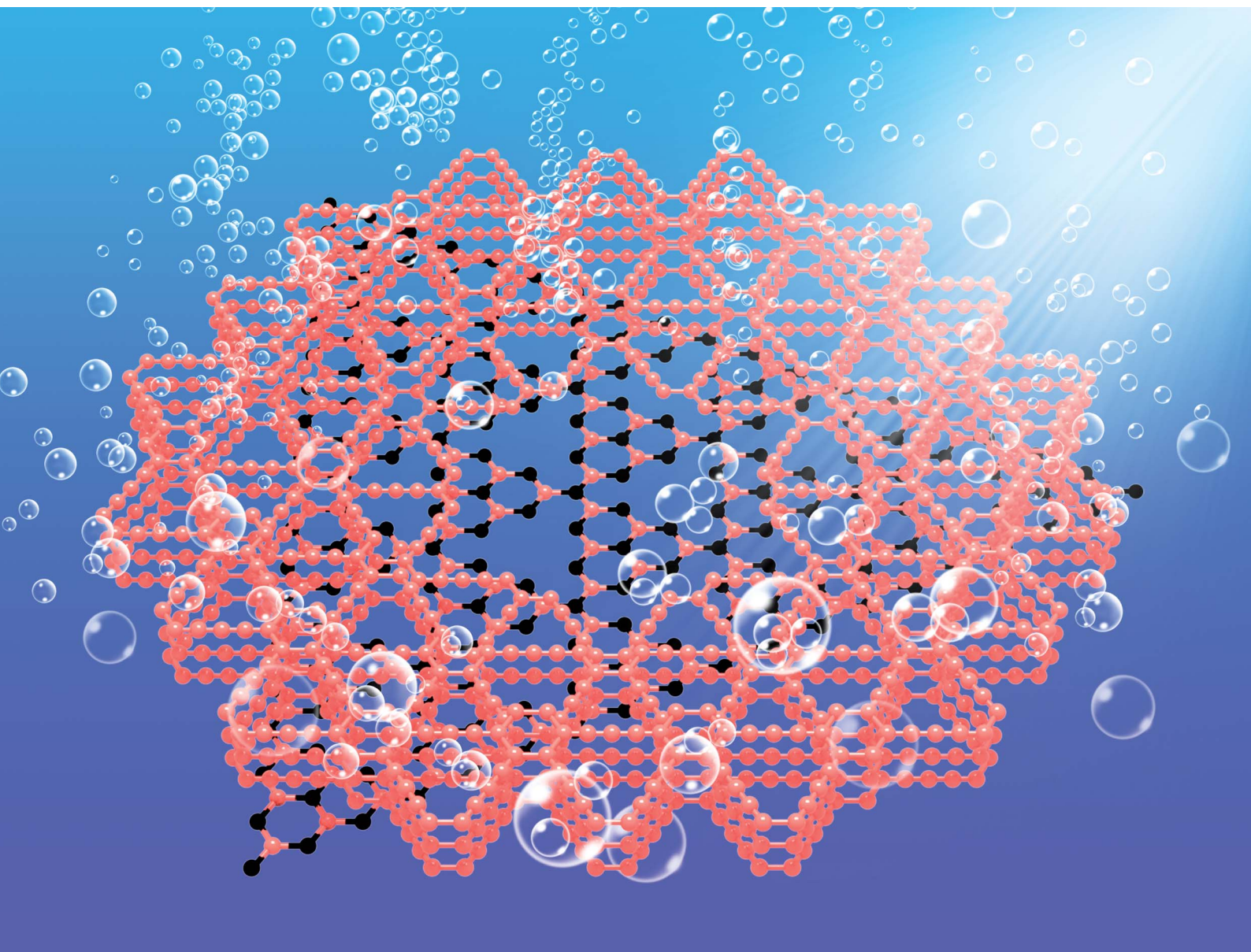


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In situ construction of graphdiyne based heterojunctions by a deprotection-free approach for photocatalytic hydrogen generation†

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Graphdiyne (GDY) with a direct bandgap, high charge carrier mobility, and ordered pore structure, is considered an excellent matrix for the construction of heterojunction photocatalysts. However, the traditional fabrication methods for GDY-based heterojunctions require a complicated deprotection of hexakis-[(trimethylsilyl)ethynyl]benzene (HEB-TMS) and usually result in localized heterojunctions. Herein, we developed a facile deprotection-free method to *in situ* grow GDY on the surface of C_3N_4 by directly using HEB-TMS as the precursor. Such a method enabled the formation of an integral GDY@ C_3N_4 heterojunction, resulting in a significantly enhanced photocatalytic activity in the visible region. The optimized GDY@ C_3N_4 showed 15.6-fold hydrogen production efficiency compared to pristine C_3N_4 , and outperformed the GDY/ C_3N_4 samples synthesized by other approaches (e.g. physical mixing, hydrothermal treatment and calcination treatment). This study provides a universal and efficient strategy for the design of GDY-based heterojunction photocatalysts for solar-to-hydrogen energy conversion.

