

Supporting Information for

**In-situ construction of 1D/2D ZnO/Graphdiyne Oxide
Heterostructure for the Enhanced Photocatalytic Reduction in
Gas Phase**

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synthesis of ZnO nanoparticle: 0.1 M of each zinc acetate dihydrate and urea solutions were prepared in deionised water, followed by mixing in a beaker maintaining a volumetric ratio of 1:4. The mixture was vigorously stirred at room temperature to get a homogeneous solution and heated at 115°C in a muffle furnace for 1.5 hrs, maintaining a closed system. As soon as the reaction was completed, a white precipitate was formed. The precipitate was centrifuged at 6000 rpm for 10 mins, pellet was collected and washed three times with deionised water to remove absorbed chemicals or ions, since the chemicals and ions help in agglomeration of NP. The washed pellet was dried at 100°C, followed by calcination in a muffle furnace at 300°C for 2 hrs.

synthesis of ZnO nanorod: Dissolve 14.87 g zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and 40 g NaOH in 100 ml deionized water to obtain an alkaline solution of zinc. Then mix 3ml of the above solution with 5.0ml deionized water and 30.0ml ethanol, and then add 5.0ml ethylenediamine ($\text{C}_2\text{H}_4(\text{NH}_2)_2$, EDA). Before transferring to a polytetrafluoroethylene lined autoclave, the solution mixture is pre-treated in an ultrasonic water bath for 30 minutes. The hydrothermal synthesis is carried out in an electric furnace at 180°C for 20 hours. After the reaction, the white crystalline product was collected by centrifugation and thorough washing with deionized water.

Catalyst characterization

An X'Pert PRO diffractometer (PANalytical B.V.) was used to record X-ray diffraction (XRD) patterns. The microscopic morphology of the samples was observed by transmission electron microscopy (TEM), a Talos F200X microscope (FEI B.V., Netherlands). An Escalab 250 Xi electron spectrometer (Thermo Scientific, USA) was

employed to obtain X-ray photoelectron spectroscopy (XPS) and the C 1 s peak (284.8 eV) was used to correct the obtained spectra. In situ XPS measurements were conducted under identical conditions, except that the samples were exposed to UV-Vis irradiation. The diffuse reflectance spectrum (DRS) of each sample was measured using a SolidSpec-3700 near-infrared spectrophotometer (Shimadzu Europa GmbH). Photoluminescence (PL) spectra were examined by a LabRAM HR800c focal laser Raman microscope (HORIBA France SAS) with a 365 nm laser. Time-resolved fluorescence was recorded under an excitation wavelength of 400 nm using an FLS980 fluorescence spectrometer (Edinburgh Instruments, UK). Transient photocurrent experiments and other photoelectric performances were measured using a CHI 660E workstation (Shanghai Chenhua Ltd., China). Electrochemical impedance spectroscopy (EIS) was conducted at a potential of 0.5 V in the frequency range of 0.1–100 kHz. The Mott-Schottky experiment was performed in 0.5 M Na₂SO₄ at 500 Hz, with an applied potential between -0.4 and 0.5 V, maintaining an AC amplitude of 10 mV at each potential.

Fourier transform infrared (FTIR) spectroscopy was obtained by a Nicolet iS5 spectrometer (Thermo Scientific). In situ DRIFTS was conducted in the Harrick reaction chamber of a Nicolet iS50 spectrometer (Thermo Fisher). Prior to the commencement of the test, the gas path and the reaction chamber were purged using nitrogen gas (200 mL/min, 1h). The reaction chamber temperature was maintained at 250 °C to remove moisture and CO₂ from the sample using a temperature-controlled device. After cooling, a mixture of CO₂ and water vapor was introduced for adsorption

into the chamber for 1 h in darkness. Thereafter, the photocatalytic reduction reaction was allowed to proceed inside the reaction chamber under a Xe lamp.

