Graphdiyne Coupled with g-C₃N₄/NiFe-Layered Double Hydroxide, a Layered Nanohybrid for Highly Efficient Photoelectrochemical Water Oxidation

Huayan Si,* Qixin Deng, Chen Yin, Mohammad Mahdi Tavakoli,* Jin Zhang, and Jing Kong

Recently discovered graphdiyne (GDY) is a unique two-dimensional (2D) planar structure with a high-degree π-conjunction network composed of sp and sp² hybridized carbon bonds. GDY has high carrier mobility, rich chemical bond properties, and having a bandgap of ≈2.1 eV. In this study, for the first time, g-C₃N₄/NiFe-layered double hydroxide (LDH) is decorated by GDY to obtain a new strongly coupled ternary nanocomposite g-C₃N₄/GDY/NiFe-LDH, which has hierarchical mesoporous layered structure, large surface area, and broad visible spectrum absorption. These properties make g-C₃N₄/GDY/NiFe-LDH nanocomposite an outstanding candidate for photoelectrochemical water oxidation. Therefore, the new architecture is analyzed and achieve a high photocurrent density of 178.66 µA cm⁻² by applying 1.4 V, a maximum incident photon-to-current efficiency (IPCE) of 3.59% at wavelength of 350 nm and 2.05% at 420 nm under standard AM 1.5G condition, which are also the best reported values in the literature. More interestingly, the proposed nanocomposite indicates a great durability, where there is nearly no dropping on the photocurrent under continuous illumination after 3600 s. This work suggests that additive engineering using GDY is an effective approach for the fabrication of efficient photoelectrochemical water oxidation devices.

1. Introduction

Photoelectrochemical (PEC) water splitting has become a desirable way to alleviate the environmental pollution and energy crisis,[1] which was proposed by Fujishima for the first time by employing TiO₂ as a photoanode to oxidize water into oxygen and hydrogen under sunlight.[2] Despite the great progress in the development of photoanodes, the solar-to-chemical energy conversion efficiency still suffers from the low number of electron–hole pairs and ineffective charge transfer ability. An effective solution to PEC research is developing novel, highly active, and efficient photoanodes materials. Among various 2D functional materials, carbon nitride (g-C₃N₄) is a great metal-free graphitic alternative as photoanode material for PEC water oxidation devices due to its proper band structure, stability, simple preparation, and low cost.[3–5] However, owing to its narrow spectral absorption (the bandgap is ≈2.7 eV), high recombination of photocarriers (due to its slow holes transfer rate) and sluggish interfacial kinetics for O₂ production, the application of pure g-C₃N₄ as a photoanode for water oxidation has still remained a challenge.[4–7] Recently, construction heterojunction[8–10] with a secondary semiconductor such as TiO₂,[11] SnO₂,[12] CdS,[13] and BiVO₄[14,15] is an effective strategy to improve the performance of g-C₃N₄ based photoanodes. Although the success has been achieved from the above heterojunctions, their stabilities were still not well controllable. 2D/2D heterojunctions which can strongly couple with g-C₃N₄ by face-to-face interface provide a more effective way to improve the PEC water splitting performance.[16] Therefore, it is imperative to find appropriate materials, which can strongly couple with g-C₃N₄ in order to improve the photogenerated holes transfer and accelerate the oxygen evolution reaction (OER) kinetics.

Graphdiyne (GDY) is a novel carbon allotrope due to its sp and sp²-hybridized π bonds carbon network and it has a large cavity structure[17] endowing the bandgap and anticipated high charge carrier mobility[18] with excellent catalytic performances.[19–21] Previously, GDY has been incorporated into BiVO₄[22] and g-C₃N₄ materials and employed as photocathodes,[7] aimed to improve the hole mobility and thus catalyzing hydrogen evolution. However, the hole extraction property of GDY for improving the performance of OER devices has not been studied yet. Recently, our group synthesized GDY, which possesses suitable bandgap (≈2.1 eV) band alignment, and analogous π-conjugated plane to g-C₃N₄.[25,26]
Figure 1. Schematics for the fabrication of g-C3N4/GDY/NiFe LDH composite. The yellow flakes in the final product is the NiFe LDH nanosheets. The top and bottom are parallel. The top is viewed from bulk perspective, while the bottom is viewed from molecular perspective. The blue sphere is carbon atom, the green sphere is nitrogen atom.