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1 Introduction

Photocatalytic solar-to-hydrogen energy conversion is one of the most promising technologies to simultaneously solve global environmental issues and energy crises.^{1–4} Along with the intensive research in the development of efficient and cost-effective photocatalysts,^{5–7} carbon-based heterojunction photocatalysts have emerged as a new class of alternative materials.⁶ Graphdiyne (GDY), consisting of both sp^2 and sp hybridized carbons, is a rising-star 2D carbon material.^{8–10} Different from zero-bandgap graphene, GDY possesses the characteristics of a semiconductor with a direct band gap, suitable band energy levels and comparable intrinsic charge carrier mobility, which enable the occurrence of efficient photocatalytic reactions.¹¹ Furthermore, the large surface area and porous structure of GDY provide huge adsorption sites for reactants and promote the mass transfer in the in-plane and out-of-plane directions

efficiently.¹² All these fascinating features make GDY an excellent host matrix to construct heterojunction photocatalysts.^{13–15}

So far, a variety of GDY-based heterojunction photocatalysts have been prepared, such as GDY/ TiO_2 ,^{16–19} GDY/CdS,²⁰ GDY/ C_3N_4 ,^{21–26} etc. These heterojunction systems were constructed by a hydrothermal method, calcination, or physical adsorption. In these processes, GDY was firstly synthesized on Cu substrates and the exfoliated GDY powder was then hybridized with other semiconductors, which is time-consuming and usually results in localized heterojunctions. Very recently, some GDY-based heterojunctions were fabricated by directly growing GDY on the other semiconductors including CuI/GDY,²⁷ CuBr/GDY²⁸ and NiTiO₃/CuI/GDY,²⁹ enabling GDY to uniformly cover other semiconductors. However, the reported *in situ* growth method is limited to Cu-based semiconductors and requires the pre-synthesis of hexaethynylbenzene (HEB) monomer *via* a complex deprotection of hexa[(trimethylsilyl)ethynyl]benzene (HEB-TMS). To the best of our knowledge, no attempt has been reported to *in situ* grow GDY on other semiconductors by directly using HEB-TMS as the precursor.

With this in mind, a straightforward deprotection-free method using HEB-TMS as the monomer for the *in situ* growth of GDY on the surface of C_3N_4 was developed. The uniform coating of GDY on C_3N_4 led to an integral GDY@ C_3N_4 heterojunction, which greatly improved the photocatalytic activity in the visible region. As a result, the optimized GDY@ C_3N_4 displayed a 15.6-fold hydrogen production efficiency compared to pure C_3N_4 . Compared to the GDY/ C_3N_4

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samples prepared by physical mixing, hydrothermal treatment and calcination treatment, the as-prepared GDY@C₃N₄ exhibited the best photocatalytic performance, further confirming the superiority of this strategy. This simple and effective method can be easily extended to other GDY-based heterojunctions, offering a promising strategy for the rational design of novel photocatalysts.

2 Materials and methods

2.1 Materials

All solvents and reagents including urea (Sigma-Aldrich), hexakis(trimethylsilyl) ethynylbenzene (HEB-TMS, purchased from Nanjing XFNANO Materials Tech Co., Ltd), tetrahydrofuran (THF, Sigma-Aldrich), *N,N*-dimethylformamide (DMF, Sigma-Aldrich), ethyl acetate (EA, Sigma-Aldrich), tetrabutylammonium fluoride (TBAF, 1 M in THF, Sigma-Aldrich), hydrochloric acid (HCl, 37%, Sigma-Aldrich), triethanolamine (TEOA, Sigma-Aldrich), ethanol (Sigma-Aldrich), methanol (Sigma-Aldrich), ultra-pure water (Millipore System, 18.2 MΩ cm), copper(i) chloride (CuCl, Sigma-Aldrich), chloroplatinic acid (H₂PtCl₆·*x*H₂O, Sigma-Aldrich) and sodium sulfate (Na₂SO₄, Sigma-Aldrich) were used without further purification.

2.2 Preparation of C₃N₄ nanosheets

Typically, urea (20 g) was placed in a crucible with a lid and then calcined at 550 °C min⁻¹ for 3 h in air (at the rate of 2 °C min⁻¹) to obtain bulk polymeric C₃N₄. The bulk polymeric C₃N₄ was milled into a powder in a mortar. Afterwards, the as-prepared C₃N₄ powder was thermally oxidized and etched in air at 550 °C for 4 h with a rate of 5 °C min⁻¹ to yield pale yellow C₃N₄ nanosheets.

2.3 Preparation of GDY@C₃N₄ and GDY/C₃N₄

GDY was grown *in situ* on C₃N₄ through a deprotection-free method.¹⁷ Briefly, 50 mg C₃N₄ nanosheets were sonicated for 20 min to evenly disperse in 10 mL DMF. Then, CuCl (10 mg) and an appropriate amount of HEB-TMS were added. Afterwards, the bottle was sealed and heated to 60 °C with stirring in an oil-bath for 24 h. After reaction, the sample was washed with fresh DMF, THF, methanol and ethanol sequentially. Finally, the sample was dried in the oven overnight and a brown powder was obtained. The GDY coated C₃N₄ (GDY@C₃N₄) was obtained by stirring in 1 M HCl for 6 hours to remove the CuO. By controlling the amount of HEB-TMS added, the mass ratio of HEB-TMS to C₃N₄ was set to 0.5, 1, 2, and 5%, and the prepared samples were denoted as GDY@C₃N₄-*x* (*x* = 1, 2, 3, and 4), respectively.

