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Van der Waals Heterojunction between Bottom-Up Grown Doped Graphene Quantum Dot and Graphene for Photoelectrochemical Water Splitting

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ABSTRACT

Van der Waals heterojunctions (vdWHs) formed between 2D materials have attracted tremendous attention recently due to their extraordinary properties which cannot be offered by their individual components or other heterojunctions. Intriguing electronic coupling, lowered energy barrier, intimate charge transfer, efficient exciton separation occurring at the atomically sharp interface promise their applications in catalysis which, however, are largely unexplored. Herein, we demonstrate a 0D/2D vdWH between 0D graphene quantum dots (GQDs) and 2D pristine graphene sheets, simply prepared by ultrasonication of graphite powder using GQDs as intercalation surfactant. And such all-carbon Schottky-diode-like 0D/2D vdWH is employed for the emerging photoelectrochemical catalysis (water splitting) with high performance. The demonstrated low-cost and scalable bottom-up growth of heteroatom-doped GQDs shall greatly promote their widespread applications. Moreover, the mechanisms underlying GQD growth and heterojunction mediated catalysis are revealed both experimentally and theoretically.

KEYWORDS: van der Waals heterojunction, graphene quantum dots, photoelectrochemical water splitting, heteroatom doping, exfoliation of pristine graphene

Van der Waals heterojunctions (vdWHs) formed between 2D materials have been an emerging focus recently. They promise various applications (*e.g.*, in electronics and optoelectronics) owing to the intriguing properties including atomically sharp hetero-interface with low energy barrier, intriguing coupling effects, gate-tunable bandgap, Moiré superlattices, efficient exciton separation.¹⁻⁴ But the study and application of vdWHs are hindered by the difficulty to readily assemble them. Despite the anticipated potential, vdWHs have seldomly been employed for catalysis (not at all for the emerging photoelectrochemical catalysis).

Herein, we construct a 0D/2D vdWH between 0D heteroatom-doped graphene quantum dots (GQDs) and 2D graphene through a facile and scalable self-assembly process, in which, single-layered pristine graphene sheets are readily exfoliated from graphite using GQDs as both intercalation agent and surfactant. Such all-carbon Schottky-diode-like 0D/2D vdWH are then employed for high-performance photoelectrochemical water splitting benefiting from the synergistic coupling at the hetero-interface. Moreover, the low-cost, scalable, and high yield bottom-up growth of GQDs demonstrated here shall promote the widespread application of this nanocarbon family.^{5, 6} The mechanisms underlying GQD growth and vdWH mediated catalysis are revealed both experimentally and theoretically.

RESULTS AND DISCUSSION

Owing to the exceptional properties (*e.g.*, highly tunable chemicophysical properties, good dispersibility, biocompatibility),⁷ graphene quantum dots (GQDs) promise a wide spectrum of applications in bioimaging, sensing, display, catalysis, energy storage and conversion, and optoelectronic devices.^{8, 9} But the widespread practical uses are hindered

by the current high cost of GQD synthesis. Wang *et al.* has reported a bottom-up strategy to synthesize GQD based on fusion of 1,3,6-trinitropyrene under hydrothermal condition.¹⁰ But the growth mechanism is not understood and pyrene is expensive. Here, we used naphthalene, which is the simplest and cheapest polyaromatic molecule, for bottom-up synthesis of undoped or heteroatom-doped GQDs (Figure 1a). The production yield of undoped GQDs is as high as 71.3%, which is much higher than that (63%) of GQDs synthesized from pyrene¹⁰ and that (20%) of GQDs synthesized from coal.¹¹ Our method shall bring down the production cost by several orders. Firstly, nitro groups were introduced onto naphthalene as the nucleophilic attack sites. As analyzed by ¹H NMR (Figure S1, Supporting Information), nitrated naphthalene is a mixture of 1,5-dinitronaphthalene (52.6%) and 1,8-dinitronaphthalene (40.3%) plus a small amount of 1-nitronaphthalene (7.1%). Subsequently, nitrated naphthalene molecules fused into GQDs in NaOH under hydrothermal condition.

