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Tuning the Electronic Bandgap of Graphdiyne by H-substitution to Promote Interfacial Charge Carrier Separation for Enhanced Photocatalytic Hydrogen Production

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Abstract: Graphdiyne (GDY), which features a highly π -conjugated structure, direct bandgap and high charge carrier mobility, presents the major requirements for photocatalytic applications. Up to now, all photocatalytic studies were performed without paying too much attention on the GDY band gap (1.1 eV at the G_0W_0 many-body theory level). Such a narrow bandgap is not suitable for the band alignment between GDY and other semiconductors, making it difficult to achieve efficient photogenerated charge carrier separation. Herein, for the first time, we demonstrate that tuning the electronic bandgap of GDY via H-substitution (H-GDY) promotes interfacial charge separation and improves photocatalytic H_2 evolution. The H-GDY

exhibits an increased bandgap energy (~ 2.5 eV) and exploitable conduction band minimum and valence band maximum edges. As a representative semiconductor, TiO_2 was hybridized with both H-GDY and GDY to fabricate a heterojunction. Compared to the GDY/ TiO_2 composite, the H-GDY/ TiO_2 heterojunction leads to a remarkable enhancement of the photocatalytic H_2 generation by 1.35 times under UV-visible illumination ($6200 \mu\text{mol h}^{-1} \text{g}^{-1}$) and 4 times under visible light ($670 \mu\text{mol h}^{-1} \text{g}^{-1}$). Such enhancement is attributed to the suitable band alignment between H-GDY and TiO_2 , which efficiently promotes the photogenerated electron and hole separation, as supported by Density Functional Theory calculations.

1. Introduction

In a response to the urgent need for sustainable and clean energy source for the up-coming generations, photocatalytic hydrogen evolution involving light-irradiated semiconductors offers both a sustainable and relatively low-cost solution.¹⁻⁶ Along with the intensive research efforts in developing photocatalysts with high performance, low cost and environmental friendliness, carbon-based hybrid photocatalysts represented by graphene have emerged as a new alternative class of materials.⁷⁻⁸ In order to maximize the charge carrier transport and separation, graphene-based hybrid photocatalysts require a preliminary opening of its zero bandgap, by either chemical modification or electric field control.⁹⁻¹¹ Compared to graphene, graphdiyne (GDY), a rapidly developing 2D carbon material, is an even more promising candidate for catalytic energy conversion, due to its inherent direct bandgap, high charge carrier mobility, and simple preparation methods.¹²⁻²⁰ Up to date, semiconductors including TiO_2 , ZnO , CdS and C_3N_4 , have been successfully hybridized with GDY for enhanced photocatalytic applications.²¹⁻²⁶ However, all these photocatalytic systems were developed without any optimization of the GDY bandgap. The narrow bandgap (around 1.1 eV at the theoretical level) of pristine GDY neither meets the requirement to overcome the theoretical endothermic change in the process of water splitting (i.e., 1.23 eV),²⁷⁻²⁸ nor achieve the interfacial separation of

photogenerated charge carriers to the maximum extent, because of the poor mismatch between the conduction/valence band edges of GDY and the donating/accepting energy levels of the other semiconductor. Tuning the bandgap of GDY in a hybrid system would provide a photosynthetic platform to mimic the “natural photosynthesis” for efficient hydrogen evolution. Type II heterostructured photocatalysts that possess adequate band alignment between two semiconductors are demonstrated to spatially separate the photogenerated charge carriers for highly efficient water reduction and oxidation to achieve water splitting.²⁹⁻³⁰ Thus, tuning the electronic bandgap of GDY, to fabricate such a type II heterostructure, represents a great potential for developing high-performance photocatalysts.

Chemical modification and element doping have been considered as effective approaches for adjusting the electronic band structure and related properties of carbon allotropes.³¹⁻³⁴ The traditional “top-down” doping method requires high temperature treatment under a specific atmosphere containing the heteroatom source, which is hard to control in term of doping sites (at either the acetylene moieties or the benzene rings) to achieve the targeted properties. Owing to the unique solution-synthesis method of GDY,³⁵⁻⁴⁰ a controllable doping/substitution method using a monomer design strategy provides an ideal bottom-up solution for adjusting the electronic bandgap of GDY. Hydrogen-substituted graphdiyne (H-GDY), prepared by the coupling reaction of 1,3,5-triethynylbenzene monomer, appears to be a good candidate. On the one hand, the introduction of hydrogen atoms on the meta-positions of benzene rings maintains the large π -conjugated structure and excellent charge carrier mobility.⁴¹ On the other hand, the introduction of H atoms has been demonstrated to enable enlarging the bandgap of carbon-based materials,⁴²⁻⁴³ which is beneficial to target the construction of type II heterostructured photocatalysts.