As reference samples, different GDY/C₃N₄ heterojunction photocatalysts were also prepared according to the previous literature.^{21,22} GDY was prepared following a previously reported approach.³⁰ Then, 30 mg C₃N₄ and 0.3 mg GDY were dispersed in 10 mL mixture of water and ethanol (*v*:*v* = 1:1), followed by sonication for 20 min and stirring for 1 h to obtain homogeneous suspensions. Thereafter, suspension-A was stirred continuously at room temperature for another 23 h to obtain

GDY/C₃N₄-Mix. Suspension-B was transferred to a 20 mL Teflon and heated at 120 °C for 3 h to synthesize GDY/C₃N₄-Hyd. Suspension-C was evaporated at 60 °C and then was calcined at 400 °C for 2 h (with a rate of 5 °C min⁻¹) to obtain GDY/C₃N₄-Cal.

All the as-prepared photocatalysts were deposited with 1 wt% Pt through a photoreduction method before photocatalytic tests. Briefly, 30 mg photocatalyst was sonicated for 20 min to evenly disperse it in 10 mL ethanol, then a certain volume of H₂PtCl₆ solution (1 mM in ethanol) was added to the photocatalyst suspension and vigorously stirred for 30 min. Subsequently, the mixture was exposed under a xenon 300 W lamp and kept stirring for 30 min to yield photocatalysts loaded with Pt nanoparticles. Finally, the samples were washed with ethanol several times and dried in the oven at 60 °C overnight.

3 Results and discussion

As shown in Fig. 1a, the *in situ* growth of GDY on C₃N₄ was achieved through a simple deprotection-free strategy by employing CuCl and DMF as the catalyst and solvent, respectively. Due to the large amount of amino groups, the surface of C₃N₄ tends to be negatively charged, which facilitates the adsorption of Cu⁺ ions on its surface. It has been demonstrated that Cu⁺ ions in DMF can promote the coupling reaction of HEB-TMS,¹⁷ thus allowing the formation of a uniform GDY layer on the C₃N₄ surface. Ultimately, the CuO generated during the process was removed by using 1 M HCl to yield GDY@C₃N₄ powders. The morphology of as-prepared C₃N₄ and GDY@C₃N₄ was investigated by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Numerous ultrathin and overlapping filamentous structures were observed in Fig. 1b and S1,[†] indicating that the C₃N₄ was successfully stripped into layers after secondary thermal oxidation and etching in air. The coating of GDY brought no structural changes to C₃N₄ but modified the color from the original pale yellow to brown, which darkens with increased usage of the HEB-TMS precursor (Fig. 1b–d and S2[†]).

To further reveal the microstructure of C₃N₄ and GDY@C₃N₄, transmission electron microscopy (TEM) measurements were carried out. As displayed in Fig. 2a, b and S3,[†] C₃N₄ showed curled edges and an abundance of pores with size of several tens of nanometers. The formation of these pores may originate from gas emissions during the thermal polymerization of urea, which contributes to the diffusion of the reactants.³¹ The elemental composition mapping of C₃N₄ was determined by electron energy loss spectroscopy (EELS) from the red square region in the HAADF-STEM micrograph (Fig. 2c). It can be seen that the C₃N₄ nanosheets showed a uniform distribution of C and N elements throughout the structure, although C₃N₄ and GDY were not easily distinguished in TEM images due to the similar atomic numbers of C and N as well as the amorphous property. Compared with the pristine C₃N₄, two different components can be clearly observed from the TEM image of GDY@C₃N₄, including the curled filamentary C₃N₄ and the flattened thinner flakes of GDY (Fig. 2d, e and S4[†]). In contrast to previous reports,^{21–23} GDY was evenly adhered

