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Electronic Supplementary Information (ESI)

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

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1. Experimental Section

1.1 Characterization

The UV−vis spectroscopy (model Cary 5000 series, Agilent Technologies) was used to analyze the optical properties of the calcined films. The transmission electron microscopy (TEM) and high angle annular dark field scanning TEM (HAADF-STEM) images were obtained in a Tecnai F20 field emission gun microscope with a 0.19 nm point-to-point resolution at 200 kV equipped with an embedded Quantum Gatan Image Filter for EELS analyses. Images have been analyzed by means of Gatan Digital Micrograph software. X-ray photoelectron spectroscopy (XPS) was performed on a Phoibos 150 analyser (SPECS GmbH, Berlin, Germany) in ultra-high vacuum conditions (base pressure 4×10-10 mbar) with a monochromatic aluminum Kα X-ray source (1486.74 eV). Binding energies (BE) were determined using the C 1s peak at 284.6 eV as a charge reference. The crystal structure of the photocatalysts was confirmed by X-ray diffraction (XRD), which was conducted on D/MAX-RB diffractometer (Rigaku, Japan) with CuKα radiation (λ =1.5405 Å). Photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (Cary Eclipse from Agilent) by using an excitation wavelength of 365 nm. FTIR was recorded on a Nicolet 6700 from ThermoFisher Scientific and a Spectrum 3 from PerkinElmer.

1.2 Photocatalytic H_2 evolution test

The hydrogen generation experiments were carried out in a 10 mL closed quartz cell. For each experiment, 4 mg sample were dispersed in 4 mL of aqueous solution containing 15 v% TEOA. Then, the cell was degassed with argon for 20 min to remove dissolved oxygen. A 100 W solar simulator (LCS-100, 94011A, AM 1.5G) was employed as the light source with a cut off filter of 420 nm for the photocatalytic reaction. A gas chromatograph (Micro GC Fusion, argon/nitrogen as the carrier gas) was used to analyze the generation of H_2 every hour. During the irradiation process, the reaction system was stirred by a magnetic stirrer and each reaction lasted for 4 hours. To evaluate the stability of as-prepared photocatalysts, the same sample was subjected to four consecutive H_2 evolution tests. After each test, the reaction system was kept overnight and degassed with argon again for the next cyclic test.

1.3 Electrochemical characterizations

All the electrochemical measurements were carried out in a three-electrode system by using a Metrohm Autolab (PGSTAT204) electrochemical station. Standard three-electrode setup was used with assembled photoelectrodes, Pt foil and Ag/AgCl (saturated KCl) as working photoelectrode, counter and reference electrodes, respectively. To prepare working photoelectrodes, the prepared photocatalysts (1 mg) were added into 1 mL ethanol (containing 5 v% Nafion solution) to form a homogeneous ink through sonication and then dropped onto 1*1.5 cm^2 ITO glasses. The photocatalyst loading was 0.05 mg cm^{-2}. For the Mott-Schottky (at 500 Hz) and impedance spectroscopy (within the range of 10 mHz to 100 kHz) tests, 0.5 M Na_2SO_4 solution was filled in the cell as electrolyte.

2 Supplementary Figures

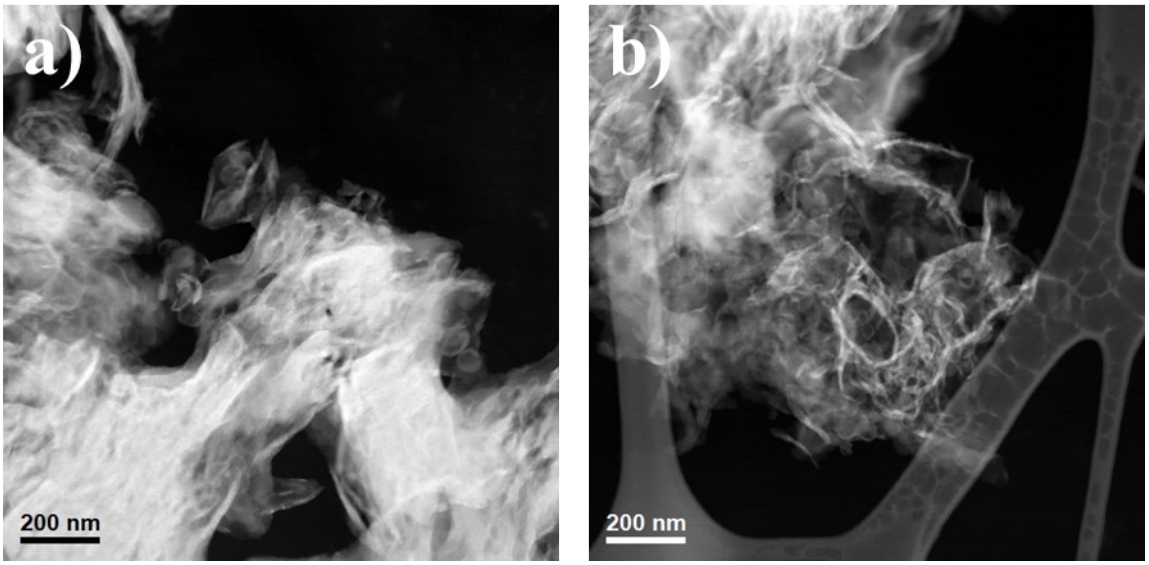

Fig. S1. HAADF-STEM general image views of pure C_3N_4.