Toward this end, H-GDY was prepared through the polymerization of 1,3,5-triethynylbenzene monomer using CuCl as a catalyst. Experiments and theoretical calculations indicated that H-GDY possessed a bandgap energy of ~ 2.5 eV and exploitable conduction band minimum (CBM)

and valence band maximum (VBM) edges. As a proof of concept, TiO_2 was combined with H-GDY to fabricate a type II heterostructured photocatalyst. The H-GDY/ TiO_2 heterojunction showed remarkable photocatalytic activity for H_2 generation, under both UV-visible and visible light excitation. DFT calculations attribute this enhancement to the suitable band alignment between H-GDY and TiO_2 , which promotes the interfacial separation of the photogenerated electrons and holes and the photosensitization of TiO_2 under visible light. TRMC measurements confirmed a longer charge carrier lifetime for H-GDY/ TiO_2 ($\sim 0.33 \mu\text{s}$), compared to GDY/ TiO_2 ($\sim 0.24 \mu\text{s}$), further evidencing an efficient interfacial charge separation between H-GDY and TiO_2 . The concept of tuning the electronic bandgap of GDY to promote interfacial charge separation opens a new avenue for GDY-based photocatalysts.

2. Results and Discussion

We have first characterized the electronic structure of an isolated sheet of H-GDY versus GDY at the Density Functional Theory (DFT) level using periodic boundary conditions and the Perdew–Burke–Ernzerhof (PBE) functional within the Generalized Gradient Approximation (GGA). The main goal here is to describe on a relative basis the changes in the electronic structure when going from GDY to H-GDY. Figure 1 displays the band structure and the corresponding Density of States (DOS) together with the shape of the HOMO and LUMO orbital of the unit cell. The bandgap of GDY is calculated to be 0.46 eV and the width of the valence band to be 1.81 eV, in good agreement with previous calculations.²⁷⁻²⁸ As expected, the bandgap calculated at the PBE level is lower than the quasi-particle bandgap of 1.1 eV found at the GW many-body theory level due to the well-established underestimation of electronic bandgaps with GGA functionals. Nevertheless, comparing at the GGA level the relative values of the bandgap of two different materials and the relative alignment of their valence or conduction band edges is meaningful, which will not thus affect the interpretation of the experimental results based on our calculations. The theoretical results reveal that the hydrogenation of graphdiyne (H-GDY) induces the opening of the bandgap up to 2.40 eV, while

the width of valence band is reduced down to 0.82 eV. Those trends are rationalized by the fact that all benzene rings are connected in meta positions in H-GDY, thus limiting the degree of conjugation and hence increasing the gap. Such change is also expected to impact the electronic coupling between the unit cells and hence the mobility of the charge carriers, as evidenced by the flattening of the CB and VB edges in Figure 1b. The positions of the VB and CB edges of GDY (H-GDY) are calculated to be -4.92 and -5.37 eV (-3.50 and -5.83 eV), respectively, which translates into a downward shift by 1.42 eV of the VB edge and an upward shift by 0.46 eV of the CB edge when going from GDY to H-GDY.