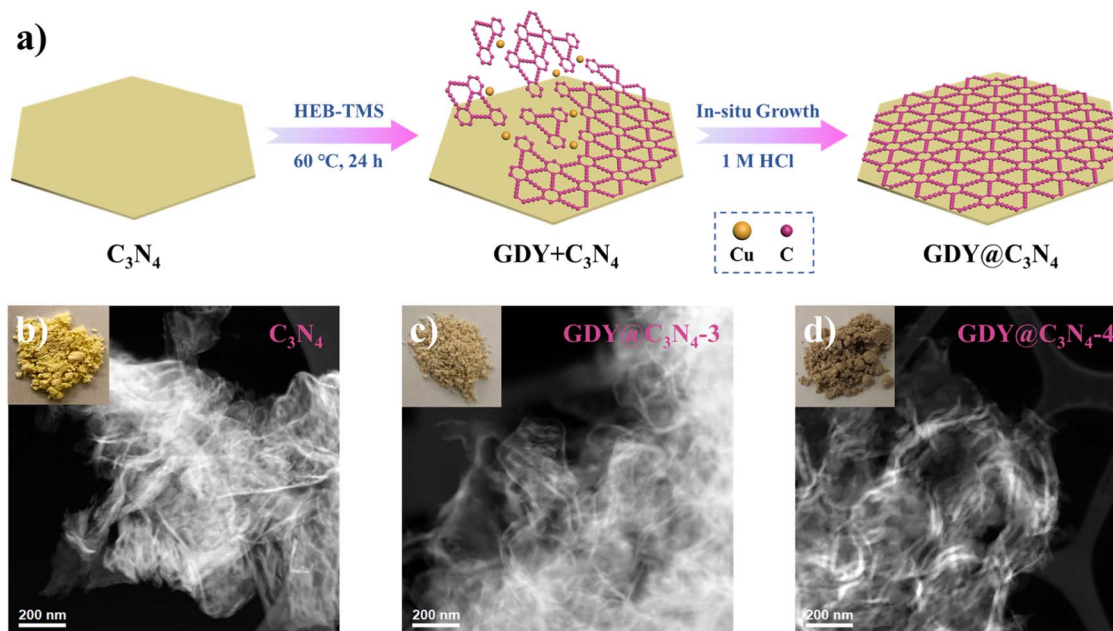


Fig. 1 (a) Schematic illustration for the preparation of $GDY@C_3N_4$ via a one-pot method. Photographs of samples and corresponding HAADF-STEM images of (b) C_3N_4 , (c) $GDY@C_3N_4-3$, (d) $GDY@C_3N_4-4$.

around the C_3N_4 rather than forming only regional interfaces, suggesting an omnidirectional growth of GDY on the surface of C_3N_4 . This view was further confirmed by the EELS mapping of the

$GDY@C_3N_4$. Fig. 2f shows a homogeneous elemental distribution of C and N, where there was an obvious expansion of the C distribution on $GDY@C_3N_4$, which indicated the

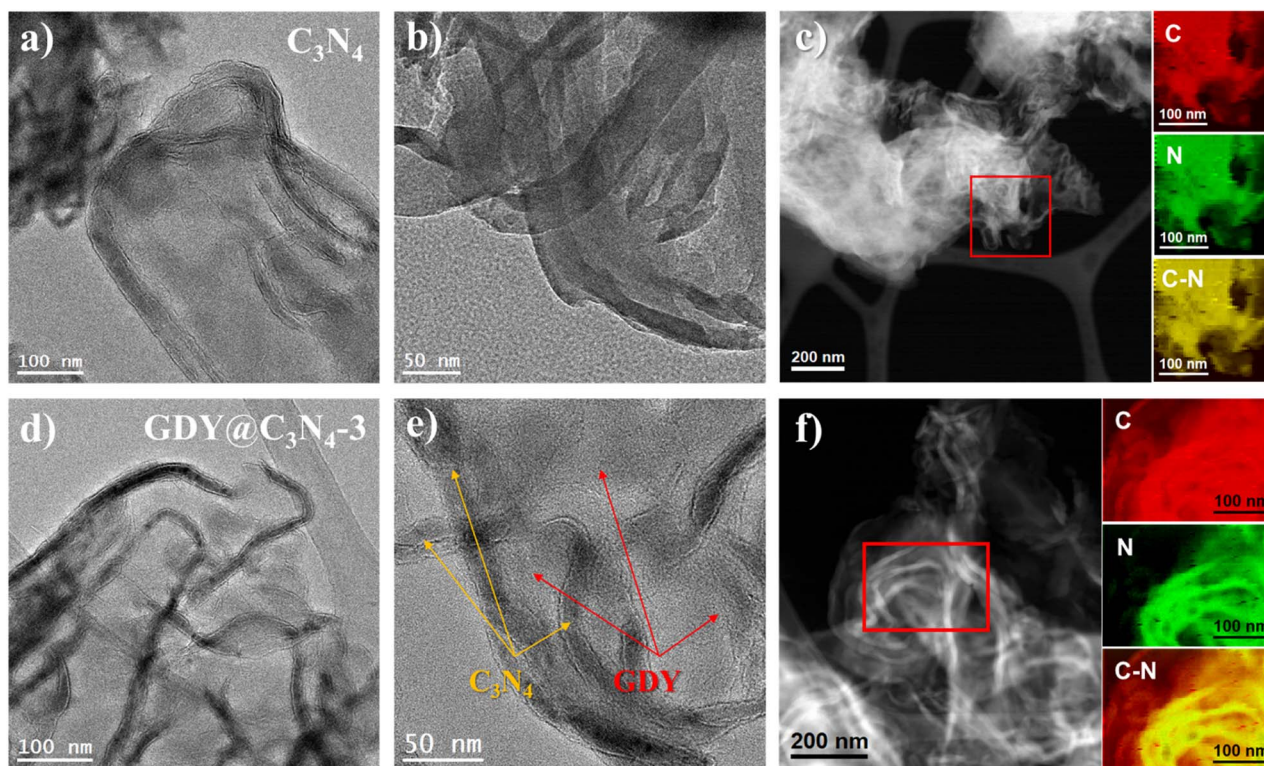


Fig. 2 TEM images showing the morphology of (a and b) C_3N_4 and (d and e) $GDY@C_3N_4-3$. (Yellow arrows point to the darker curly filamentous areas, belonging to C_3N_4 . Red arrows point to the shallower flattened flake areas, belonging to GDY.) HAADF-STEM images of (c) C_3N_4 and (f) $GDY@C_3N_4-3$, and the corresponding representative EELS chemical composition mapping obtained from the red squared area in the STEM images. In dividual mapping obtained from the C K-edge at 284 eV (red), N K-edge at 402 eV (green) and C-N composite mapping (yellow).