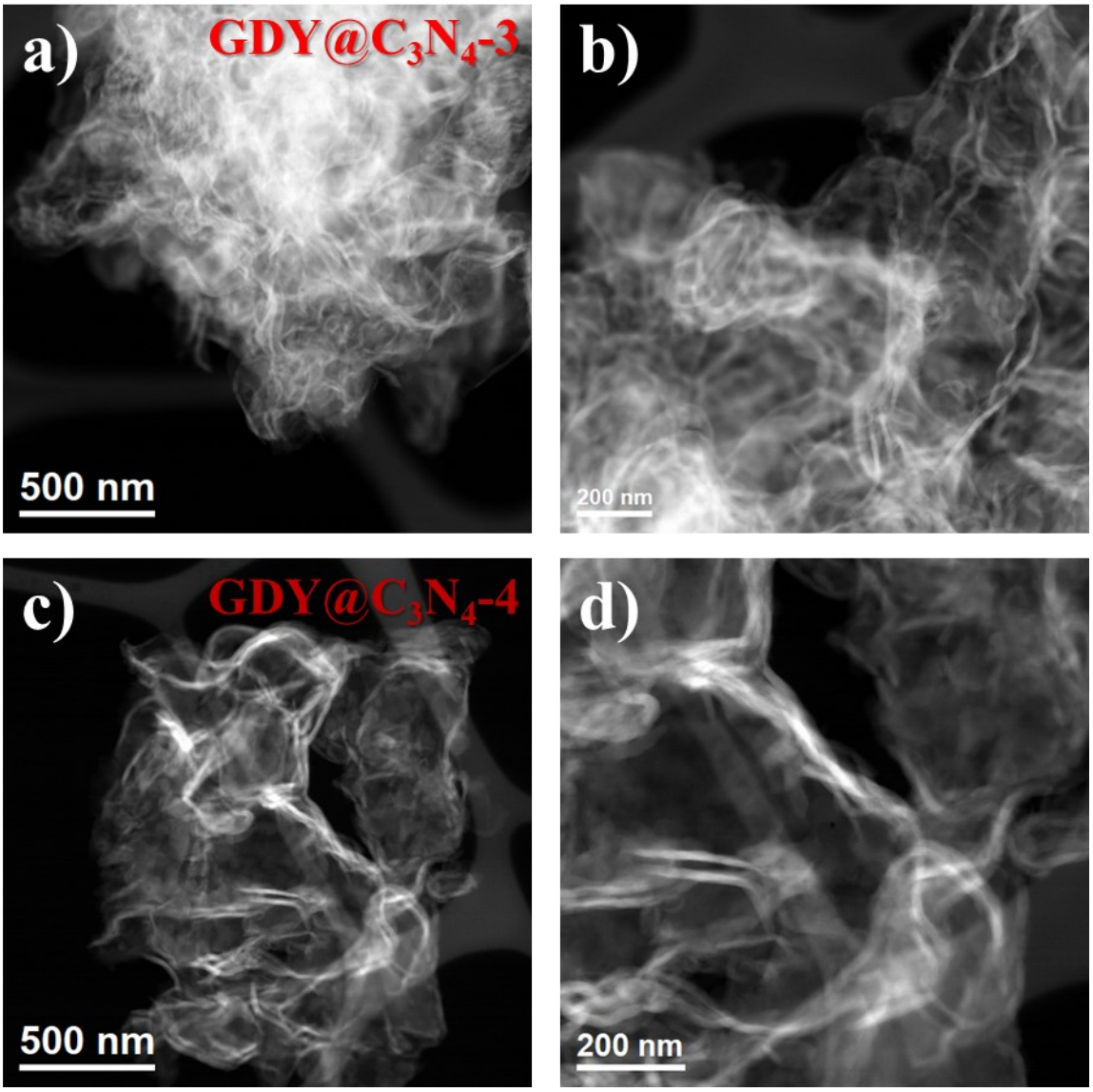

Fig. S2. HAADF-STEM general image views of (a, b) GDY@C_3N_4-3 and (c, d) GDY@C_3N_4-4.

