) and multivalent Ni$^{\delta+}$ (860.2, 872.5, and 878.5 eV), close to the Ni state in Ni$_3$S$_2$/NF (Figure S7D, Supporting Information).[36] Compared the S 2p XPS spectra of Ni$_3$S$_2$/NF (Figure S7E, Supporting Information) to Ni$_3$S$_2$-NGQDs/NF (Figure 4D), it can deduce that S$^{2-}$ and S$^{3-}$ are primary forms in Ni$_3$S$_2$/NF, while S$^{2-}$, S$^{3-}$, and SO$_4^{2-}$ are main species in Ni$_3$S$_2$-NGQDs/NF due to the introduction of NGQDs carrying more oxygen-species.[16,36,37] The C=C and C=O/C=N active sites for OER and HER, and thus can be anticipated with decent electrocatalytic performance.

Firstly, the Ni$_3$S$_2$-NGQDs/NF was directly employed as an electrode to catalyze the OER. For comparison, Ni$_3$S$_2$/NF, NGOQDs/NF, RuO$_2$/NF, and NF were also investigated under the same conditions. The polarization curves of these samples were shown in Figure 5A. Except for RuO$_2$/NF and NF, an oxidation peak observed around 1.35 V versus reversible hydrogen electrode (RHE) before the water oxidation is contributed to the transformation of Ni (II) to Ni (III or IV) species of these samples, which is considered as the active sites of Ni-based materials for OER.[44] Of note, the intensity of the oxidation peak from Ni (II) increases in the sequence of Ni$_3$S$_2$/NF, NGOQDs/NF, and Ni$_3$S$_2$-NGQDs/NF. In consequence, the Ni$_3$S$_2$-NGQDs/NF exhibits the overpotential of 216 mV at 10 mA cm$^{-2}$ (Figure 5B), much lower than those of the RuO$_2$/NF (265 mV), NF (388 mV), Ni$_3$S$_2$/NF (317 mV), and NGOQDs/NF (314 mV). As compared to the recently reported OER noble-metal-free electrocatalysts (Table S2, Supporting Information), the Ni$_3$S$_2$-NGQDs/NF performs amongst the best. Meanwhile, the current densities at the overpotential of 420 mV of these samples were compared in Figure 5B. The Ni$_3$S$_2$-NGQDs/NF reaches 143 mA cm$^{-2}$ under the same conditions. The polarization curves of these samples were shown in Figure 5C. Evidently, the Ni$_3$S$_2$-NGQDs/NF displays a lower Tafel slope (95.5 mV dec$^{-1}$) relative to Ni$_3$S$_2$/NF (115.2 mV dec$^{-1}$), NGOQDs/NF (123.9 mV dec$^{-1}$), RuO$_2$/NF (107.1 mV dec$^{-1}$), and NF (147.0 mV dec$^{-1}$), respectively. This suggests the reaction kinetics for Ni$_3$S$_2$-NGQDs/NF is more favorable, further implying its higher OER activity.[45]
To evaluate the electrocatalytic stability of the Ni$_3$S$_2$-NGQDs/NF toward OER, the chronoamperometry curve at 1.45 V versus RHE for over 60,000 s was shown in Figure 5D. It depicts the impressive OER stability of the Ni$_3$S$_2$-NGQDs/NF without evident current degradation. Besides, the polarization curve nearly keeps the same after the stability measurement for 60,000 s (Figure 5E), confirming the excellent stability of the Ni$_3$S$_2$-NGQDs/NF. The improved electrocatalytic performance and strong durability reveal that the Ni$_3$S$_2$-NGQDs/NF is an efficient OER catalyst. This can be mainly ascribed to its higher electrochemically active surface areas (ECSA) and its enhanced electron transfer rate as indicated respectively by the comparison of corresponding geometric double layer capacitance $C_{dl}$ (Figure S8, Supporting Information) and charge transfer resistance $R_{ct}$ (Figure 5F; Table S1, Supporting Information).[36,46]