successful coating of C_3N_4 by GDY. The unique encapsulation structure of $GDY@C_3N_4$ photocatalysts predicts excellent charge separation/transfer ability and promising photocatalytic performance can be expected.³²

X-ray diffraction (XRD) was used to investigate the crystal structures of the synthesized samples (Fig. 3a). GDY exhibited a typical broad and weak diffraction peak centred at around 21.2° , corresponding to the characteristic (002) plane of the graphite-type carbon, which reveals a distortion of the ordered arrangement of GDY along its stacking direction.^{17,33} Two obvious diffraction peaks at 13.1° and 27.4° can be observed from the XRD diagram of C_3N_4 , which are assigned to the (100) plane from the interplanar stacking of the conjugate segments and the (002) plane originating from interlayer structural packing units, respectively.^{7,34,35} The characteristic peaks of C_3N_4 were retained in the $GDY@C_3N_4$ samples, suggesting that the presence of GDY did not disrupt the crystal structure of C_3N_4 . Diffraction peaks belonging to GDY cannot be detected in $GDY@C_3N_4$ composites due to the poor crystallinity and low content.²⁶ However, it is worth mentioning that the characteristic peaks corresponding to C_3N_4 decreased with increased amount of GDY, which could be attributed to the partial shielding effect of the GDY, further validating the homogeneous growth of the GDY. The chemical composition of $GDY@C_3N_4$ was analyzed by X-ray photoelectron spectra (XPS). The XPS general survey indicated the presence of C, N and O (Fig. S5†). No peaks attributed to Cu were observed, which suggested the complete removal of Cu after acid treatment (Fig. S6†). The high-resolution C 1s XPS spectra of $GDY@C_3N_4$ display four sub-peaks (Fig. 3b), where the peaks located at 284.5 and

286.0 eV can be assigned to $C=C$ (sp^2) and $C-O$, while the peaks at 287.5 and 288 eV can be attributed to $C-N$ (sp^2) in C_3N_4 , respectively.^{21,36–39} The N 1s XPS spectra of $GDY@C_3N_4$ can also be deconvoluted into four sub-peaks at 399.1 eV for sp^2 -hybridized N in the $C-N$ heterocycle ($C=N-C$), 400.7 eV for sp^3 -hybridized N ($N-C_3$), 401.7 eV for amino groups ($-NH$) and 405.1 eV for charge effects, respectively (Fig. 3c).^{40–42} Fourier-transform infrared (FT-IR) spectroscopy was conducted to further examine the functional groups of as-prepared samples (Fig. 3d and e). The peaks located at 1381 and 1610 cm^{-1} in GDY were assigned to the stretching vibrations of $C-C/C-O$ bonds and the skeletal vibrations of the aromatic ring, respectively.³⁰ A series of peaks can be observed in the range of $1200\text{--}1700\text{ cm}^{-1}$ in pristine C_3N_4 ascribed to the typical stretching vibrations of $C-N$ heterocycles, while the peak located at 805 cm^{-1} can be attributed to the characteristic breathing mode of s-triazine units.⁴³ In addition, several broad peaks in the range $3000\text{--}3400\text{ cm}^{-1}$ are designated as the stretching vibrations for amino groups.⁴⁴ No significant changes were observed in the FT-IR spectra of $GDY@C_3N_4$, indicating that the *in situ* growth of GDY has no effect on the structure of C_3N_4 . Similarly, no distinct peaks belonging to GDY can be observed in the $GDY@C_3N_4$ samples due to the peak overlap between the $C-N$ heterocycle and aromatic ring as well as the low content of GDY, which is consistent with the XRD results. Of note, the peaks belonging to $C-N$ heterocycles shifted to higher wavenumbers in $GDY@C_3N_4$ compared to the pure C_3N_4 , indicating a strong interaction between GDY and C_3N_4 (Fig. 3e). This result demonstrates the formation of chemical bonds and hetero-junctions between C_3N_4 and GDY, which serves as charge