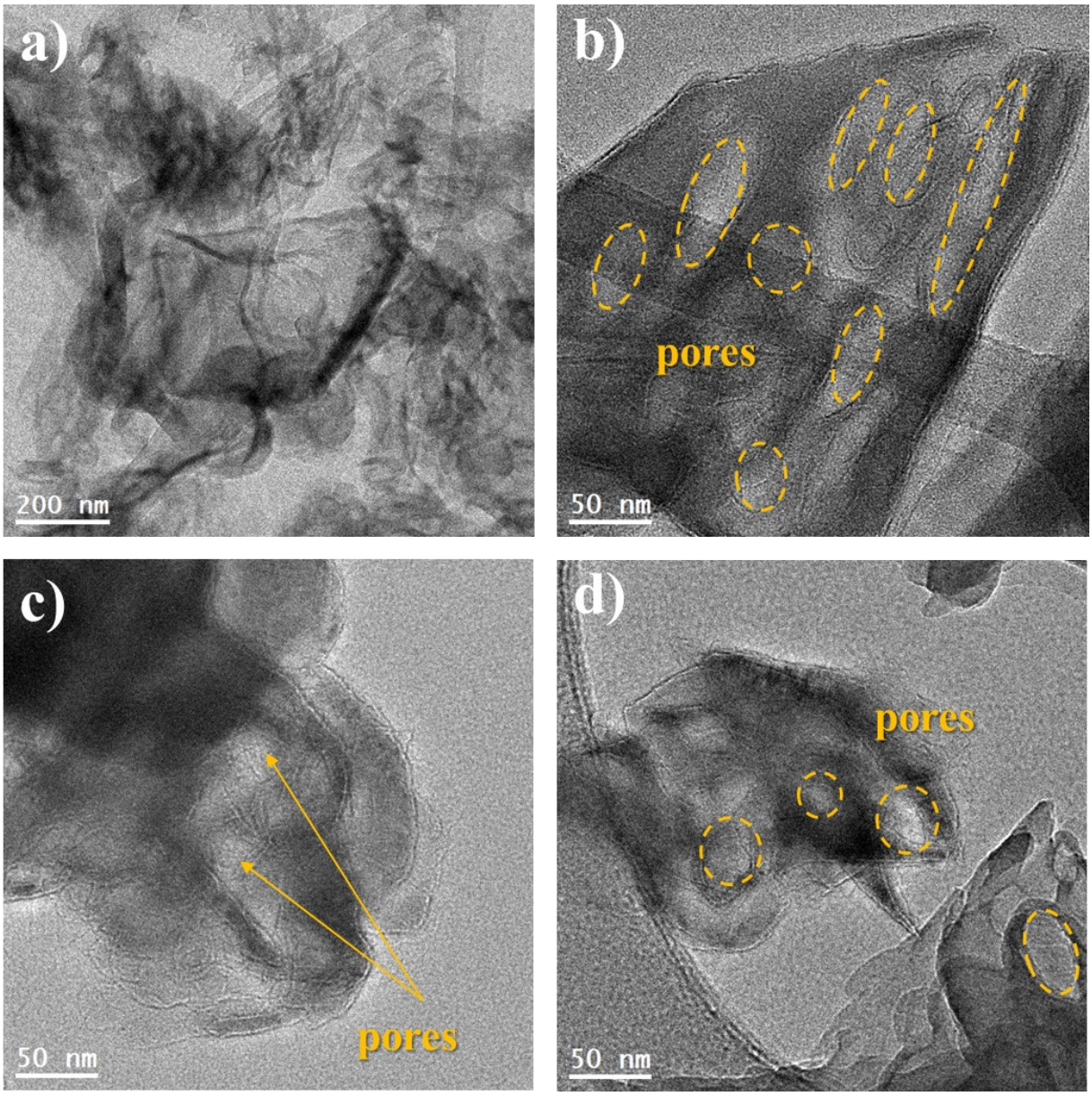

Fig. S3. TEM images of pure C_3N_4.

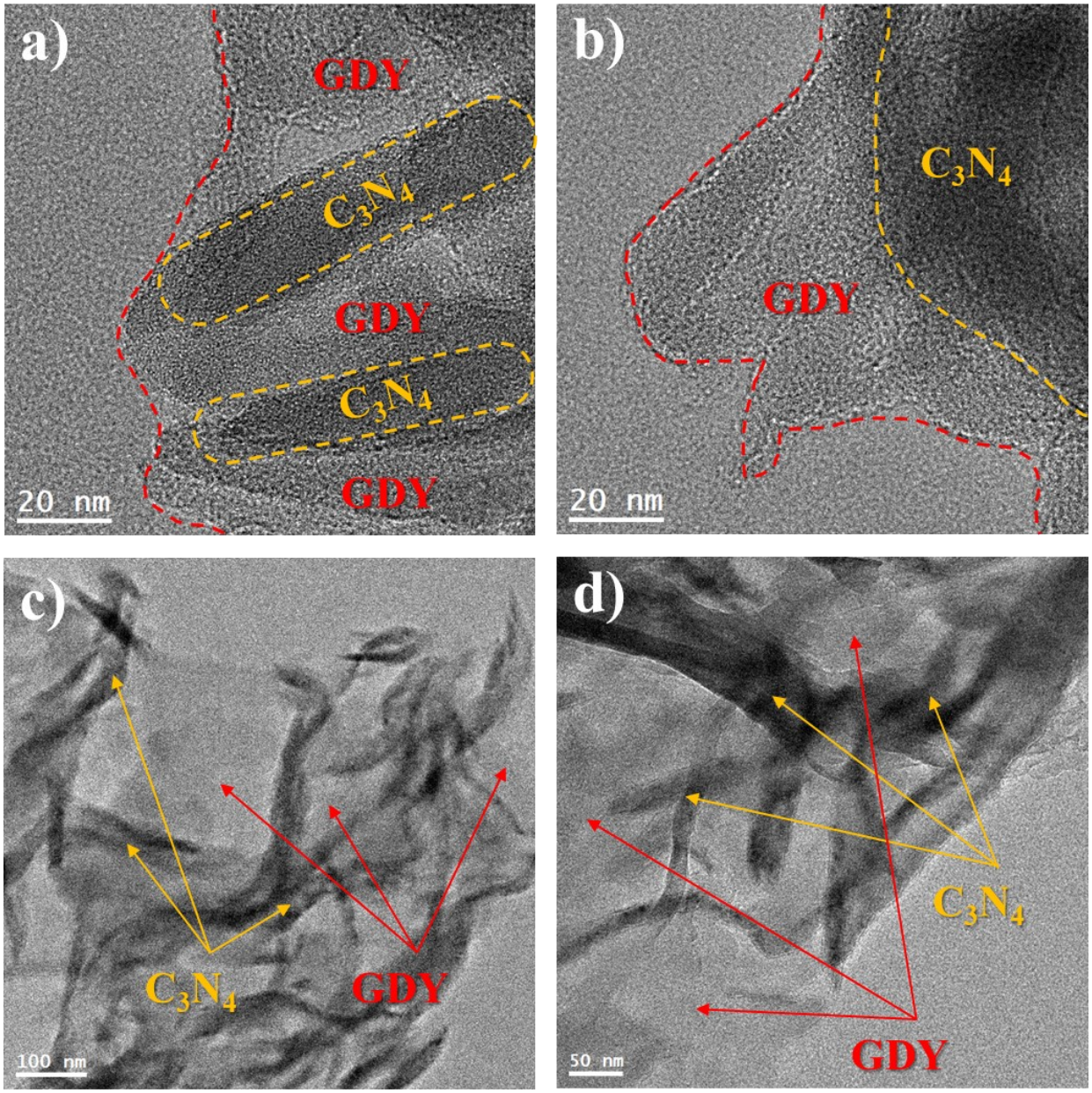

Fig. S4. TEM images of (a, b) GDY@C_3N_4-3 and (c, d) GDY@C_3N_4-4.

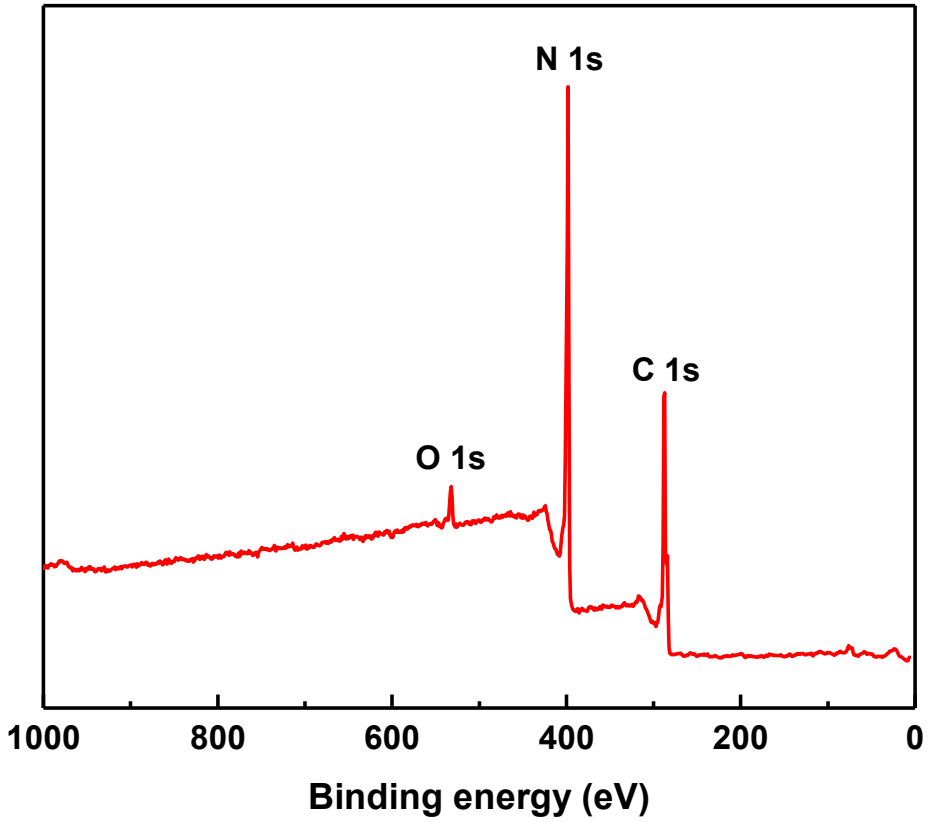

Fig. S5. XPS survey spectra of the as-prepared GDY@C_3N_4.

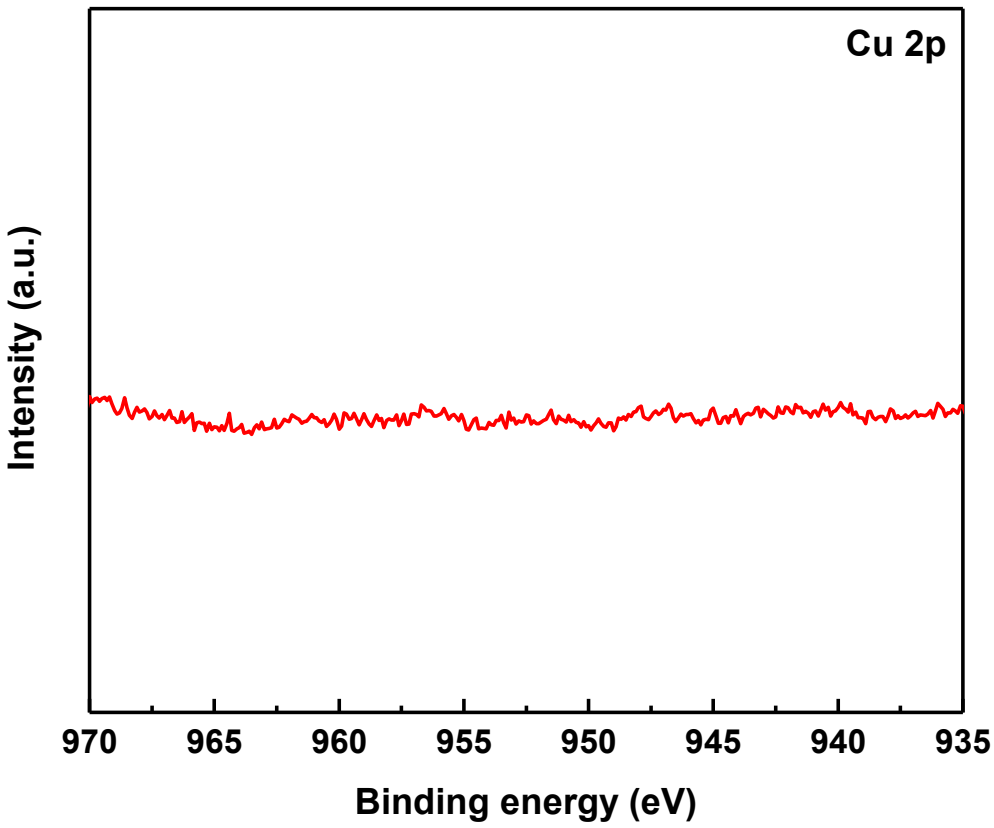

Fig. S6. High-resolution Cu 2p spectrum of GDY@C_3N_4.

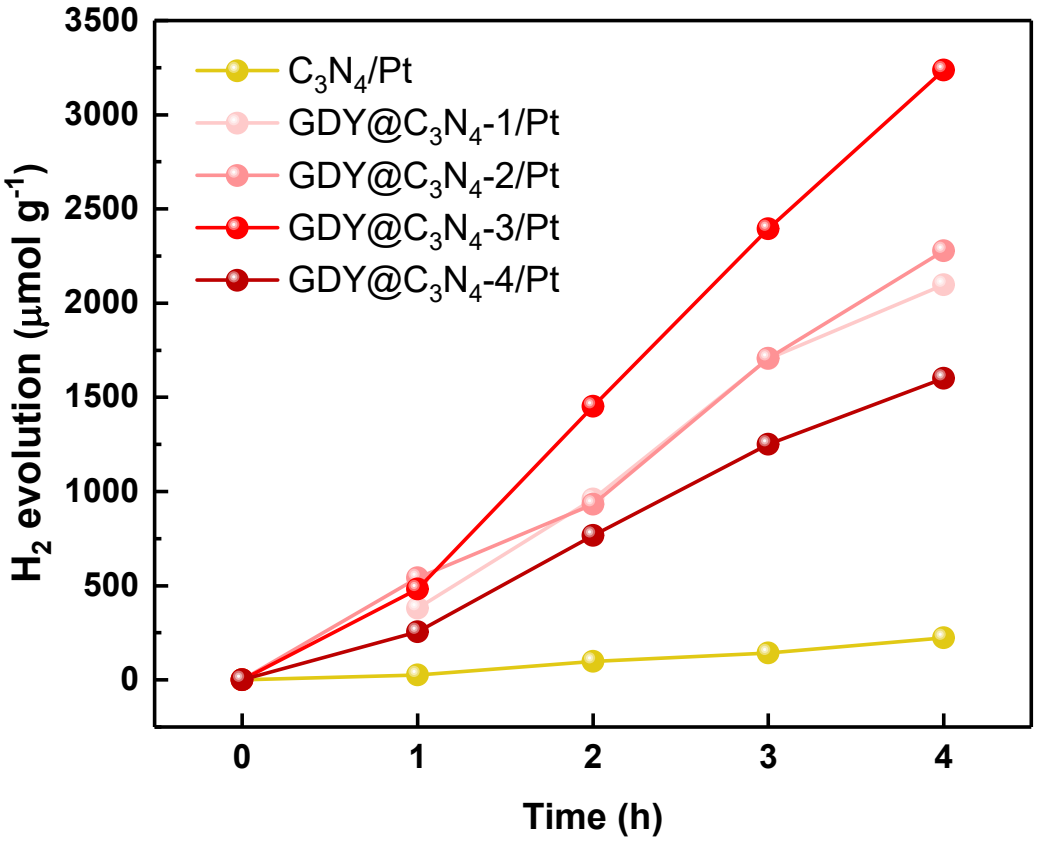

Fig. S7. H_2 evolution of as-prepared C_3N_4/Pt and GDY@C_3N_4/Pt photocatalysts under visible light ($\lambda > 420$ nm).

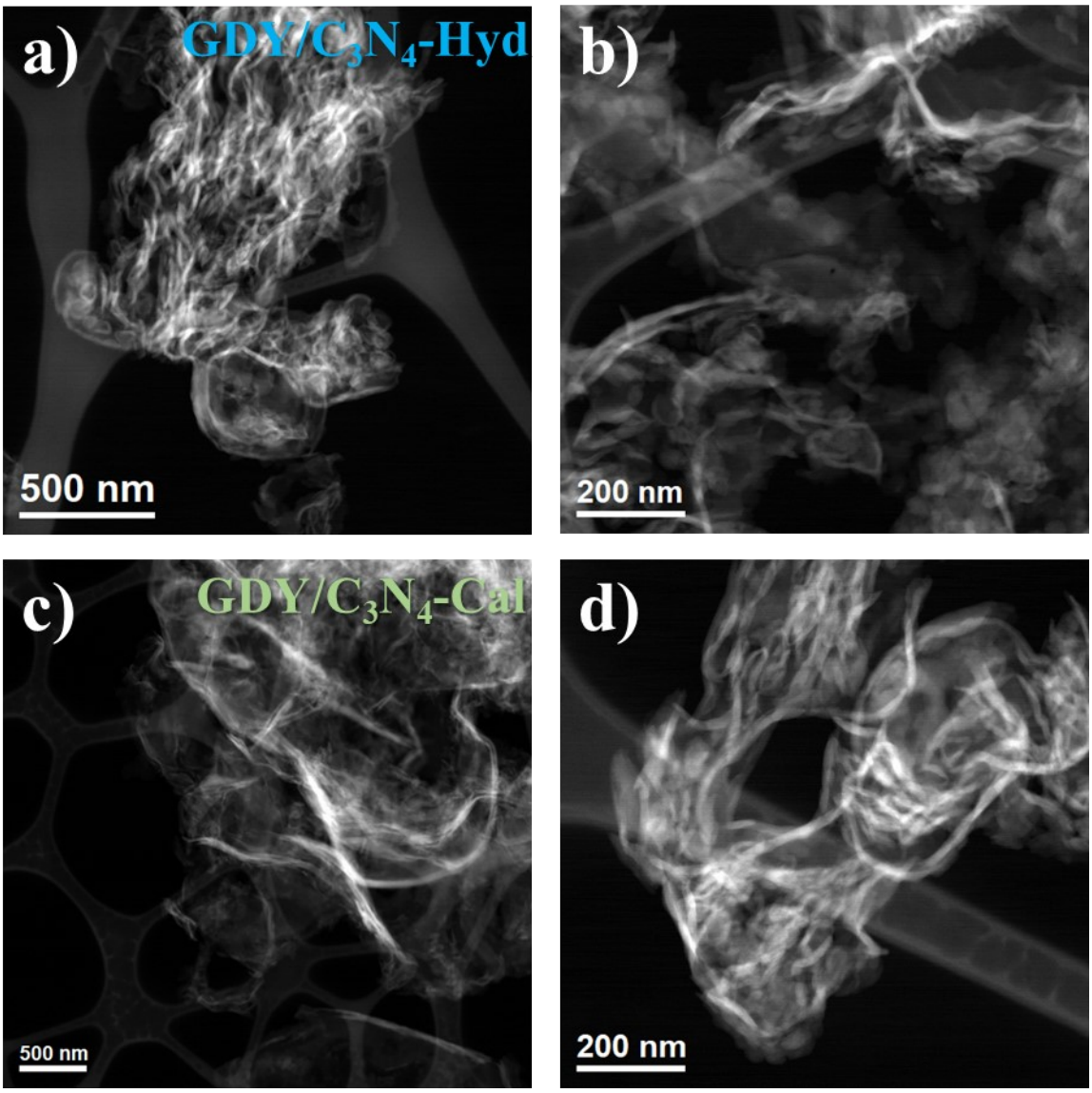

Fig. S8. HAADF-STEM general image views of (a, b) GDY/C_3N_4-Hyd and (c, d) GDY/C_3N_4-Cal.

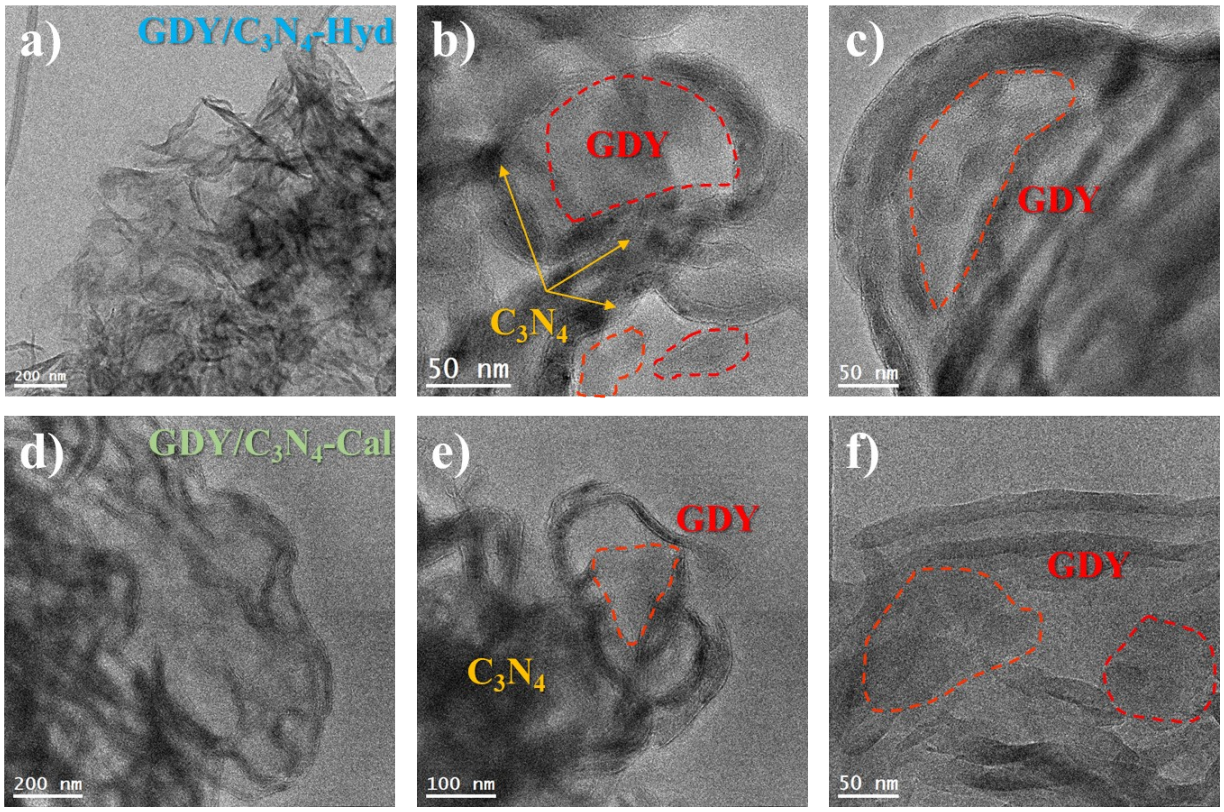

Fig. S9. TEM images of (a-c) GDY/C_3N_4-Hyd and (d-) GDY/C_3N_4-Cal.