Therefore, 2D GDY could be joined in 2D g-C3N4 to form an exceptional 2D/2D g-C3N4/GDY heterojunction, in which they have a strong coupling by the face-to-face π–π stacking interaction. Using g-C3N4/GDY photoanode, we expect to have broader solar light absorption, suppressed photocarriers recombination in g-C3N4 and the improved photoinduced holes transfer from g-C3N4 to GDY.

The slow surface reaction kinetics in PEC device can be addressed by using a suitable OER catalyst, which can accept the transferred holes by GDY in order to improve the PEC activity.[1,27–29] However, there is still a big challenge to effectively introduce OER catalysts into photoanode because of inefficient and unstable hole transfer through the interfaces. The incorporation of 2D GDY in g-C3N4 is expected to be a promising scaffold between the photoanode and the OER catalyst. Because GDY has two advantages at the same time: (1) Its 2D unique periodic framework within networks of sp and sp² hybridized carbon–carbon bonds, which could form strong chemical bonds between transition metals and surrounding acetylenic bonds and thus possessing much efficient catalytic performances and stability.[30–33] Therefore, NiFe-layered double hydroxide (NiFe-LDH) may be the best candidate due to its amazing nature catalytic activity for OER and its distinctive layered structure, which can form strong chemical bonds between transition metals and GDY. Despite the fact that there are many research works on hybrid GDY/NiFe-LDH as electrocatalysts with composite structure, only a few of them have been applied in photoanodes.[34] To the best of our knowledge, however, there is still no report on integrating GDY into g-C3N4 photocatalyst and NiFe LDH OER catalyst together to form stable and efficient g-C3N4/GDY/NiFe LDH photoanodes toward photoelectrochemical water oxidation. Notably, due to GDY unique periodic framework within networks of sp and sp² hybridized carbon atoms, by combining GDY with 2D g-C3N4 and layered structure of NiFe-LDH, a strongly coupled 3D hierarchical g-C3N4/GDY/NiFe LDH photoanodes is expected to be constructed with the extraordinary synergetic photoelectrochemical water oxidation and high solar energy conversion efficiency.

2. Results and Discussions

Figure 1 illustrates the preparation process for the 3D g-C3N4/GDY/NiFe-LDH. First, GDY was obtained through a cross-coupling method.[37] Meanwhile, pyrolysis of urea was used to form the g-C3N4. Then, g-C3N4, GDY, and the precursor of NiFe-LDH were mixed in the distilled water and ethanol solvent under stirring. After sonication for another 0.5 h, the obtained homogeneous suspension was transferred into a Teflon-lined autoclave for heating and further processing. Generally, g-C3N4 and GDY could make a couple to form the g-C3N4/GDY heterojunction through the π–π stacking interaction. The π bond of acetylenic bond is very active, which can adsorb the Ni²⁺ and Fe²⁺ on the GDY surface due to its strong chemisorption.[35] Since 2D g-C3N4/GDY is flexible, a 3D hierarchical mesoporous structure of g-C3N4/GDY/NiFe-LDH can be formed through a hydrothermal method.