The HER activities of the as-prepared samples were subsequently assessed in N$_2$-saturated 1.0 m KOH electrolyte. The polarization curves in Figure 6A shows that the onset potentials of Ni$_3$S$_2$/NF (128 mV), NGQDs/NF (160 mV), and NF (248 mV) are all much higher than that of the Ni$_3$S$_2$-NGQDs/NF (125 mV), which is approaching the Pt-C/NF. Moreover, except inferior to the Pt-C/NF, the Ni$_3$S$_2$-NGQDs/NF reaches the current density of 10 mA cm$^{-2}$ at a lower overpotential of 218 mV and displays greater current density at the overpotential of 300 mV than other control samples and some recently reported catalysts (Figure 6B; Table S2, Supporting Information). On the other hand, the lower Tafel slope (Figure 6C) and $R_{ct}$ (Figure 6F; Table S1, Supporting Information) suggest that the Ni$_3$S$_2$-NGQDs/NF possesses a higher HER kinetics and a more rapid electron transfer rate, respectively.[36]
Furthermore, the HER stability measurement of the Ni$_3$S$_2$-NGQDs/NF was conducted by the chronoamperometry and the related curve was shown in Figure 6D. The current densities at 10 mA cm$^{-2}$ almost have no attenuation for 60 000 s test, revealing its gratifying durability for HER in alkaline media. Meanwhile, the improved durability of the Ni$_3$S$_2$-NGQDs/NF toward HER can be further testified by the polarization curves obtained before and after the chronoamperometry test. No variations can be observed in the overpotential at 10 mA cm$^{-2}$ and the current densities. Additionally, the Faradic efficiency of the Ni$_3$S$_2$-NGQDs/NF during O$_2$ and H$_2$ evolution was probed by the comparison of the volume of experimentally generated gas and the theoretical gas volume. The examined results show that Faradic yield of O$_2$ and H$_2$ production is nearly 100% over the time scale of the measurements, suggesting the pure OER and HER occurred on the anodic and cathodic electrode (Figure S9, Supporting Information), respectively.$^{[47,48]}$

It is worth noting that the Ni$_3$S$_2$-GQDs/NF prepared by replacing the NGQDs with the GQDs displays inferior electrocatalytic performance for OER and HER as compared to the Ni$_3$S$_2$-NGQDs/NF, even it has the analogous ECSA and $R_{ct}$ (Figure S10 and Table S1, Supporting Information). This phenomena manifests the key role of N-doped species in enhancing the electrocatalytic activity by altering the composition and electron structure of the obtained nanocomposite.$^{[49]}$

Synchronously, the effect of NGQDs content on the OER and HER activities was also investigated. It can be observed that Ni$_3$S$_2$-NGQDs/NF obtained in 0.05 mg mL$^{-1}$ NGOQDs aqueous gives much higher OER and HER performance than those of the Ni$_3$S$_2$-NGQDs-0.01/NF with 0.01 mg mL$^{-1}$ of NGOQDs and Ni$_3$S$_2$-NGQDs-0.1/NF with 0.1 mg mL$^{-1}$ of NGOQDs (Figure S11, Supporting Information). These might be due to the less formation of active species with low NGOQDs content, while too much NGOQDs cover the active species.

For the evaluation of the catalytic activity toward overall water splitting, a two-electrode configuration was applied