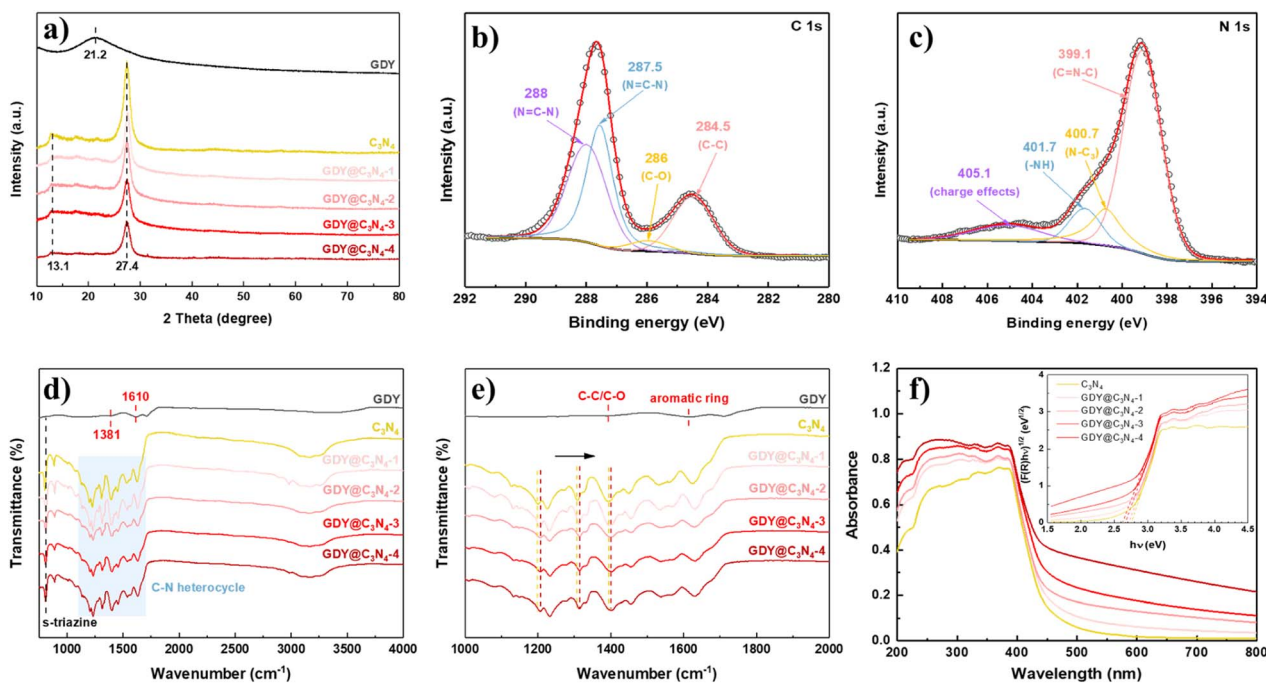


Fig. 3 (a) XRD patterns of the prepared samples. High resolution XPS spectra of $GDY@C_3N_4$: (b) C 1s and (c) N 1s. (d) FT-IR spectra of prepared samples. (e) Enlarged FT-IR spectra from (d). (f) UV-vis diffuse reflectance spectra of prepared samples (inset is the corresponding Kubelka–Munk plot).

transfer channels to enhance the photocatalytic performance.^{21,37,45}

To evaluate the light absorption capacity of the as-prepared samples, UV-vis diffuse reflectance spectroscopy (DRS) was carried out. Compared to pure C_3N_4 , the introduction of GDY significantly improves the absorption in the visible region owing to its excellent visible light absorption, and the intensity simultaneously enhances with the increased amount of GDY.²⁵ The optical bandgaps were estimated through the Kubelka-Munk (K-M) method, where the bandgap of C_3N_4 was determined to be 2.7 eV, while the bandgap for $GDY@C_3N_4$ samples reduced to 2.6 eV. The strong visible light absorption and narrow bandgap make $GDY@C_3N_4$ a promising visible-light driven photocatalyst.

The photocatalytic activities of C_3N_4 and $GDY@C_3N_4$ were estimated towards the hydrogen evolution reaction (HER) under visible light illumination (>420 nm), employing 1 wt% of Pt as a cocatalyst. Triethanolamine was used as the sacrificial reagent

to deplete the photogenerated holes. The photocatalytic H_2 production rate of C_3N_4 , which showed negligible H_2 generation, was significantly improved when covered by GDY. The photocatalytic activity increased with the content of GDY and reached an optimal photoactivity of $798 \mu\text{mol g}^{-1} \text{h}^{-1}$ for $GDY@C_3N_4$ -3/Pt (Fig. 4d and S7†), exceeding that of C_3N_4 /Pt by approximately 15.6-fold. A further increase in GDY reduced the H_2 evolution rate, probably because an excessively thick GDY layer disrupts the delicate balance between photogenerated carrier separation and light utilization efficiency (Fig. 4a-c).²¹ In addition, no significant deactivation was observed after four consecutive cycles, implying the robust stability of $GDY@C_3N_4$ -3/Pt (Fig. 4e). Such enhancement in photocatalytic performance and high stability is attributed to the excellent conductivity and protection of the GDY layer, which can effectively facilitate the transfer of photogenerated carriers and also can inhibit the photocorrosion.^{46,47}