Figure 2a presents the scanning electron microscopy (SEM) image of g-C3N4/GDY/NiFe-LDH composite. The 3D flower-shaped hierarchical mesoporous structure is beneficial to expose lots of accessible active sites and ensure mass transport. The composition of g-C3N4/GDY/NiFe-LDH structure was analyzed by Energy dispersive X-ray (EDX) (Figure S1, Supporting Information), confirming the uniform distribution of C, N, O, Fe, and Ni elements in this structure. Moreover, the oxygen-containing functional groups in GDY could also contribute to form the strong chemical bonds between Ni²⁺, Fe²⁺, and surrounding acetylenic bonds, which are beneficial to fast charge transfer from GDY to NiFe LDH, lead to promote the photoelectrochemical catalytic performance.[33] The wrinkle strips in the transmission electron microscopy (TEM) images illustrate the thin flake feature of NiFe-LDH (Figure 2b). Figure 2c shows high resolution TEM (HRTEM) image of g-C3N4/GDY/NiFe-LDH, indicating the close interfacial contact among three components. The HRTEM image shows curved fringe with a lattice spacing of 0.365 nm, ascribed to the interlayer spacing of GDY[36] In Figure 2c, we also observed a d-spacing of 0.26 nm, which is corresponded to the (012) crystal planes of NiFe-LDH.[38] Notably, no apparent crystal fringe is observed for g-C3N4. The selected area diffraction of the g-C3N4/GDY/NiFe-LDH heterostructure (Figure 2d) contains the GDY and NiFe-LDH diffractions. These images confirm the formation of the g-C3N4/GDY/NiFe-LDH heterostructure. This unique 3D hierarchical mesoporous structure of g-C3N4/GDY/NiFe-LDH supplies large face-to-face interface among each component, which can shorten the charge transfer distance and provide abundant channels for the mass transport.[35–37]

The chemical composition and structure of g-C3N4/GDY/NiFe-LDH were further characterized by X-ray photoelectron spectroscopy (XPS). Figure 3a shows that there are C, N, O, Fe, and Ni elements in g-C3N4/GDY/NiFe-LDH heterostructure.
and the Ni/Fe atomic ratio is \(\approx 3.0\), which proves the presence of NiFe-LDH.[13] The high-resolution spectra of Fe 2p and Ni 2p in NiFe-LDH are shown in Figure 3b,c.[30,31] The binding energies of both Fe 2p and Ni 2p in the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH are blue-shifted as compared to NiFe LDH, confirming the strong electronic interactions between the metallic species in the LDHs and GDY. There are five subpeaks in the C 1s in the LDHs and GDY. There are five peaks at 284.23, 285.57, and 288.10, respectively. The peaks at 287.90 and 287.19 eV are belong to C−O of GDY, respectively. The peaks at 287.90 and 287.19 eV are belong to C−N (sp\(^2\)) of g-C\(_3\)N\(_4\).[31,32] indicating the successful formation of g-C\(_3\)N\(_4\)/GDY/NiFe-LDH composites. The structure of g-C\(_3\)N\(_4\)/GDY/NiFe-LDH composites were also characterized by the Raman spectra as seen in Figure 3c. There are four typical peaks around 1388, 1572, 1930, and 2176 cm\(^{-1}\) in GDY.[17] g-C\(_3\)N\(_4\)/GDY/NiFe-LDH shows the same Raman peaks as the NiFe LDH excluding 1386 and 1578 cm\(^{-1}\) peaks, which are ascribed to GDY, suggesting that the NiFe LDH was successfully combined with GDY. Coupled with X-ray diffraction (XRD) (Figure 3e), the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH shows a stronger peak at 27.6° than g-C\(_3\)N\(_4\) due to the overlaid with two diffraction peaks of g-C\(_3\)N\(_4\) and GDY, presenting the successful incorporation of g-C\(_3\)N\(_4\) in the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH. There are several weak diffraction peaks for NiFe-LDH and GDY, which are ascribed to their relatively low content in the present XRD pattern (Figure 3f). Figure 3g shows the Fourier transform infrared (FTIR) spectra of the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH heterostructure, which has the characteristic peaks of all components, confirming the strong interaction of g-C\(_3\)N\(_4\), GDY, and NiFe-LDH. Figure 3h and Figure S4 (Supporting Information) show the characterization of surface area and porosity properties of the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH. All the isotherms show type IV isotherms with a Brunauer–Emmett–Teller (BET) and their corresponding surface areas are 208.75, 126.32, 95.03, and 42.63 m\(^2\) g\(^{-1}\), respectively. The surface area of g-C\(_3\)N\(_4\)/GDY/NiFe-LDH is much higher than those of g-C\(_3\)N\(_4\), GDY, and NiFe LDH. As seen, the pore size (initial size is 3 nm) is increased for by the formation of the NiFe LDHs in the acetylenic bond of GDY frameworks. The high BET surface area and nonuniform mesoporous porosity in the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH hybrid would produce more exposure and active sites to the molecules, thereby give rise to a novel and superior candidate for efficient PEC water oxidation.[38]