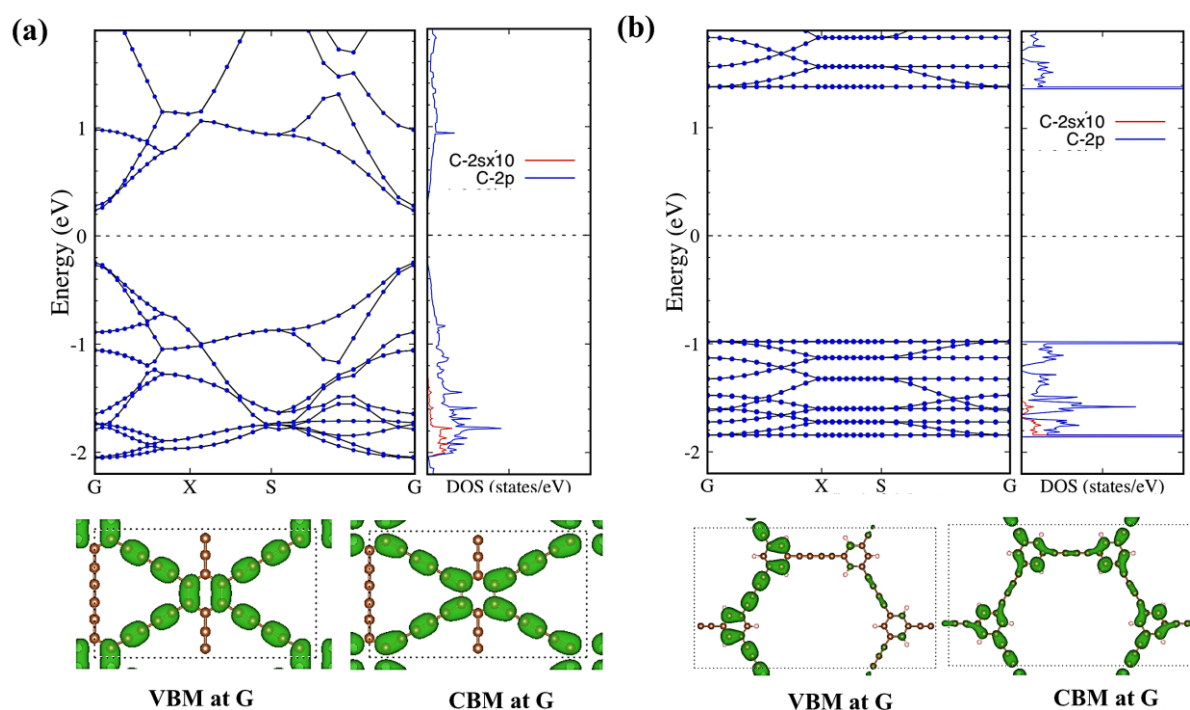


Figure 1. Band structure and projected density of states on the carbon orbitals of GDY (a) and H-GDY (b) calculated at the DFT level and shape of the HOMO and LUMO levels of the unit cell.

H-GDY was then synthesized via the coupling reaction of 1,3,5-triethynylbenzene monomer. In brief, 1,3,5-triethynylbenzene and CuCl were firstly added in pyridine and then heated at 60 °C for 24 h (Figure 2a). The presence of oxygen stimulated the formation of Cu I/II species, which catalysed the coupling reactions of the monomer to yield a yellowish powder (H-GDY). Raman spectroscopy, a useful technique for carbon materials, was used to study the bonding

structure of the prepared H-GDY. Compared to the terminal $\text{C}\equiv\text{C}$ stretching mode at 2123 cm^{-1} in the monomer (Figure S1), the shifted peak at 2224 cm^{-1} in H-GDY confirmed the successful formation of conjugated diacetylenic linkages (Figure. 2b). The peaks located at 997 and 1589 cm^{-1} are attributed to the ring breathing and ring stretching of aromatic moieties, respectively.⁴⁴ Transmission electron microscopy (TEM) displayed that the prepared H-GDY was composed of dispersed thin layers, which promote the adsorption of solvent and fast charge transfer (Figure S2). X-ray photoelectron spectroscopy (XPS) revealed that the prepared H-GDY powder mainly contained elemental carbon and oxygen while no Cu species were detected, indicating that they were successfully removed (Figure 2c). Deconvolution of the high-resolution C 1s spectra displayed the major fractions of sp and sp^2 hybridized carbons with binding energies at 284.5 and 285.1 eV , respectively (Figure 2d). The additional oxygen atoms could originate from the partial oxidation of terminal alkyne units. In comparison to the monomer, an obvious bathochromic shift was observed in the UV–visible spectrum (Figure 2e), suggesting enlarged electron delocalization by the extended π -conjugated system. The optical bandgap (E_g) estimated from the Tauc plot is 2.50 eV (Figure 2f), which is in agreement with the DFT calculations. Such a bandgap is large enough to overcome the theoretical endothermic change associated to the process of water splitting (i.e., 1.23 eV). The valence band edge of H-GDY was determined by high resolution XPS to be 1.24 V vs NHE (Figure 2g). Combined to the bandgap of 2.50 eV , the conduction band and valence band edges of H-GDY are calculated at -1.26 V and 1.24 V vs NHE (-3.24 eV and -5.74 eV vs vacuum level), respectively. The DFT calculations and the experimental determination of the bandgap, CB and VB energy levels are found to be in good quantitative agreement.