**Figure 5.** A) Polarization curves for OER of (a) Ni$_3$S$_2$-NGQDs/NF, (b) Ni$_3$S$_2$/NF, (c) NGQDs/NF, (d) NF, and (e) RuO$_2$/NF. B) Comparison of overpotential at 10 mA cm$^{-2}$ and current density at overpotential of 420 mV for all as-obtained samples, C) corresponding Tafel plots with associated linear fittings, D) chronoamperometric curve of Ni$_3$S$_2$-NGQDs/NF at overpotential of 220 mV, E) polarization curves of Ni$_3$S$_2$-NGQDs/NF before and after stability measurement, and F) Nyquist plots of these electrodes in 1.0 M KOH at a potential of 1.55 V (vs RHE, inset is equivalent circuit used for fitting the Nyquist plots).
with Ni$_3$S$_2$-NGQDs/NF as both anode and cathode electrode materials, along with the Ni$_3$S$_2$/NF, RuO$_2$-Pt-C/NF, and NF as references. The polarization curves in Figure S12A (Supporting Information) show that the Ni$_3$S$_2$-NGQDs/NF gives much more negative onset potential and higher catalytic current density than those of the Ni$_3$S$_2$/NF, RuO$_2$-Pt-C/NF, and NF. Moreover, the Ni$_3$S$_2$-NGQDs/NF shows a superior durability with negligible degradation over 12 h galvanostatic electrolysis at the current density of 10 mA cm$^{-2}$ and the applied potential almost maintains at 1.58 V versus RHE (Figure S12B, Supporting Information). This potential surpasses Ni$_3$S$_2$/NF (1.64 V), RuO$_2$-Pt-C/NF (1.62 V), and many advanced electrocatalysts reported recently for overall water splitting, such as Ni/NiP (1.61 V vs RHE),[1] NiS/Ni foam (1.64 V vs RHE),[45] NiCo$_2$S$_4$ NW/NF (1.63 V vs RHE),[36] NiCo$_2$O$_4$/NF (1.65 V vs RHE),[50] and NiFe LDH/Ni foam (1.7 V vs RHE).[51] Additionally, gas bubbles can be obviously observed at the Ni$_3$S$_2$-NGQDs/NF-constructed anode and cathode with an applied voltage of ≈1.65 V versus RHE (Movie 1) or powered by an AAA battery (Figure S12C,D, Supporting Information). The electrolyzer using the Ni$_3$S$_2$-NGQDs/NF nanocomposite shows a low overpotential and satisfactory stability, making it a promising practical electrocatalyst for overall water splitting.

Altogether the Ni$_3$S$_2$-NGQDs/NF exerts enhanced OER and HER activity than the Ni$_3$S$_2$-GQDs/NF, Ni$_3$S$_2$/NF, NGQDs/NF, NF samples, and some non-noble-metal-based catalysts (Table S2, Supporting Information). This can be originated from the following aspects as illustrated in Figure 7. The 3D free-standing nanosheets of Ni$_3$S$_2$-GQDs/NF interlace together to form numerous pore passages (Figure 7A), which are in favor of the mass transfer, infiltration of electrolytes, and the diffusion of gaseous products. Besides, the striking thin nanosheets render itself with much larger specific surface area and thereby provide more reaction sites.

And more importantly, the decoration of NGQDs on the Ni$_3$S$_2$ nanosheets promotes the electron transfer (Figure 7A).
Furthermore, the abundant edge sites of NGQDs could bring many catalytic active species, such as Ni$_x$N$_y$, pyridinic-N, NiO$_x$, Ni(OH)$_2$, etc., which can be explicated by the FT-IR, XRD, XPS, Raman, and UV results (Figure 4; Figures S6B,C and S7C, Supporting Information). Thus, the OER and HER intermediates adsorption and desorption occur more easily.[44] Synchronously, the well stability of the morphology, composition, and crystalline structures throughout the electrocatalysis process determine the Ni$_3$S$_2$-NGQDs/NF with pronounced durability for OER (Figure S13, Supporting Information) and HER (Figure S14, Supporting Information). Moreover, it can be found that the content of Ni=OH and Ni=O species increased during the catalysis process for OER and HER based on the FT-IR and XRD results (Figures S13C,D and S14C,D, Supporting Information), further promoting the electrocatalytic performance of the Ni$_3$S$_2$-NGQDs/NF.[19,52]