As revealed by transmission electron microscopy (TEM), the average size of obtained GQDs is 5.62 nm ($\pm$ 1.60 nm, n= 179) (Figure 1b), with lattice spacing of 0.21 nm corresponding to the (100) facet of graphene (Figure 1c).¹² Atomic force microscopy (AFM) shows that these GQDs are single- or double-layered with an average thickness of 1.23 nm ($\pm$ 0.42 nm, n=153) (Figure 1d). They show maximum photoluminescence (PL) emission at 546 nm under 467 nm excitation (Figure 1e). The XRD spectrum of GQDs (Figure S2, Supporting Information) shows the characteristic peak of (002) facet that identifies the graphitic crystallinity of GQDs.¹⁰ While the Raman spectrum (Figure S3, Supporting Information) presents that the intensity ratio of G to D bands (I_G/I_D) is 1.6, implying a high percentage of graphitic carbon. Directly using commercial 1,5-

dinitronaphthalene or 1,8-dinitronaphthalene as the precursor, similar GQDs were obtained without the nitration step (Figure S4, Supporting Information). In contrast, 1-nitronaphthalene was not able to produce GQDs presumably because the benzene ring without nitro group cannot be activated for dehydrogenation. Compared with dehydrogenation of 1,5-dinitronaphthalene (Figure S5a, Supporting Information), naphthalene without nitration cannot grow into GQD as the density functional theory (DFT) calculation shows the absence of bonding energy release (Figure S5b, Supporting Information).

DFT calculations suggest that under alkaline hydrothermal condition dinitronaphthalene undertake dehydrogenation first and then more energy-costly denitration (Figure 2). The resulting naphthalene alkyne with two dangling bonds sequentially conjugates with two other naphthalene alkyne molecules. Subsequent dehydrogenation and denitration of the resulting polyaromatic molecule allows further growth similarly. Note that the fusion between naphthalene alkyne and dinitronaphthalene is unlikely to occur due to daunting energy barrier (Figure S6, Supporting Information). Generation of naphthalene alkyne is confirmed by electron paramagnetic resonance (Figure S7, Supporting Information).

Dimerization of naphthalene alkyne molecules is exothermic (Figure S8a, Supporting Information). Various dimer structures can form depending on the fusion orientations. C-C bonding gives a *cis* configuration for type I dimers, while *trans* configuration forms for type II dimers (Figure S8b, Supporting Information). The remaining dangling bonds are available for further fusion. In contrast, type III dimers are not favorable to grow into GQDs because all the dangling bonds are consumed and

unstable non-hexagonal carbon rings are formed. Continuous growth of GQD leads to increase of the total energy cost for dehydrogenation and denitration (Figure S9, Supporting Information). This shall cause self-limiting of GQD size. This is confirmed by TEM and AFM observations that doubling the react time (to 16 h) only slightly increases the average GQD size by ~0.3 nm and red-shifts the PL emission by ~5 nm (Figure S10, Supporting Information).

The obtained GQDs are decorated with –OH groups because of nucleophilic attack by OH^- . Indeed, Fourier-transform infrared spectroscopy (FTIR) spectrum of GQDs shows stretching vibrations of –OH at 3500 cm^{-1} , C=C at 1650 cm^{-1} , C-O at 1375 cm^{-1} (Figure 3a). The elemental mapping also shows that O is populated on both basal plane and edge (Figure 3b). The defects created by addition of –OH groups offer the opportunity for heteroatom doping which confers GQD with interesting properties. Here, ammonia and thiourea were used as the sources of N and S dopants, and these heteroatom sources also replaced NaOH to provide alkaline condition. As revealed by TEM and AFM (Figure S11, Supporting Information), N-, S- and NS-doped GQDs have similar size and thickness as undoped GQD. FTIR spectra in Figure 3a demonstrate stretching vibrations of N-H at 3160 cm^{-1} , C-N at 1150 cm^{-1} , and C-S at 1120 cm^{-1} , confirming successful introduction of heteroatom dopants.

As demonstrated in Figure 3b, S and N are densely distributed on GQD basal plane and even more at edge. Consistently, X-ray photoelectron spectroscopy (XPS) spectra reveal C 1s (284 eV), O 1s (532 eV), N 1s (400 eV), and S 2p (164 eV) peaks (Figure 3b). O contents of undoped, N-doped, S-doped and NS-doped GQDs are 21.7%, 8.25%, 7.92% and 7.43% respectively. Decrease of O content implies that doping utilizes O-containing

defect sites. N contents of N-GQDs and NS-GQDs are 9.73% and 9.01%, while S contents of S-GQDs and NS-GQDs are 4.96% and 4.17%. As seen, doping of N and S doesn't affect each other, probably implying that they don't compete for the same type of doping sites. It is noteworthy that such *in situ* doping is more effective and convenient than post-synthesis doping.¹³⁻¹⁵

The high-resolution C 1s peak of undoped GQD can be deconvoluted into C=C and C-O peaks due to the presence of –OH groups (Figure 3c). For N-GQD (or S-GQD), C 1s peak is separated into C=C, C-N (or C-S) and C-O peaks. For NS-GQD, C 1s peak is deconvoluted into C=C, C-S, C-N and C-O peaks. Its high resolution N 1s peak is summation of NH₂ peak from –NH₂ groups at edge and N-C peak from graphitic N while S 2p peak is summation of C=S at edge and C-S from both edge and basal plane (Figure 3d). The absence of binding energy >166 eV indicates the absence of oxidized state of S (*e.g.* SO₃²⁻, SO₄²⁻).

Doping of N and S causes PL redshift because GQD bandgap is narrowed due to introduction of intermediate n orbital between π and π^* orbitals by these electron-donating elements (Figure 3e).¹² As S has stronger electron donating ability, S-GQD emits longer wavelength than N-GQD (585 vs. 570 nm). Co-doping of N and S causes the greatest redshift to 610 nm, implying the joint effects from the two dopants. Interestingly, doping also enhances the absolute PL quantum yield (10.38% for undoped GQD, 14.72% for N-GQD, 16.91% for S-GQD and 19.54% for NS-GQD), presumably due to decrease of O moieties which act as non-radiative centers.⁷ Linear sweep voltammetry was used to determine the conduction band (CB), valance band (VB), thus bandgaps of GQDs (Figure 3f).¹²⁻¹³ As shown in Figure 3g, the bandgaps of GQD, N-GQD, S-GQD and NS-GQD

are 2.31, 2.18, 2.12 and 2.04 eV, respectively. Naturally, bandgap narrowing by heteroatom doping enhances light absorption (Figure 3h).

GQD is essentially amphiphilic as chemical moieties render it hydrophilicity and its carbon plane is intrinsically hydrophobic. In addition, GQD can strongly interact with π -conjugated materials through π - π interaction. Taking advantage of these properties and its atomically thin planar structure, GQDs were employed as the intercalation agent and surfactant to exfoliate and disperse pristine graphene sheets from graphite powders simply by bath sonication (Figure S12, Supporting Information). As observed by scanning electron microscope (SEM), the graphite powders have an average size of $47.8 \pm 3.5 \mu\text{m}$ ($n=146$; Figure S13 in supporting information). As uncovered by AFM (Figure 4a), the exfoliated pristine graphene sheets are large and uniformly single layered ($0.71 \pm 0.32 \text{ nm}$ thick, $n = 126$). They are decorated with numerous GQDs as evidenced by intermittent step-like increase of thickness and can stably disperse in aqueous solution. GQDs are enriched at edges presumably because GQD intercalation into graphite starts from edges and the initial stage requires more frequent attacking by GQDs. This method provides a solution to the currently unmet need for readily and scalable exfoliation of pristine single-layered graphene sheets, promising the applications such as nanoelectronic devices and printable conducting ink.

Recent studies have demonstrated that graphene and 2D semiconducting materials (*e.g.*, transition metal dichalcogenides, graphitic carbon nitride, boron nitride) can form Schottky-diode-like vdWHs.^{2, 4, 16} The intimate electronic coupling at vdWHs offers interesting properties for widespread application opportunities, such as, tunable work function and Schottky barrier, formation of superlattice structure, fast carrier transfer, and

efficient charge separation.¹⁷ GQD as semiconducting 0D graphene naturally forms tight vdWH with 2D graphene. To confirm the electronic coupling at such 0D/2D vdWHs, XPS and X-ray absorption near edge structure (XANES) characterizations were conducted (Figure S14, Supporting Information). Both high-resolution C 1s XPS spectra and XANES C K edge spectra demonstrate an obvious shift of C=C peak from GQD/graphene or NS-GQD/graphene towards lower binding and photon energy, compared to commercial pristine graphene free of chemical moieties. And the shift caused by NS-GQD is more significant than undoped GQD. These observations indicate charge transfer from GQDs to graphene, which is further promoted by NS co-doping.¹⁸ And charge transfer lowers the work function and increases carrier density.

GQD/graphene vdWH shall be promising for widespread optoelectronic applications, using GQDs as the light harvester, graphene sheet as highly conductive collector for photogenerated carriers, and the fact that vdWH with reduced Schottky barrier are favorable for photogenerated charge separation and transfer. As a proof-of-concept demonstration, we employed such all-carbon 0D/2D vdWHs for photoelectrochemical water splitting because the electronic bandgap of GQDs are wide enough (>1.6 eV) to simultaneously drive both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) yet not too wide to ensure a broad range of light absorption.¹⁹ To construct the photoelectrochemical electrodes, GQD decorated graphene sheets were coated onto Ni mesh.

As shown in Figure 4b, NS-GQD/graphene electrode exhibits the smallest Tafel slope (71.2 mV dec^{-1}) for HER, indicating the occurrence of fast Volmer-Heyrovsky pathway which consists of water adsorption, dissociation into adsorbed H (H_{ads}) and OH^-

(Volmer reaction: $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^-$), OH^- desorption and recombination of H_{ads} to form H_2 (Heyrovsky reaction: $\text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$).^{20, 21} In comparison, the relatively larger Tafel slopes of GQD (395.6 mV dec⁻¹), GQD/graphene (167.3 mV dec⁻¹), N-GQD/graphene (119.1 mV dec⁻¹), and S-GQD/graphene (98.5 mV dec⁻¹) suggest the slower Volmer-Tafel pathway, consisting of the Volmer reaction and Tafel reaction ($2\text{H}_{\text{ads}} \rightarrow \text{H}_2$).²² Similarly, NS-GQD/graphene electrode also offers the smallest Tafel slope for OER (63.5 mV dec⁻¹). This fast kinetic is ascribed to the two-step mechanism consisting of dissociation of OH^- into adsorbed O ($2\text{OH}^- \rightarrow \text{O}_{\text{ads}} + \text{H}_2\text{O} + 2\text{e}^-$) and subsequent combination between O_{ads} and OH^- to form O_2 ($\text{O}_{\text{ads}} + 2\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$).²³ Larger Tafel slopes of GQD (417.9 mV dec⁻¹), GQD/graphene (257.3 mV dec⁻¹), N-GQD/graphene (219.4 mV dec⁻¹) and S-GQD/graphene (118.2 mV dec⁻¹) electrodes are resulted from the slow four-step mechanism: (1) $\text{OH}^- \rightarrow \text{OH}_{\text{ads}} + \text{e}^-$, (2) $\text{OH}^- + \text{OH}_{\text{ads}} \rightarrow \text{O}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$, (3) $\text{OH}^- + \text{O}_{\text{ads}} \rightarrow \text{OOH}_{\text{ads}} + \text{e}^-$, (4) $\text{OH}^- + \text{OOH}_{\text{ads}} \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{e}^-$.²⁴ Bare Ni mesh is inert for both HER (Tafel slope of 574.6 mV dec⁻¹) and OER (Tafel slope of 683.9 mV dec⁻¹), ruling out the implication of possible catalytic activity of Ni. The superior performance of GQD/graphene than GQD testifies the importance of the heterojunction. The observations also highlight the facilitation roles of N and S doping for both HER and OER.

Further, the 0D/2D hybrids are utilized as the bifunctional electrodes for overall water splitting in the same alkaline solution (Figure 4c). The overpotentials of NS-GQD/graphene electrode for HER (η_{HER}) and OER (η_{OER}) at a current density of 100 mA cm⁻² are 205 and 237 mV, which are much lower than N-GQD/graphene, S-GQD/graphene, GQD/graphene. Particularly to be pointed out, the η_{OER} is much smaller than

GQD-engineered NiCo₂P₂ nanosheets, commercial RuO₂ and other photosensitizers modified graphene²⁵⁻²⁸ (Table S1, Supporting Information). It is worth noting that the onset potential of NS-GQD/graphene (1.09 V) for OER is lower than the theoretical minimum of electrochemical reaction (1.23 V) because of the effective utilization of light energy by the heterojunction.

As schematically illustrated in Figure 4d, at anodic vdWHs, the Dirac point of graphene moves downwards due to voltage bias. The Fermi level of GQD also shifts downwards to align with Dirac point, causing upward band bending which promotes transfer of photogenerated holes on VB of GQD to graphene.^{29, 30} Subsequently, the holes are utilized to oxidize water to O₂. Similarly at cathode, upshift of graphene Dirac point causes downward band bending of GQD,³⁰ which promotes transfer of photogenerated electrons on CB of GQD to graphene for reduction of water to H₂.

As shown in Figure 4e, the photocurrent amplitudes without voltage bias follows the order of NS-GQD/graphene > S-GQD/graphene > N-GQD/graphene > GQD/graphene, suggesting doped GQDs is superior to undoped GQD because of stronger light absorption with narrower bandgap and better charge separation at the heterojunction. Charge transfer resistance is decreased by the electron-donating dopants on GQD, following the same order as above (Figure 4f). The Faradaic efficiencies of NS-GQD/graphene for HER and OER are measured to be 95.7% and 98.4%, respectively (Figure S15, Supporting Information).

Density functional theory calculations were performed with Perdew-Burke-Ernzerhof using Vienna *Ab-Initio* Simulation Package to investigate the Schottky barrier of the 0D/2D vdWHs (Figure 5a-d). Note that GQD (~270 hexagonal rings) is simplified

to a seven-ring structure to reduce the computational burden without losing generality to provide qualitative insights and comparisons. Undoped GQD is a *p*-type semiconductor because Fermi level (E_F) is closer to HOMO than LUMO, caused by abundant electron-withdrawing –OH groups. GQD/graphene vdWH shows a much reduced Schottky barrier of 0.32 eV (Figure 5b), compared to 1.10 eV for heterojunction between graphene and pristine GQD free of chemical moieties (Figure 5a). In comparison, co-doping by electron-donating N and S atoms transforms GQD to an *n*-type semiconductor and further reduces Schottky barrier with graphene. Separation between N and S dopants gives smaller Schottky barrier (0.10 vs. 0.11 eV) and narrower bandgap (1.17 vs. 1.38 eV), as compared to the case that N and S are adjacent (Figure 5c and d). Low Schottky barrier favors rapid transfer of photogenerated carriers. The differential charge density maps demonstrate that pristine GQD is not an effective charge donor while GQD with –OH groups can obviously transfer charge to graphene when H atom is in the immediate vicinity, and heteroatom dopants are strong donors particularly in the case of N, S co-doping (Figure 5). Taken together, consistent with the experimental observations, DFT calculations confirm that NS doping significantly lowers Schottky barrier and increases carrier density. And the strong electronic coupling between the electron-donating N,S-codoped GQDs and the graphene sheet as electron acceptor causes the charge redistribution at the vdWH interface.

Figure 6a shows the current response from NS-GQD/graphene electrode during the water splitting process with intermittent chopping of light illumination, which is exactly enveloped by the responses with continuous illumination and without illumination. As seen, the photoelectrochemical process outperforms pure electrochemical process by 2.39

folds for HER and 1.75 folds for OER. This observation indicates that photogenerated carriers are effectively utilized by the electrochemical reactions and significantly enhance the output. Comparing to GQD/graphene, NS-GQD/graphene displays much higher electrochemical activity without illumination (Figure 6a), because these dopants increase carrier density and also facilitate electrocatalysis. For HER, N dopants can well adsorb H_2O and dissociate it into H_{ads} and OH^- *via* hydrogen bonding, while S dopants favor charge transfer and recombination of H_{ads} to form H_2 due to its strong electron-donating ability.^{31, 32} For OER, N and S with lone pairs adsorb electron-deficient O_{ads} from dissociated OH^- on anode, which combines with O_{ads} to form O_2 .^{32, 33}

Using ethanol containing 0.1M KOH as the electrolyte, the cathodic photocurrent response is purely due to transfer of photo-excited electrons from CB of NS-GQD to graphene, without implication of HER (Figure 6b). As seen, the photocurrent increases exponentially with increase of negative voltage bias, implying the nonlinear electrical promotion of charge separation. This is because the upward shift of graphene Dirac point causes downward band bending of CB of NS-GQD whereby leading to reduction of Schottky barrier for the transfer of photoexcited electrons from CB to graphene. Similarly, the anodic photocurrent is exponentially enhanced by positive voltage bias because of reduction of Schottky barrier for transfer of photoexcited holes from up-bent VB of NS-GQD to graphene (Figure 6c). As seen from Figure 6a-c, the photoelectrochemical water splitting is achieved through synergistic cooperation between photo- and electro-chemical processes.

The chronoamperometry measurement demonstrates the high stability of NS-GQD/graphene electrode. As shown in Figure 6d, the efficiency of both HER and OER

fully maintains after 20 h, benefiting from the all carbon structure. The performance of NS-GQD/graphene is superior to other all-carbon catalysts^{31, 32, 34-36} (Table S2 in Supporting Information). Although a few catalysts show slightly better performance,^{37, 38} their practical application is limited by high cost, difficulty in synthesis, and poor stability.

CONCLUSIONS

In summary, we developed a GQD synthesis which may bring down the current cost by several orders. The revealed growth mechanism and self-limiting phenomenon shall provide insights and guidance to other bottom-up synthesis methods. A spectrum of GQDs with different PL colors (*i.e.*, bandgaps) or catalytic properties may be obtained by selection of dopants and combinations. In addition to single-layered pristine graphene, the synthesized GQDs could serve as the intercalating agent and surfactant to rapidly exfoliate and disperse other layered materials and simultaneously form various heterojunctions. Light is the most abundant and renewable energy source. But photocatalysis suffers from low efficiency. On the other hand, electrochemical catalysis consumes electricity. Photoelectrochemical catalysis may harvest light energy to promote electrochemical process and thus has attracted tremendous attention.^{19, 39, 40} Schottky-diode-like 0D/2D vdWH formed between NS-codoped GQDs and exfoliated graphene sheets was employed for photoelectrochemical water splitting which is amenable for industrial use. The outstanding performance is attributed to narrowed bandgap (thus enhanced light absorption), efficient separation of photoexcited electron-hole pairs, small charge transfer resistance, low Schottky barrier for charge transfer, increased charge density, catalytic activities from the dopants, synergistic cooperation between

photochemical and electrochemical processes, synergistic cooperation between N and S dopants, and the all-carbon nature of the catalyst. Such 0D/2D vdWH shall also promise other applications in optoelectronics and catalysis. This study provides the insights to the emerging research and application of 0D/2D vdWHs. Currently, it is highly difficult to construct vdWHs. The simple method used here presents the avenue for studying GQD based 0D/2D vdWHs. In addition, 0D/2D vdWHs may also be formed between other 2D materials derived quantum dots ⁹ and various 2D materials ⁴¹.

METHODS

Synthesis of undoped or doped GQDs. Naphthalene (1g) was suspended in 80 mL concentrated nitric acid (70%) and stirred at 80 °C for 12 h. The resulting nitro-naphthalene product is filtered, dried. 20 mg nitro-naphthalene was dispersed in 10 mL NaOH solution (0.25 M) and hydrothermally treated at 200 °C for 8 h to form GQDs decorated with –OH groups. To achieve heteroatom doping, NaOH was replaced with 1.5 M ammonia solution or 0.12 M thiourea solution or both above to produce N-doped GQDs or S-doped GQDs or NS-doped GQDs. After dialysis (MWCO 500 Da) for 48 h and freeze-drying, GQD powders were obtained.

Exfoliation of pristine graphene from graphite. 50 mg of graphite powders were added into 50 mL of GQD (or doped GQD) solution (1 mg/mL) and bath ultrasonicated for 2 h. The dispersion of exfoliated pristine graphene sheets was centrifuged to remove the unexfoliated graphite particles (11.5%) and freeze-dried.

Characterizations. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were conducted with JEOL JEM 2100F and Bruker ICON AFM, respectively. Scanning electron microscope (SEM) uses the field emission scanning

electron microscope JEOL6700F (FESEM). X-ray photoelectron spectroscopy (XPS) measurement was performed on VG Multilab 2000 spectrometer (Thermo) with an Al K α 1846.6 eV anode. Elemental mapping was recorded using energy-dispersive X-ray spectroscopy (EDX) on JEOL JEM 2100 F. Fourier-transform infrared spectroscopy (FTIR) and UV-vis absorption spectroscopy were obtained from PerkinElmer FTIR spectrometer (Spectrum One) and Shimadzu UV-2450, respectively. The UV-vis absorption used GQD suspensions at the concentration of 0.1 mg/mL and the absorbance intensities were normalized. ^1H NMR (nuclear magnetic resonance) was conducted on Bruker Avance 300 NMR. Electron paramagnetic resonance (EPR) was conducted on a cw-EPR spectrometer (Bruker A300). Photoluminescence spectroscopy and quantum yield measurements were carried out by a Fluorolog TCSPC fluorescence spectrometer (HORIBA). X-ray absorption near edge structure (XANES) was recorded using the QuantumLeap X-ray absorption spectroscopy with synchrotron-like performance (Sigray). X-ray diffraction (XRD) was conducted on Bruker AXS D8 diffractometer using a filtered CuK α radiation ($\lambda = 0.15406$ nm) source at 40 mA, 40 kV. Raman spectrum was obtained by Renishaw Raman spectrometer using an Ar excitation laser light with wavelength of 514.5 nm (detection depth ~ 150 nm). Electrochemical measurements were obtained from Chenhua Electrochemical Station.

Photoelectrochemical water splitting. Hybrids of GQDs and exfoliated graphene sheets (2 mg) was dispersed in 400 μL Nafion solution (5%) under ultrasonication for 30 min. 100 μL of the ink is loaded onto Ni mesh and dried overnight. Photoelectrochemical measurements are performed with CHI 660D electrochemical analyzer equipped with 300 W Newport Xe lamp (2.4 W/cm^2 of visible light), using Ni mesh coated with hybrid

sheets (GQD/graphene or N-GQD/graphene, S-GQD/graphene, NS-GQD/graphene) as working electrode, Ag/AgCl as reference electrode and graphite rod as counter electrode. Potentials are referenced to a reversible hydrogen electrode (RHE) following the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.197$. The overpotential of OER (η_{OER}) follows the equation: $\eta_{\text{OER}} = E_{\text{RHE}} - 1.23\text{V}$. H_2 and O_2 gas produced from water splitting was detected by Agilent gas chromatography (GC Model 6890N).

Computation methods. DFT calculations for growth mechanism of GQD were carried out using Gaussian 09 software⁴². We used M06-2X exchange-correlation functional⁴³ with 6-311++G** basis set to determine geometry optimizations, vibrational frequencies, and transition states. Solvation effects were included in the calculations using SMD solvation model⁴⁴ with water dielectric constant of 78.355. The Berny algorithm was used to locate the transition states in reactions. We confirmed all stationary structures by vibrational analyses, yielding no imaginary frequencies for stable structures and only one imaginary frequency for transition states. In order to reduce the computational burden for large-sized GQDs in consideration of their self-limiting growth, we used PBE-D2/DNP level of theory⁴⁵⁻⁴⁷ with COSMO solvation model⁴⁸⁻⁴⁹ implemented in DMol³ module⁵⁰⁻⁵¹ of Materials Studio 8.0 to perform the DFT calculations. Reaction energies of denitration of various nitropolycyclic aromatic hydrocarbons with different sizes were obtained.

The calculations of density of states of pristine GQD/graphene, undoped GQD/graphene, adjacent NS-GQD/graphene, and separated NS-GQD/graphene were performed with Perdew-Burke-Ernzerhof (PBE) using Vienna *Ab-Initio* Simulation Package^{45, 52-53}. The valence electrons were expanded in a plane-wave basis set within a cutoff energy of 500

eV⁵⁴⁻⁵⁵. To avoid lateral interactions between adjacent GQDs due to the periodic boundary, a 7×7 supercell ($17.22 \text{ \AA} \times 17.22 \text{ \AA}$) of graphene was used (Fig. 5), leading to sufficient large distance ($> 6.6 \text{ \AA}$) between adjacent GQDs. Thus, the GQD/graphene systems contain totally at least 134 atoms. Van der Waals (VDW) correction of Grimme (D2)⁴⁶ was applied to model GQD/graphene interfacial interaction. The structures were relaxed till all residual forces are less than $0.02 \text{ eV/\AA}$. A vacuum thickness of at least $15 \text{ \AA}$ and dipole corrections were included to prevent unphysical interaction between periodic images. Γ -centered $3 \times 3 \times 1$ and $7 \times 7 \times 1$ k-meshes were respectively used for geometry optimization and electronic structure calculations. The isosurface value is 5×10^{-4} electron per $\text{\AA}^3$.

ASSOCIATED CONTENT

The supporting information is available free of charge on the ACS Publications website at DOI: XXX.

Details on ^1H NMR, XRD, Raman, EPR, the DFT calculations on synthesis mechanism, control experiments using different precursors and for different reaction time, exfoliation results, XPS and XANES of vdWHs, gas production of HER and OER are provided.

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Figure 1 Synthesis and characterization of GQDs. (a) Schematic illustration of the bottom-up synthesis of undoped and N,S-codoped GQD. TEM image and size distribution (b), High-resolution TEM image (c), AFM image with inset showing the height profile along the red-line and the height distribution (d), and Photoluminescence spectra with inset showing GQD dispersion under UV lamp (e) for undoped GQDs, 546 nm is the maximum emission peak at excitation of 467 nm.

Figure 2 Schematic illustration of GQD growth from naphthalene. The numbers (unit kcal/mol) stand for reaction energy. The green patterns represent the isosurface plots of the spin density distributions of the unpaired electrons.

Figure 3 Characterizations of doped and undoped GQDs. (a) FTIR spectra. (b) XPS spectra and elemental mapping from STEM-EDX (inset, scale bars = 5 nm). (c) High-resolution C 1s XPS spectra. (d) High-resolution N 1s (upper) and S 2p (bottom) XPS spectra of NS-GQD. (e) PL spectra. (f) Cathodic (left) and anodic (right) linear sweep voltammetry to determine CB and VB (scan rate at 5 mV/s in 0.5 M Na₂SO₄). (g) Energy diagrams. (h) UV-vis absorbance spectra.

Figure 4 Heterojunctions between exfoliated graphene and doped or undoped GQDs. (a) AFM image of the exfoliated graphene by undoped GQDs. Inset shows the height profile along the red line. (b) Tafel plots for HER (upper) and OER (bottom). (c) Photoelectrochemical HER and OER linear scan curves at scan rate of 2 mV s^{-1} in 1.0 M KOH , under stimulated visible light from 300 W Xe lamp . (d) Energy band diagram of GQD/graphene vdWH for photoelectrochemical anodic OER and cathodic HER. (e) Photocurrent responses (in 1.0 M KOH , at 0 V bias, and with illumination chopping every 50 s). (f) Nyquist plots from electrochemical impedance spectroscopy (EIS).

Figure 5 The density of states (left), top-view of the atomic models (middle) and side view differential charge density map (right) of vdWHs. (a) Pristine GQD/graphene. (b) undoped GQD/graphene. (c) NS-GQD/graphene with N and S dopants localized adjacently. (d) NS-GQD/graphene with N and S dopants separated. Dashed line indicates the Fermi level as the reference.

Figure 6 High-performance photoelectrochemical water splitting resulting from synergistic addition of electrochemical and photochemical processes. (a) HER and OER linear scan curves of NS-GQD/graphene at scan rate of 2 mV s⁻¹ in 1.0 M KOH with Xe lamp illumination (black), with intermittent illumination (blue), without illumination (red). Electrochemical performance of GQD/graphene without illumination (green) is shown for comparison. (b and c) Cathodic (b) and anodic (c) current densities of NS-GQD/graphene in ethanol containing 0.1 M KOH in ethanol with intermittent illumination. (d) HER and OER current densities over time from NS-GQD/graphene under the static overpotential of -150 mV (HER) and 150 mV (OER) respectively, in 1.0 M KOH solution with Xe lamp illumination.