Figure 4a shows the optical properties of the representative samples measured by the UV–Vis diffuse reflectance spectra. The g-C\(_3\)N\(_4\) and GDY show an absorption edge at 460 and 800 nm, respectively. To obtain the best photoanodes, we optimized the mass ratio of g-C\(_3\)N\(_4\)/GDY. NiFe-LDH and 9:3:1 is the optimum value for the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH heterostructure, which has the highest enhanced light absorption over the whole range of wavelengths. We find that there is a red-shift in the absorption edge by increase the amount of GDY in the composition, indicating the light absorption ability of the hybrid structure.[39] These results imply that the hybrid may produce more electron–hole pairs and thus improve catalytic activity. The photoluminescence (PL) spectra shown in Figure 4b indicate that the PL signal nearly disappears in the g-C\(_3\)N\(_4\)/GDY/NiFe-LDH hybrid, indicating that the photogenerated electron–hole pairs have been effectively separated in the hybrid. This phenomenon could be due to the proper coupling bond between GDY and NiFe LDH, which allows more holes to transfer from g-C\(_3\)N\(_4\) to NiFe LDH through the GDY, which is mainly due to the high hole mobility of GDY.[7,25] The efficient hole transfer suppresses the photoinduced electron–holes pairs recombination in g-C\(_3\)N\(_4\) and improves the PEC water oxidation reaction.

To verify the superior PEC water oxidation property of g-C\(_3\)N\(_4\)/GDY/NiFe-LDH hybrid, the transient photocurrent density–potential curves were measured. As shown in Figure 5a, g-C\(_3\)N\(_4\)/GDY/NiFe-LDH hybrid displays a much superior current density than other samples in the entire potential range. It can be seen that the g-C\(_3\)N\(_4\) itself produces a photocurrent density of 4.02 \(\mu\)A cm\(^{-2}\) at 1.4 V. In contrast,
g-C_{3}N_{4}/GDY/NiFe-LDH hybrids with different mass ratios of g-C_{3}N_{4}/GDY/NiFe-LDH (1:1:8, 3:1:1, 6:2:1, 9:3:1, 12:4:1) show photocurrent densities of 12.14, 7.71, 20.32, 178.66, and 53.46 µA cm^{-2}, respectively. Among them, the g-C_{3}N_{4}/GDY/NiFe-LDH with the mass ratio 9:3:1 has the maximum photocurrent density, which is nearly 45 times higher than that of the