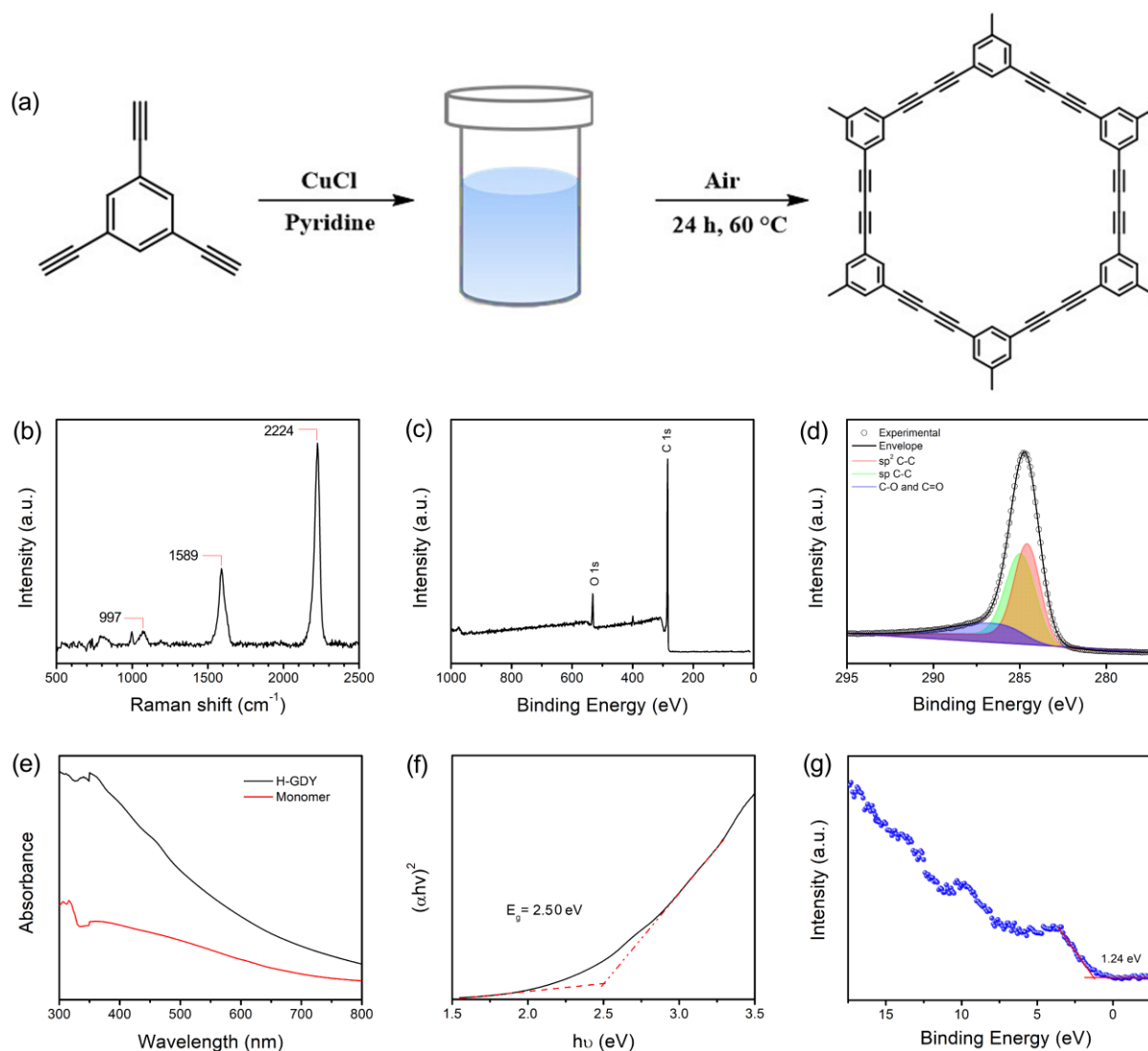


Figure 2. The synthesis and characterization of H-GDY. (a) Schematic illustration of the synthesis of H-GDY powder; (b) Raman spectrum of H-GDY; (c) XPS survey spectrum and (d) high-resolution C 1s spectrum of H-GDY; (e) UV-vis absorption spectrum and (f) Tauc plot of H-GDY; (g) high-resolution XPS valence band spectrum of H-GDY.

In order to demonstrate the potential of tuning the bandgap of GDY by H-substitution to fabricate type II heterojunction, TiO_2 was chosen as a model semiconductor to be interfaced with H-GDY. The microstructure of H-GDY/ TiO_2 composite was firstly characterized by transmission electron microscopy (TEM) and the results are shown in Figures 3a and 3b. The images indicated that the TiO_2 nanoparticles were dispersed with particle size of about 20 nm (Figure 3a). The high resolution TEM (HRTEM) micrograph taken from one of them in Figure 3b revealed that this nanoparticle has a crystal phase in agreement with TiO_2 Anatase (space

group = I41/AMDS) with $a=3.7850 \text{ \AA}$ $b=3.7850 \text{ \AA}$ and $c=9.5140 \text{ \AA}$ (Figure 3b). The electron energy loss spectroscopy (EELS) compositional mapping of the selected region displayed a homogeneous distribution of both Ti and O. The spatial distribution of C was different from that of Ti and O elements, indicating that the sample had two composite phases (Figure 3c). X-ray diffraction (XRD), Raman spectra, and XPS were performed to investigate the composition and chemical state of H-GDY/TiO₂ composite. The XRD of TiO₂ exhibited a mixture of anatase and rutile crystalline phase, typical of P25, with the anatase (101) preferential orientation. No typical diffraction patterns for H-GDY were observed, probably due to their relatively low amount and crystallinity (Figure 3d). Compared to pristine TiO₂, the H-GDY/TiO₂ composites exhibit enhanced characteristic peaks of H-GDY at 1587 cm⁻¹ and 2223 cm⁻¹ with the increase of H-GDY content, confirming the successful blending (Figure 3e). The high-resolution Ti 2p peak for H-GDY/TiO₂ was resolved at the same binding energy, indicating that the valence band states of Ti have not changed upon coupling (Figure S3). UV-visible diffuse reflectance spectra demonstrated that the introduction of H-GDY red-shifted the absorption of TiO₂ (Figure S4).

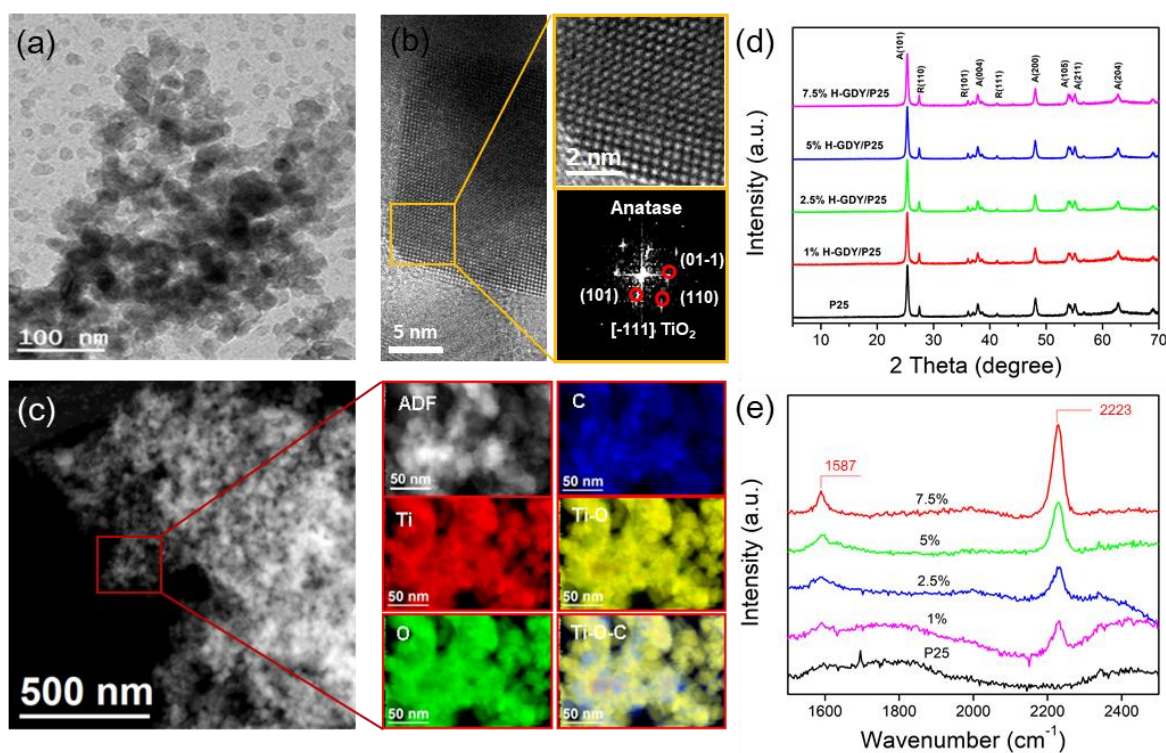


Figure 3. Characterization of H-GDY/TiO₂; (a) TEM image of H-GDY/TiO₂; (b) HRTEM micrograph, detail of the orange squared region and its corresponding power spectrum; (c) EELS mapping of selected region in H-GDY/TiO₂; (d) XRD patterns and (e) Raman spectra of TiO₂ and H-GDY/TiO₂ with different contents of H-GDY.

The photocatalytic activity of the H-GDY/TiO₂ nanocomposite was evaluated towards H₂ generation in methanol/water solution (1:3 v/v) under Xenon lamp illumination. The photocatalytic activity of pristine TiO₂, which showed negligible H₂ generation, was improved remarkably when mixed with H-GDY. The photocatalytic activity increased with the content of H-GDY and reached an optimal efficiency for 5% H-GDY/TiO₂ (Figure 4a). The total amount of H₂ generated is up to 370 μmol after 6 hours, corresponding to $\sim 6200 \mu\text{mol h}^{-1} \text{g}^{-1}$ H₂ production rate (Figure 4b). A further increase in the H-GDY content reduces the photocatalytic performance. This result suggests that a higher coverage of the TiO₂ surface reduces the accessibility to the active sites on the TiO₂ surface. In order to assess the stability of the photocatalysts, the optimal 5% H-GDY/TiO₂ sample was subjected to four consecutive test cycles of hydrogen evolution (Figure 4c). The 5% H-GDY/TiO₂ sustained a stable photoactivity for hydrogen evolution after four cycles under identical experimental conditions.

For comparison, GDY was synthesized and hybridized with TiO₂ under the same conditions. The hybridization of GDY and TiO₂ was also characterized and the Raman spectra and HRTEM images of 5% GDY/TiO₂ were presented in Figure S5 and S6. Both H-GDY/TiO₂ and GDY/TiO₂ composites displayed much higher photocatalytic activities than that of pure TiO₂ (Figure 4d, 4e), which is attributed to the synergetic charge transfer processes in the composites. Notably, the H₂ generated rate of the 5% H-GDY/TiO₂ were 1.35 times and 4 times higher than those of the 5% GDY/TiO₂ under UV-visible and visible light, respectively. Such results point to the more efficient interfacial separation of photogenerated carriers between H-GDY and TiO₂. Excitingly, the H-GDY/TiO₂ even generate nearly 11 μmol H₂ from pure water after 8 h illumination, nearly 1.6 times that of GDY/TiO₂ (Figure 4f), further indicating the great potential of bandgap engineering of GDY for enhancing the photocatalytic efficiency.