Density functional theory (DFT) calculations were performed to better understand the origin of improved catalytic performance of the Ni$_3$S$_2$-NGQDs/NF. The correlative Ni–N coordination bond on the interface between Ni$_3$S$_2$ and NGQDs was chosen as the theoretical model. For the chemisorption of the oxygen-containing intermediates (*O) in the OER process, the edge Ni atom near the Ni–N coordination bond between the constructed interfaces was demonstrated to be more active than the others (Figures S15 and S16, Supporting Information). The Ni–N binding interaction between the NGQDs and Ni$_3$S$_2$ can be found in the calculated partial density of states (PDOS) as presented in Figure 7B.[3] Some p orbital peaks of N atoms in NGQD are induced near the Fermi level when composited onto the Ni$_3$S$_2$. The Ni 3d orbital is shifted toward higher energy, which leads to an increase of the overall DOS at the Fermi level for the Ni$_3$S$_2$-NGQDs prototype. These results reveal that the introduction of NGQDs to the Ni$_3$S$_2$ can change the electronic structure of Ni$_3$S$_2$ and add more active edge sites to improve the electrical conductivity and catalytic performance, consistent well with our experimental results.[53]

Additionally, the calculated free energy diagram for the four intermediate steps in the OER displays that all the steps are uphill except the OH* absorption as no voltage given (Figure 7C). Once the voltage of 1.23 or 1.81 V is applied, almost all the steps are energetically downhill and the chemisorption energy for each reaction is more energetically favorable as compared to the pure Ni$_3$S$_2$ and N-doped graphene from previous reports.[16,54] Besides, we investigated the effect of the oxidized Ni$_3$S$_2$-NGQDs toward OER, since the surface Ni$_3$S$_2$ in Ni$_3$S$_2$-NGQDs/NF would be partly oxidized into NiO$_x$ during the OER process as aforementioned. The catalytic performance of the oxidized Ni$_3$S$_2$-NGQDs complex could be evidently improved because the four steps of the OER are more energetically favorable (Figure S17, Supporting Information) than those of the Ni$_3$S$_2$-NGQDs (Figure 7C). These results indicate the more facile absorption of the intermediates on Ni$_3$S$_2$-NGQDs in OER process, suggesting that the existence of NGQDs on Ni$_3$S$_2$ or oxidized Ni$_3$S$_2$ can highly accelerate the OER process.[19,55] Meanwhile, the chemisorption free energies of hydrogen (ΔG(H*)) for different catalytic species in HER process were also evaluated by the DFT (Figure S17, Supporting Information). It can be found that the ΔG(H*) of Ni$_3$S$_2$-NGQDs is much more close to zero than those of sole Ni$_3$S$_2$ and NGQDs, verifying the higher HER catalytic activity of the Ni$_3$S$_2$-NGQDs.[56]

As such, the NGQDs anchored on the Ni$_3$S$_2$ nanosheets can favorably improve the conductivity and produce more active edge sites. The synergistic effects between NGQDs and Ni$_3$S$_2$ nanosheets are primarily proved to endow the Ni$_3$S$_2$-NGQDs/NF with remarkable electrocatalytic performance toward OER, HER, as well as the overall water splitting reaction. This work provides a new route to construct noble-metal-free nanocomposites through coupling the heteroatom
doing graphene quantum dots with transition metal-based nanomaterials, which can be extended to design other functional electrocatalysts.

3. Conclusion

In summary, the coupling of NGQDs and Ni$_3$S$_2$ nanosheets in situ on Ni foam was achieved and it was investigated as an advanced bifunctional OER and HER electrocatalyst. The NGOQDs were obtained in gram-scale by using the inexpensive and earth-abundant biomass (watermelon fleshes) as raw materials. Thanks to the graphene backbones, N doping sites and numerous edges with enriched oxygen functional groups of the NGOQDs, the NGQDs were successfully introduced into Ni$_3$S$_2$ nanosheets to regulate its electrocatalytic activity for water splitting reaction. The synergistic effects between NGOQDs and Ni$_3$S$_2$ nanosheets are experimentally and theoretically demonstrated the key factor to improve the electrocatalytic performance of Ni$_3$S$_2$-NGQDs/NF toward OER and HER. This work will pave a way to developing advanced bifunctional complex catalysts to replace noble metals for specific applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was sponsored by the National Natural Science Foundation of China (21335004, 21673111, and 11404037) and the International cooperation foundation from Ministry of Science and Technology (2016YFE0130100).

Conflict of Interest

The authors declare no conflict of interest.


Received: January 23, 2017
Revised: March 11, 2017
Published online: