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Supporting Information

HOF-Ni-GDY Dual-Ohmic-Junction Engineering: Inducing Photogenerated Electron–Hole Dual Channel Separation for Boosted Hydrogen Evolution

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2.1 Materials

Trimethylsilylacetylene (98.0%), tetri(triphenylphosphine) palladium (99.0%), tetrabutylammonium fluoride (1.0 mol·L−1 in THF), $ZnCl_2$ (0.7 mol·L−1 in THF), n-butyllithium (1.6 mol·L−1 in hexane), tetrahydrofuran (99.5%), pyridine (99.5%), ethyl acetate (99.5%), dichloromethane (99.5%) and n-hexane (99.5%) were purchased from Anhui Zesheng Technology Co., LTD. Hexabromobenzene (99.0%) and L-ascorbic acid (99.0%) were purchased from Shanghai McLean Biochemical Technology Co., LTD. $Ni(Cl)_2 \cdot 6H_2O$ and 1,3,6,8-tetrakis(4-carboxyphenyl)pyrene were purchased from Aladdin and Adamas, respectively.

2.2 Characterizations

The morphology and microstructure of the materials were characterized using transmission electron microscopy (TEM, JEM-2100) and scanning electron microscopy (SEM, thermal field emission Apreo 2). The crystal structure of the samples was investigated via X-ray diffraction (XRD, Rigaku INT-2000) with a scanning rate of 8°/min within the range of 3° to 80°. The successful synthesis of GDY was verified by Fourier transform infrared spectroscopy (FTIR-650) and Raman spectroscopy (Hrobia XploRA™ Plus Raman, Japan). The elemental composition, electronic transport properties, and valence states of the catalyst were analyzed using X-ray photoelectron spectroscopy (XPS ESCALAB 250Xi). Ultraviolet-visible diffuse reflection spectra of the prepared catalyst were recorded on a UV-2550 Shimadzu spectrophotometer with $BaSO_4$ as the reference background. Photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectras were measured using a FluoroMAX-4 (Horiba, France) spectrometer for further characterization of the catalyst. The Zeta potential of samples was determined using a Litesizer 500.

2.3 Electrochemical test

Electrochemical measurements were performed using a three-electrode system on an electrochemical workstation (VersaStat 4-400, AMETEK) equipped with self-calibrating capabilities. The as-prepared catalyst was evaluated electrochemically with indium tin oxide (ITO) conductive glass (1×1 cm^2) serving as the working electrode and a 0.2 M sodium sulfate solution employed as the electrolyte. In detail, 5 mg of the catalyst was dispersed in 300 μL of a 10% Nafion ethanol solution and subjected to ultrasonication to achieve a homogeneous suspension. This suspension was then uniformly deposited onto the ITO substrate to fabricate the working

electrode. Subsequently, the transient photocurrent response was recorded under illumination from a 300 W xenon lamp.

2.4 Test of AQE

The apparent quantum efficiency (AQE) of the photocatalyst was evaluated at wavelengths of 420, 450, 475, 500, 520, and 550 nm under irradiation from a 300 W xenon lamp. The distance between the light source and the sample was maintained at 15 cm, with an illuminated area of 3 cm × 4 cm. The AQE was calculated according to the following formula:

$$AQE(\%) = \frac{The\ number\ of\ evolved\ hydrogen\ molecules * 2}{The\ number\ of\ incident\ photons} * 100\%\#$$

2.5 DFT calculation

The density functional theory (DFT) framework was employed for first-principles calculations. Specifically, the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was utilized to treat the exchange-correlation interaction. The kinetic energy cutoff for the plane-wave basis set of the expanded Kohn-Sham electron wave function was set to 400 eV. In the computation of the work function, the self - consistent field (SCF) method is utilized to acquire the ground - state electronic structure of the system. A vacuum layer with a thickness of 15 Å is established to eradicate the periodic image interaction. The Monkhorst - Pack k - point grid is applied to comprehensively sample the surface Brillouin zone (k - point density = 0.04 $Å^{-1}$).

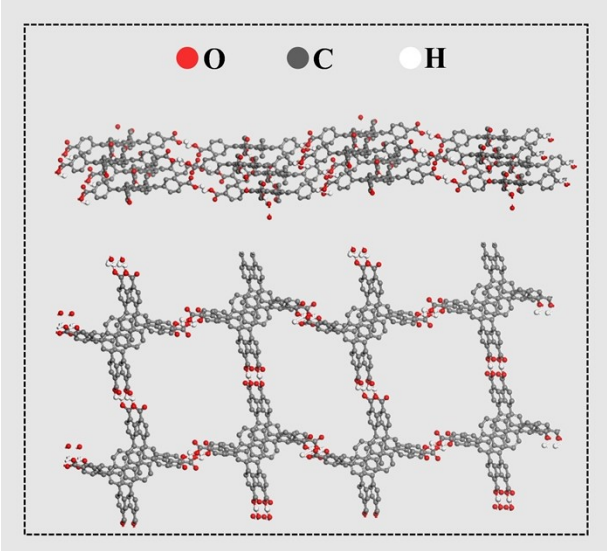

Fig. S1 AA-stacked model of TCP.

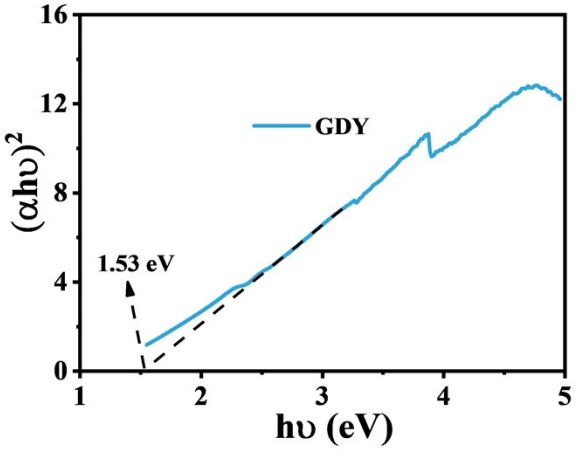

Fig. S2 Band gap of GDY.

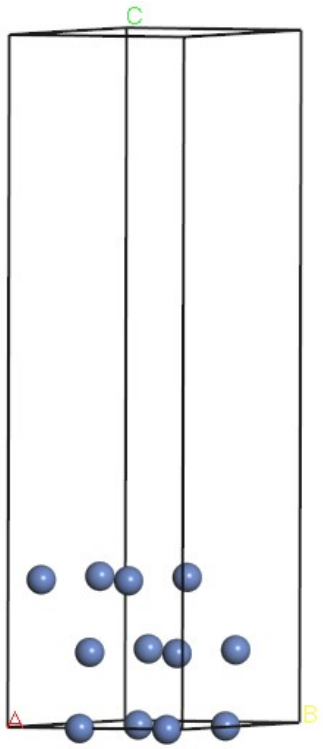

Fig. S3 The calculation model of the work function of Ni.

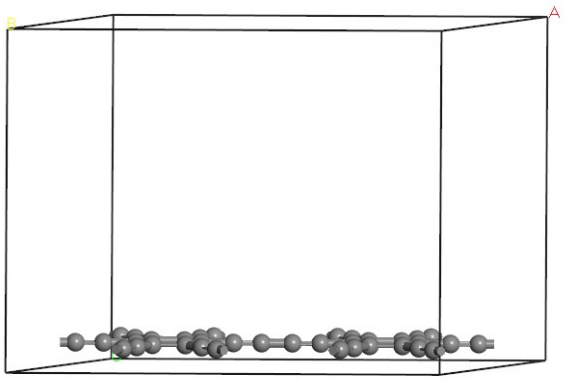

Fig. S4 The calculation model of the work function of GDY.

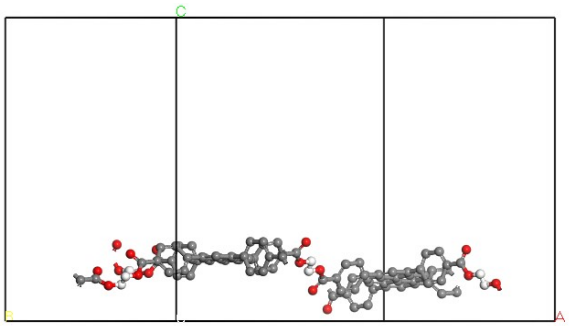

Fig. S5 The calculation model of the work function of TCP.