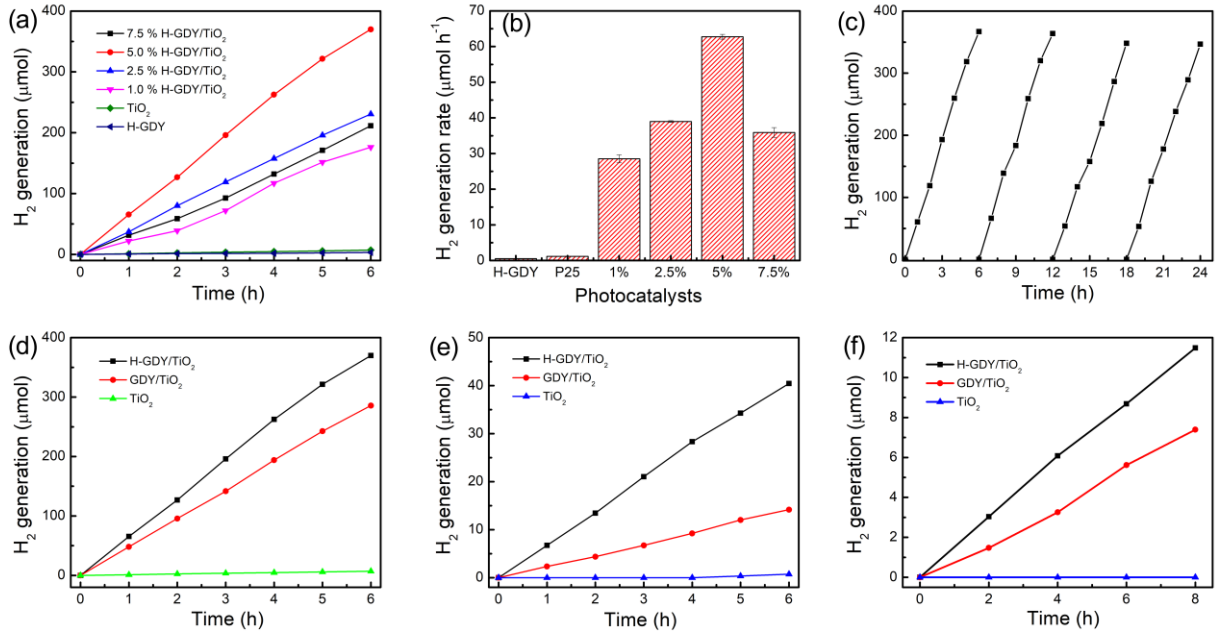


Figure 4. Photocatalytic characterization of different samples. (a) Photocatalytic activity and (b) H₂ generation rate for H-GDY/TiO₂ composites with different contents; (c) stability test of 5% H-GDY/TiO₂ photocatalyst; (d) photocatalytic activity of H-GDY/TiO₂, GDY/TiO₂ and TiO₂ composites under Xenon lamp illumination; (e) photocatalytic activity of H-GDY/TiO₂, GDY/TiO₂ and TiO₂ composites under visible light illumination (Xenon lamp equipped with 405 filter); (f) photocatalytic activity of H-GDY/TiO₂, GDY/TiO₂ and TiO₂ composites in pure water under Xenon lamp illumination.

DFT calculations were performed to shine light on the effect of H-substitution of the GDY on the properties of the hybrid systems made with TiO₂. For the sake of comparison with our experimental observations, we considered electron transfer processes only over the main exposed surface (101) of TiO₂, which is non polar. The optimized structures of the built TiO₂/GDY (H-GDY) interfaces are given in Figure S7 and the projected band structure of the hybrid system in Figure S8. We have calculated at DFT/PBE level with van der Waals corrections the interaction energy between the two components by the following equation:

$$E_{int} = E_{tot} - E_{TiO_2} - E_{(GDY/H-GDY)} \quad (1)$$

where E_{tot} , E_{TiO_2} and $E_{(GDY/H-GDY)}$ are the total energies of the heterostructure, individual TiO₂ and individual GDY (H-GDY) layers, respectively, in the geometry of the fully relaxed heterostructure.

The GDY (H-GDY) monolayer and the top layer of the TiO_2 surface undergo only a negligible buckling at the interfaces. The distance between H-GDY and TiO_2 ($2.57 \text{ \AA}$) is smaller than that computed between GDY and TiO_2 ($2.75 \text{ \AA}$). The calculated binding energies are found to be relatively comparable in TiO_2/GDY and $\text{TiO}_2/\text{H-GDY}$ heterostructures ($-7.32 \text{ meV/\AA}^2$ versus $-4.20 \text{ meV/\AA}^2$ per unit cell, respectively). This points that the H-substituted GDY does not perturb thermodynamically the interaction with TiO_2 .

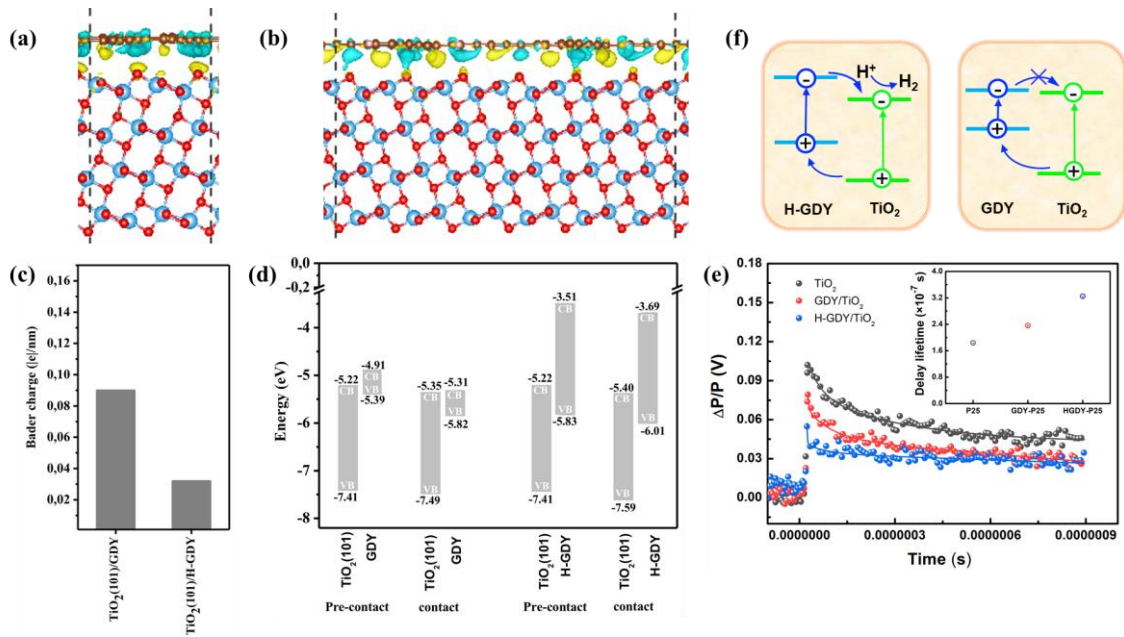


Figure 5: Side views of the 3D charge density difference in the (a) $\text{TiO}_2(101)/\text{GDY}$ and (b) $\text{TiO}_2(101)/\text{H-GDY}$ heterostructures; isosurface values for 3D charge density difference plots are $0.09 \text{ e/\AA}^3$; the accumulation and depletion of electrons are represented in cyan and yellow, respectively; (c) calculated Bader charge accumulated on the GDY (H-GDY) monolayer in the heterostructure; (d) relative band alignment of VB and CB band edges before and after the formation of the heterostructure. (e) TRMC measurements of TiO_2 , GDY/TiO_2 and $\text{H-GDY}/\text{TiO}_2$ at 360 nm excitation wavelength; insert: the fitting of the decay lifetime of the three samples; (f) schematic illustration of the interfacial charge transfer between TiO_2 and H-GDY/GDY.

The amount of interfacial charge transfer in the ground state in the two different systems has been quantified by using a Bader charge analysis (Figure 5c). In both cases, there is a charge transfer in the ground state between the two components, with the positive charge systematically localized in the H-GDY or GDY monolayer while the negative charge is localized in the TiO_2 slab, acting thus as the acceptor layer. This trend is rationalized by the

small energy difference between the VB edge of GDY/H-GDY with respect to the CB edge of TiO₂. Interestingly, although the size of unit cell is smaller when considering GDY, the hole accumulation in GDY in the ground state is larger than that in H-GDY, most probably due to the larger carbon areal density in GDY; this is in full consistency with the larger binding energy computed for the GDY/TiO₂ hybrid system. The pronounced hole accumulation in GDY also explains the large downward shifts of the VB and CB edges when going from the individual components to the blend (Figure 5d). It is also of prime interest to analyse the alignment of the band edges, which are key parameters that govern the charge transfer processes at the interfaces. As shown in Figure 5d, there is a large valence band offset ΔE_{VB} in the GDY/TiO₂ heterostructure while the conduction band minimum (CBM) of GDY is lying very close to that of TiO₂. Under UV-visible light excitation of TiO₂, charges can be generated following an efficient photoinduced hole transfer between the valence bands of the two components whereas electron transfer processes between the conduction bands are expected to be much less efficient due to the absence of a significant driving force. For H-GDY/TiO₂ interfaces, there is a large offset between both the CBM and VBM of the two layers, leading to a type-II band alignment; photogenerated charge carriers are thus expected to be observed, originating from both efficient photoinduced hole transfer processes between the valence bands (from TiO₂ to H-GDY) upon photoexcitation of TiO₂ and efficient photoinduced electron transfer processes between the conduction bands (from H-GDY to TiO₂) upon excitation of H-GDY. In turn, these two available pathways are expected to make the hydrogen evolution reaction more efficient.

To further elucidate and confirm the interfacial charge transfer between TiO₂ and H-GDY (GDY), a Time Resolved Microwave Conductivity (TRMC) analysis was performed under laser-pulsed excitation at 360 nm, which enables exciton generation in both materials. Compared to the well-known photoluminescence time resolved measurements, TRMC enables evaluating the dynamics of charge carriers in TiO₂-based composites.⁴⁵⁻⁴⁶ Upon laser excitation of the samples, the concentration of the photogenerated charge carriers increased during the

pulse, and then a subsequent decay is observed due to the decrease in the amount of excess charges, either by recombination, trapping or surface reaction processes. It is worth noting that no TRMC signal was observed for pristine H-GDY (GDY), probably due to the low sensitivity of the change in the conductivity of the carbon-based material. As shown in Figure 5e, pure TiO_2 shows a higher maximum value of the signal compared to GDY/ TiO_2 and H-GDY/ TiO_2 , which is probably attributed to the shield effect. However, these effects, usually harmful for the photoactivity, can be compensated by the influence on the charge carriers' lifetime (decay), a limiting factor in the photocatalytic reaction.

In contrast to pure TiO_2 , GDY/ TiO_2 and H-GDY/ TiO_2 exhibited much slower global decay, leading to a higher number of charge carriers exploitable for photocatalytic reactions. Notably, a lifetime of charge carriers of $\sim 0.33 \mu\text{s}$ was observed in H-GDY/ TiO_2 , much longer than that for GDY/ TiO_2 ($\sim 0.24 \mu\text{s}$), thus indicating that the heterojunction between H-GDY and TiO_2 is more efficient for the charge separation than that between GDY and TiO_2 , in full consistency with the theoretical analysis and experimentally observed photocatalytic activity. All in all, the charge carrier separation in the H-GDY/ TiO_2 and GDY/ TiO_2 photocatalysts can be rationalized in the following way: GDY acts solely as a hole transport layer, while the H-substitution enables to markedly increase the bandgap and provide a proper positioning of the CB and VB bands to construct an efficient type II heterojunction with TiO_2 ; this fully promotes a full charge carrier separation (Figure 5f), which subsequently improves the photocatalytic activity towards H_2 generation.

3. Conclusions

In conclusion, the electronic bandgap of GDY was adjusted by H-substitution and the obtained H-GDY was hybridized with TiO_2 to form a type II heterojunction. The prepared H-GDY/ TiO_2 displayed excellent photocatalytic activity with H_2 production rate of $\sim 6200 \mu\text{mol h}^{-1} \text{g}^{-1}$ under UV-visible illumination and $\sim 670 \mu\text{mol h}^{-1} \text{g}^{-1}$ under visible illumination, which were 1.35 times higher and 4 times higher than that of GDY/ TiO_2 composite, respectively. DFT calculations

revealed that the superior activity of H-GDY is attributed to the suitable band alignment between H-GDY and TiO_2 , which promote photogenerated electron and hole separation via different pathways compared to the GDY/ TiO_2 heterojunction. TRMC evidenced the longest lifetime of charge carriers in H-GDY/ TiO_2 , further evidencing the successful fabrication of type II heterojunction. The concept of tuning the electronic bandgap of GDY to construct efficient heterojunctions enhancing interfacial carrier separation is certainly not confined to H-substitution and TiO_2 but should be extended to other element doping and semiconductors for photocatalytic applications. Related works are in progress in our laboratory.

Supporting Information

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

Conflict of Interest

The authors declare no conflict of interest.

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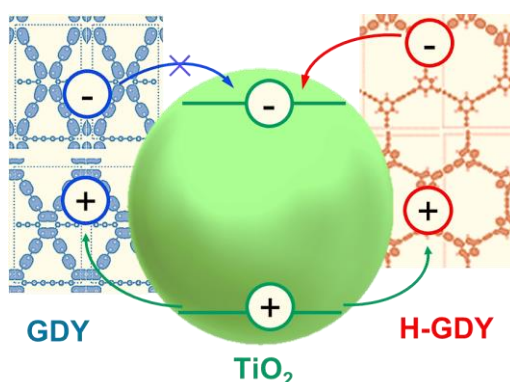
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Table of Contents:

Title: Tuning the Electronic Bandgap of Graphdiyne by H-substitution to Promote Interfacial Charge Carrier Separation for Enhanced Photocatalytic Hydrogen Production

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Adjusting the electronic bandgap of graphdiyne is the next step to move forward and expand the use of graphdiyne in photochemical reactions. The H-substitution of graphdiyne maintains the large π -conjugated structure and enable widen the bandgap, which is beneficial to target the construction of type II heterostructured photocatalysts for efficient charge carrier separation and H_2 generation.