Figure 3. a) XPS survey spectra of GDY and g-C_{3}N_{4}/GDY/NiFe-LDH. b) High-resolution Fe 2p XPS and c) high-resolution Ni 2p XPS of NiFe LDH and g-C_{3}N_{4}/GDY/NiFe LDH. d) Raman spectra and e) XRD patterns of GDY, NiFe-LDH, g-C_{3}N_{4}, g-C_{3}N_{4}/GDY/NiFe LDH. f) Enlarged XRD pattern of g-C_{3}N_{4}/GDY/NiFe LDH extracted from panel (e). g) FTIR spectra, and h) nitrogen adsorption-desorption isotherm curves of GDY, NiFe-LDH, g-C_{3}N_{4}, and g-C_{3}N_{4}/GDY/NiFe LDH.
g-C₃N₄. In order to investigate the role of the GDY and NiFe LDH, the PEC water oxidation property of g-C₃N₄/GDY and GDY/NiFe-LDH was also measured. As expected, Figure S5a in the Supporting Information shows that the photocurrent density of the g-C₃N₄/GDY, which is higher than that of g-C₃N₄ and GDY and the optimal mass ratio of g-C₃N₄:GDY is 3:1. Higher photocurrent density verifies that more charges are effectively separated in the g-C₃N₄/GDY. Moreover, there was no saturation of photocurrent density viewed within the voltage scanning range, further indicating efficient charge separation in the heterojunction.[5,40] These results indicate GDY plays an important role in suppressing the photocarriers recombination of the g-C₃N₄. Figure S5b in the Supporting Information shows that the photocurrent density of the g-GDY/NiFe LDH heterostructure, which is higher than that of GDY and NiFe, implying that NiFe-LDH has a dual role in the g-C₃N₄/GDY/NiFe-LDH structure, which not only could accelerate the charge transfer, but also could play as a cocatalyst to promote the surface reaction kinetics.[41] All these performances are consistent with the results of both UV−Vis diffuse reflectance and PL measurements. However, only when g-C₃N₄, GDY, and NiFe LDH were effectively coupled together, the g-C₃N₄/GDY/NiFe-LDH hybrid structure can exert the optimal PEC water oxidation reaction. As far as we know, this PEC water oxidation performance

![Figure 4. a) UV−vis diffuse reflectance spectra of NiFe LDH, GDY, g-C₃N₄, and g-C₃N₄/GDY/NiFe-LDH with different mass ratio. b) Photoluminescence spectra of g-C₃N₄, NiFe LDH, g-C₃N₄/GDY, and g-C₃N₄/GDY/NiFe-LDH.](image)

![Figure 5. a) Transient photocurrent density versus applied voltage plots for the different mass ratios of g-C₃N₄/GDY/NiFe-LDHs a) 1:1:8, b) 3:1:1, c) 6:2:1, d) 9:3:1, e) 12:4:1, f) g-C₃N₄. b) IPCE spectra of g-C₃N₄, g-C₃N₄/GDY, and g-C₃N₄/GDY/NiFe-LDH 9:3:1. c) EIS Nyquist plots of g-C₃N₄, g-C₃N₄/GDY, and g-C₃N₄/GDY/NiFe-LDH 9:3:1, with an equivalent circuit (CPE, Rₛ, and Rₘₚ represent constant phase element, solution resistance, and charge transfer resistance, respectively) in inset and d) the photocurrent steady of g-C₃N₄, g-C₃N₄/GDY, and g-C₃N₄/GDY/NiFe-LDH 9:3:1 at 1.0 V versus RHE bias under AM 1.5G illumination.](image)
(178.66 $\mu$A cm$^{-2}$ at 1.4 V) of g-C$_3$N$_4$/GDY/NiFe-LDH is the best reported values in the literature (Table S1, Supporting Information). This high PEC performance is due to the unique 3D nanostructure that not only has hierarchical mesoporous structure, but also g-C$_3$N$_4$, GDY, and NiFe-LDH strongly couples to each other, which increases the light absorption, improves charge transfer, and reduces overpotential. The PEC activities of as-prepared samples were further investigated using the incident-photon-to-current-conversion-efficiency (IPCE) measurement. g-C$_3$N$_4$/GDY/NiFe-LDH hybrid shows a maximum IPCE over the whole range of wavelengths, as shown in Figure 5b. The IPCE for the g-C$_3$N$_4$/GDY/NiFe-LDH hybrid is 3.59% at 350 nm and 2.05% at 420 nm, respectively, while both g-C$_3$N$_4$ and g-C$_3$N$_4$/GDY show quite low photoresponse. Notably, the IPCE for the g-C$_3$N$_4$/GDY/NiFe-LDH is also the highest value among the reported values in the literature (Table S2, Supporting Information), which is consistent with the result of photocurrent density–potential curves.

Electrochemical impedance spectroscopy (EIS) is an effective technique to characterize the charge transfer in the heterostructure. Figure 5c shows the Nyquist plots of samples, fitted with an equivalent circuit using charge transfer resistance ($R_{ct}$). The value of $R_{ct}$ is determined by the electro-catalytic kinetics at the catalyst/electrolyte interface. The lower value means the faster electron transfer. Figure 5c shows the smallest arc for the g-C$_3$N$_4$/GDY/NiFe-LDH hybrid both under dark and illumination. This phenomenon indicates that incorporation of GDY and NiFe-LDH extremely decreases the charge-transfer resistance, which manifests that a valid separation of photocarriers and interfacial charge transfer took place in the g-C$_3$N$_4$/GDY/NiFe-LDH interface. The GDY plays the role in accelerating interfacial hole transfer between g-C$_3$N$_4$ and NiFe-LDH.

The steady property for g-C$_3$N$_4$/GDY/NiFe-LDH heterostructure was surveyed over time, as shown in Figure 5d. There is no obvious photocurrent decay for all the samples after 3600 s of irradiation. The SEM image of g-C$_3$N$_4$/GDY/NiFe-LDH was collected (Figure S6, Supporting Information) and showed no significant morphological change after the irradiation. The excellent durability of g-C$_3$N$_4$/GDY/NiFe-LDH may be attributed to the coupling interaction between 3D transition metal atoms and the carbon–carbon triple bonds and carboxyl bonds in GDY. The generation rates of O$_2$ by g-C$_3$N$_4$/GDY/NiFe-LDH is measured to be 1.1 mmol h$^{-1}$, with Faradic efficiency of 97.73%.

Based on the above experimental results, combined with the Mott–Schottky plots (Figure S7, Supporting Information), the band configuration for g-C$_3$N$_4$ and GDY is plotted in Scheme 1a. An ideal PEC reaction mechanism for the g-C$_3$N$_4$/GDY/NiFe-LDH hybrid could be proposed (Scheme 1b). As g-C$_3$N$_4$ has a face-to-face contact with GDY, a built-in electric field can be formed with a direction from g-C$_3$N$_4$ to GDY in equilibrium state. When the ternary g-C$_3$N$_4$/GDY/NiFe-LDH hybrid is irradiated by the visible light, the photogenerated holes will easily flow to GDY under the built-in field. Due to the high hole mobility of GDY and the powerful coupling interaction between each component, GDY can play a high way role in transferring the hole from g-C$_3$N$_4$ to NiFe LDH, where the trapped holes will oxidize the water to produce oxygen. Meanwhile, the direct transfer of some holes from g-C$_3$N$_4$ to NiFe-LDH is also possible (Scheme S1, Supporting Information). Therefore, the synergetic catalytic effect has been exerted in 3D ternary g-C$_3$N$_4$/GDY/NiFe-LDH hybrid by combining interfacial regulation, hole transport design, and the bandgap engineering, leading to high PEC performance for water oxidation.

3. Conclusions

In summary, we synthesize a new powerful ternary hierarchical mesoporous heterostructure, i.e., g-C$_3$N$_4$/GDY/NiFe-LDH based on the unique structure of 2D GDY, embodying sp and sp$^2$-hybridized $\pi$ bonds carbon network for efficient solar conversion. In addition to structural advantages, GDY has a bandgap and high hole mobility, which not only extends the absorption spectrum of g-C$_3$N$_4$, but also forms a built-in field, extracting the holes from the photocarrier in g-C$_3$N$_4$ and conducting them to NiFe LDH. The chemical bond formation between GDY and NiFe-LDH provides effective kinetic transportation of the photocarrier. This unique structure together with coupling effect leads to a high durability. The g-C$_3$N$_4$/GDY/NiFe-LDH hybrid shows a record value of photocurrent density of 178.66 $\mu$A cm$^{-2}$ at 1.4 V under AM 1.5G irradiation. This type of GDY based 3D ternary hierarchical mesoporous photoelectrodes promises a new insight into water splitting applications.

Supporting Information

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

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
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