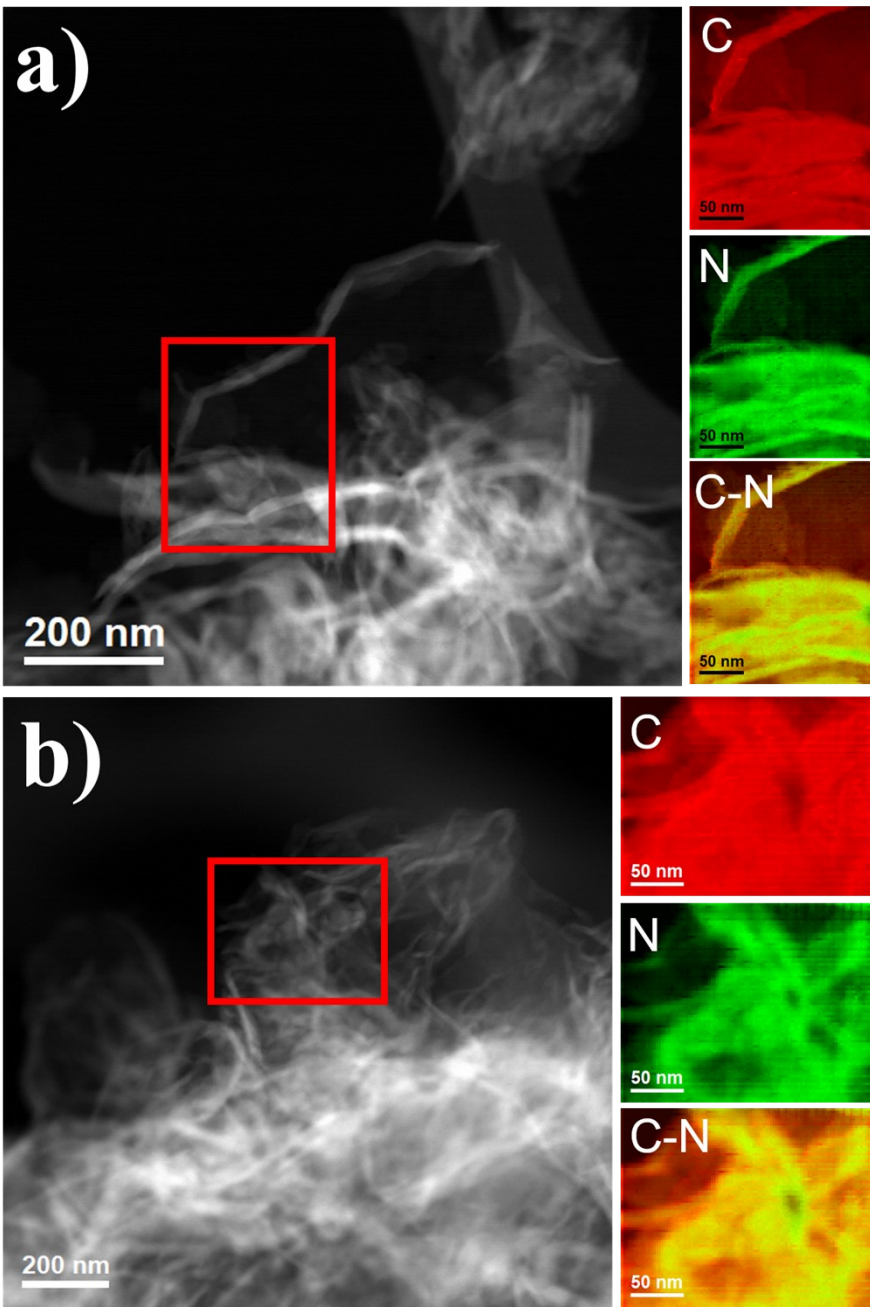

Fig. S10. HAADF-STEM images of (a) GDY/C_3N_4-Hyd and (b) GDY/C_3N_4-Cal, and the corresponding representative EELS chemical composition mapping obtained from the red squared area in the STEM images.

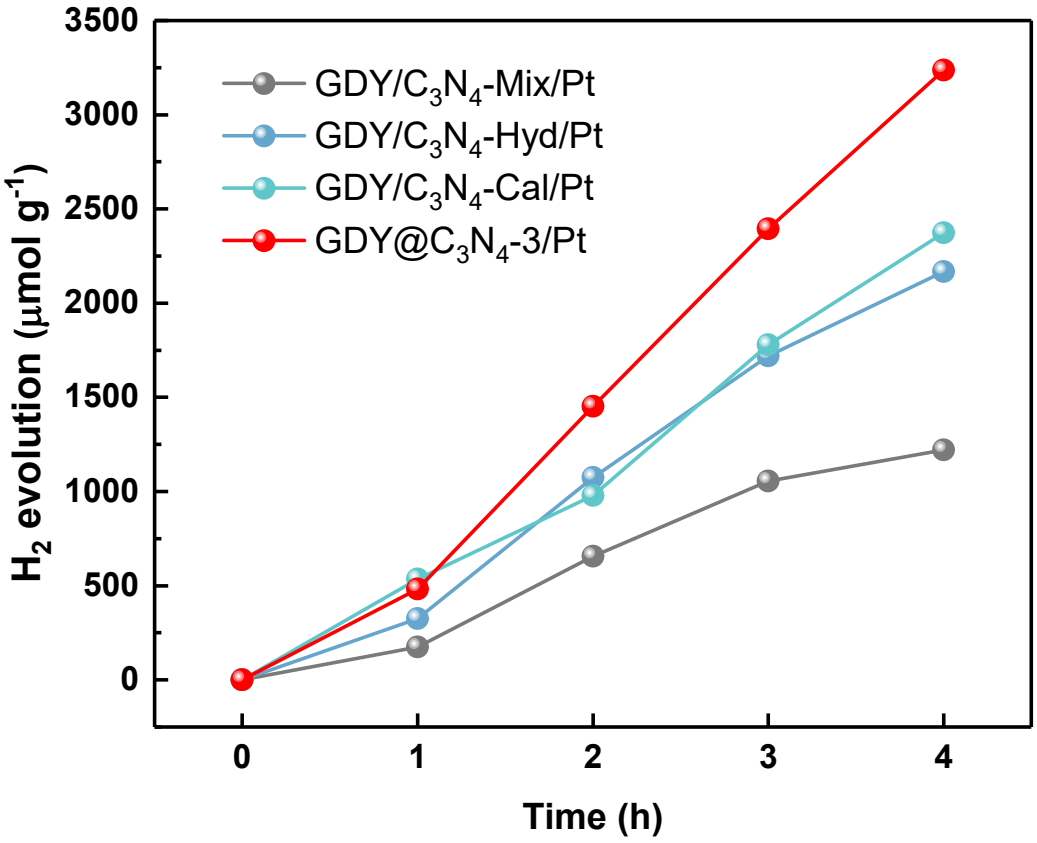

Fig. S11. H_2 evolution of GDY@C_3N_4-3/Pt and GDY/C_3N_4/Pt photocatalysts under visible light ($\lambda > 420$ nm).