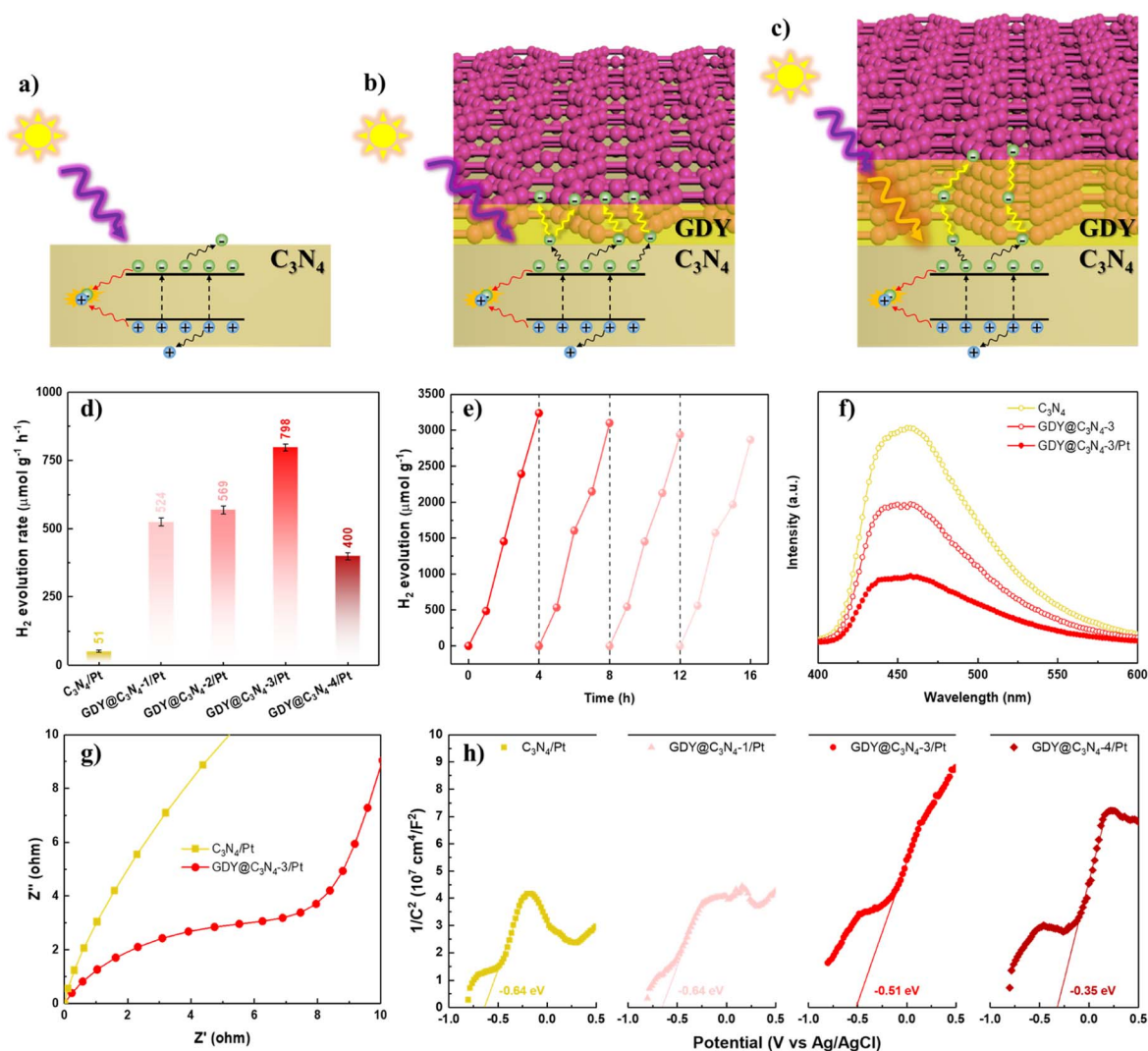


Fig. 4 (a–c) Schematic illustrations of the charge transfer pathways on the C_3N_4 and $GDY@C_3N_4$. (d) H_2 evolution rate of as-prepared photocatalysts under visible light ($\lambda > 420$ nm). (e) Long-term HER test with $GDY@C_3N_4$ -3/Pt. (f) PL spectra of C_3N_4 , $GDY@C_3N_4$ -3 and $GDY@C_3N_4$ -3/Pt. (g) EIS Nyquist plots of C_3N_4 /Pt and $GDY@C_3N_4$ -3/Pt in the dark. (h) MS plots of C_3N_4 /Pt and $GDY@C_3N_4$ /Pt composites.

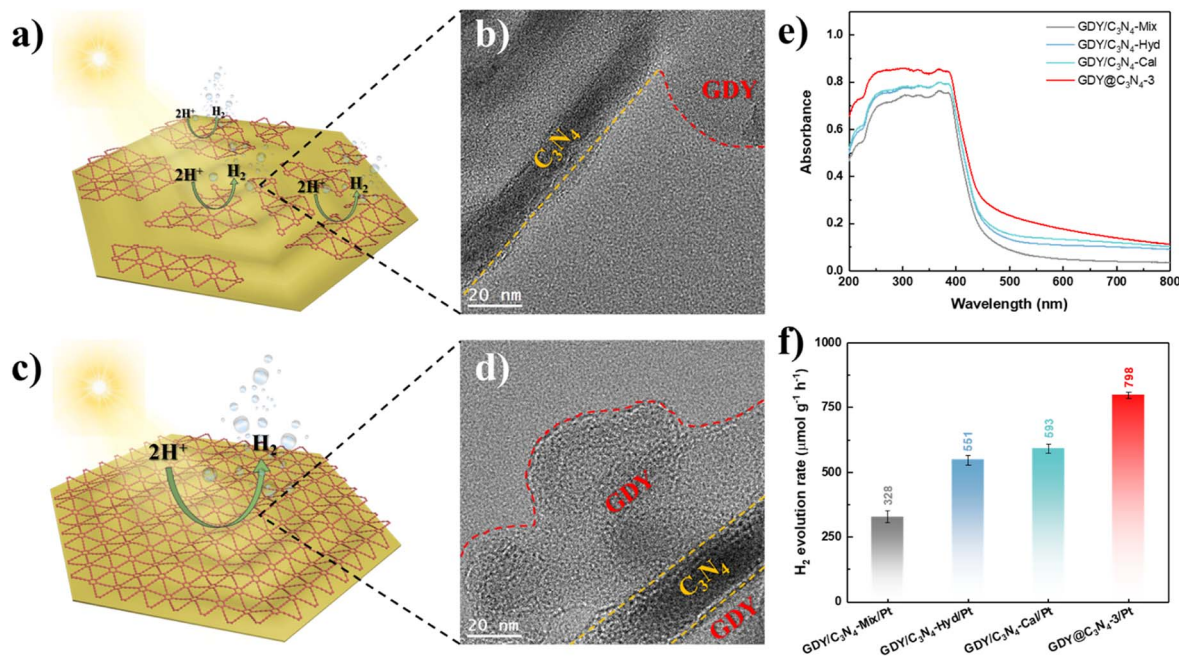


Fig. 5 (a) Schematic diagram of GDY/C₃N₄-Hyd and (b) corresponding TEM image. (c) Schematic diagram of GDY@C₃N₄-3 and (d) corresponding TEM image. (e) UV-vis diffuse reflectance spectra of GDY@C₃N₄-3 and GDY/C₃N₄ samples. (f) H₂ evolution rate of GDY@C₃N₄-3/Pt and GDY/C₃N₄/Pt photocatalysts under visible light ($\lambda > 420$ nm).

To further validate the role of the GDY layer in the GDY@C₃N₄ heterojunction, photoluminescence (PL) spectroscopy and photoelectrochemical measurements were carried out. As exhibited in Fig. 4f, GDY@C₃N₄-3 showed an obvious PL quenching compared with pure C₃N₄, which suggested that GDY could efficiently extract the photogenerated carriers from C₃N₄.⁴⁸ The introduction of Pt nanoparticles further facilitated charge carrier separation. Electrochemical impedance spectroscopy (EIS) was performed to reveal the charge carrier transfer capability.⁴⁹ The smaller radius of curvature for GDY@C₃N₄-3/Pt indicated a lower charge transfer resistance than C₃N₄/Pt (Fig. 4g). Mott-Schottky (MS) measurements were employed to evaluate the band structure of the photocatalysts.^{50,51} All the MS plots showed positive slopes, indicating that both C₃N₄/Pt and GDY@C₃N₄/Pt are n-type semiconductors (Fig. 4h). Compared to C₃N₄/Pt, there was a positive shift of -0.29 V in the flat-band potential of GDY@C₃N₄/Pt samples, and more positive shift was observed with increased GDY content. This positive shift can be attributed to the construction of an internal electric field at the GDY-C₃N₄ interface, which is beneficial for the separation of photogenerated carriers, consistent with previous results.⁵²

Based on the above-mentioned results, the *in situ* growth of GDY on the surface of C₃N₄ is an effective method for enhancing its photocatalytic activity. To further demonstrate the superiority of this strategy, three samples were synthesized using physical mixing, hydrothermal treatment and calcination treatment according to previous studies, namely GDY/C₃N₄-Mix, GDY/C₃N₄-Hyd and GDY/C₃N₄-Cal, respectively.^{21,22} C₃N₄ still maintained the same filamentous morphology after treatments due to its thermal stability (Fig. S8†). Although these methods

can achieve the hybridization of GDY with C₃N₄ through the π - π stacking interaction, the formed GDY/C₃N₄ heterojunction exhibited locality, which may be filled in the voids of C₃N₄ or partially attached to its surface (Fig. 5a, b and S9†). The EELS mappings of GDY/C₃N₄-Hyd and GDY/C₃N₄-Cal showed a homogeneous elemental distribution of C and N, indicating that most of the GDY was present in the voids of C₃N₄ and cannot be distinguished (Fig. S10†). These results are strikingly different from those observed in GDY@C₃N₄ samples, which achieved a complete coating of GDY on C₃N₄ (Fig. 5c, d and 2f). The GDY/C₃N₄ samples with localized heterojunctions displayed lower light absorption capability and H₂ generation efficiency compared with the uniformly coated GDY@C₃N₄ sample (Fig. 5e, f and S11). Therefore, the *in situ* growth of GDY enabled an integral GDY@C₃N₄ heterojunction instead of localized heterojunctions, which maximizes the advantages of GDY to promote the photogenerated carrier separation and transfer efficiently.

4 Conclusions

In summary, we have developed a deprotection-free strategy directly using HEB-TMS as a precursor to *in situ* grow GDY on C₃N₄. This one-pot method realized the uniform coating of GDY, which efficiently promotes the photogenerated carrier separation/transfer and greatly improves the photocatalytic activity in the visible region. The optimized GDY@C₃N₄ achieved 15.6-fold hydrogen production efficiency compared to pure C₃N₄. Moreover, the as-prepared GDY@C₃N₄ exhibited much better photocatalytic activity than the GDY/C₃N₄ samples constructed by physical mixing, hydrothermal treatment and

calcination treatment, further demonstrating the excellence of this approach. This work provides a facile and universal strategy for the design of GDY-based heterojunctions for photocatalytic hydrogen generation.

Conflicts of interest

There are no conflicts to declare.

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