Photocatalytic CO₂ reduction

The solid-gas photocatalytic reaction system (Fig. S1) included a water bath, a photocatalytic reactor located in an oven, a 300 W Xe lamp, and an online gas chromatograph (GC). The top of the reactor was a piece of quartz glass, and the Xe lamp coupled to a visible cutoff filter ($\lambda < 400$ nm) was located approximately 10 cm above the reactor. Before turning on the light, the reactor was blown using CO₂ mixed with steam (200 mL/min, 1h). The light illuminated a Petri dish containing 10 mg of catalyst at a stable CO₂ flow rate (5 mL/min). During the photocatalytic reaction, the reaction temperature was 50 °C, and water bath temperature was 30 °C. The composition of the gaseous products was analyzed every 0.5 h using gas chromatography (GC).

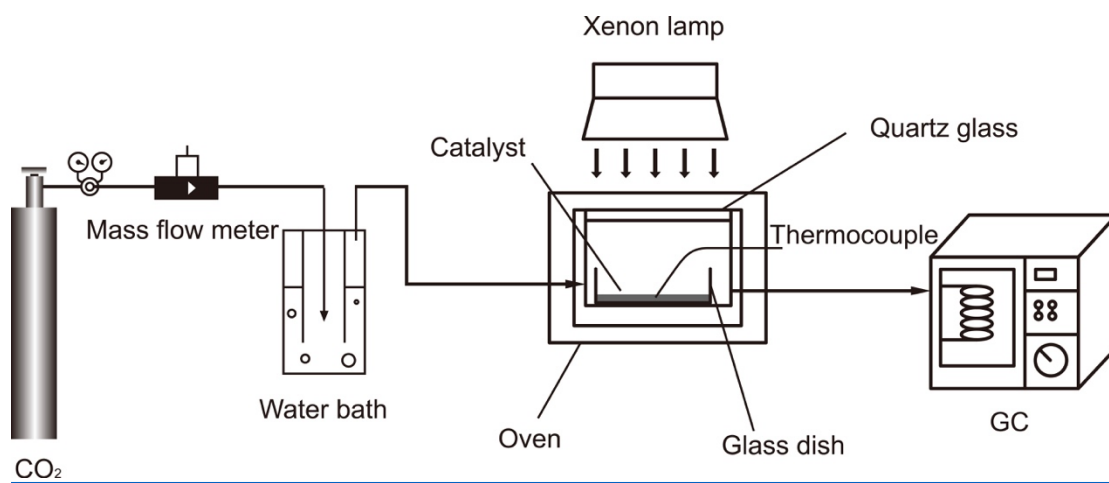


Figure S1. Schematic diagram of photocatalytic reaction system

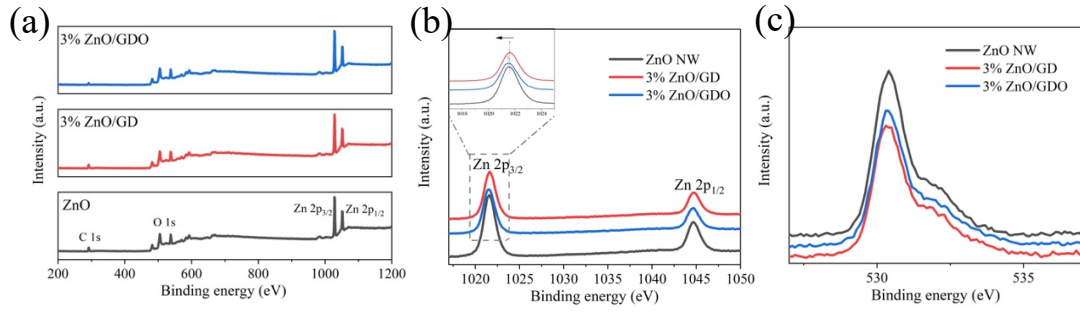


Figure S2. XPS of (a) survey, (b) Zn and (c) O 1s spectra of ZnO, ZnO/GD and ZnO/GDO.

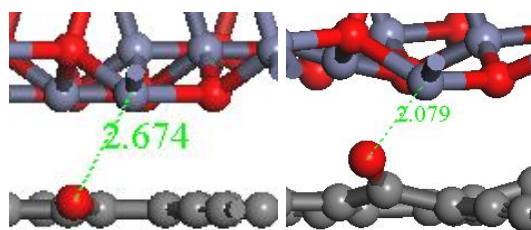


Figure S3 The magnified graph of theoretical model before and after optimization.

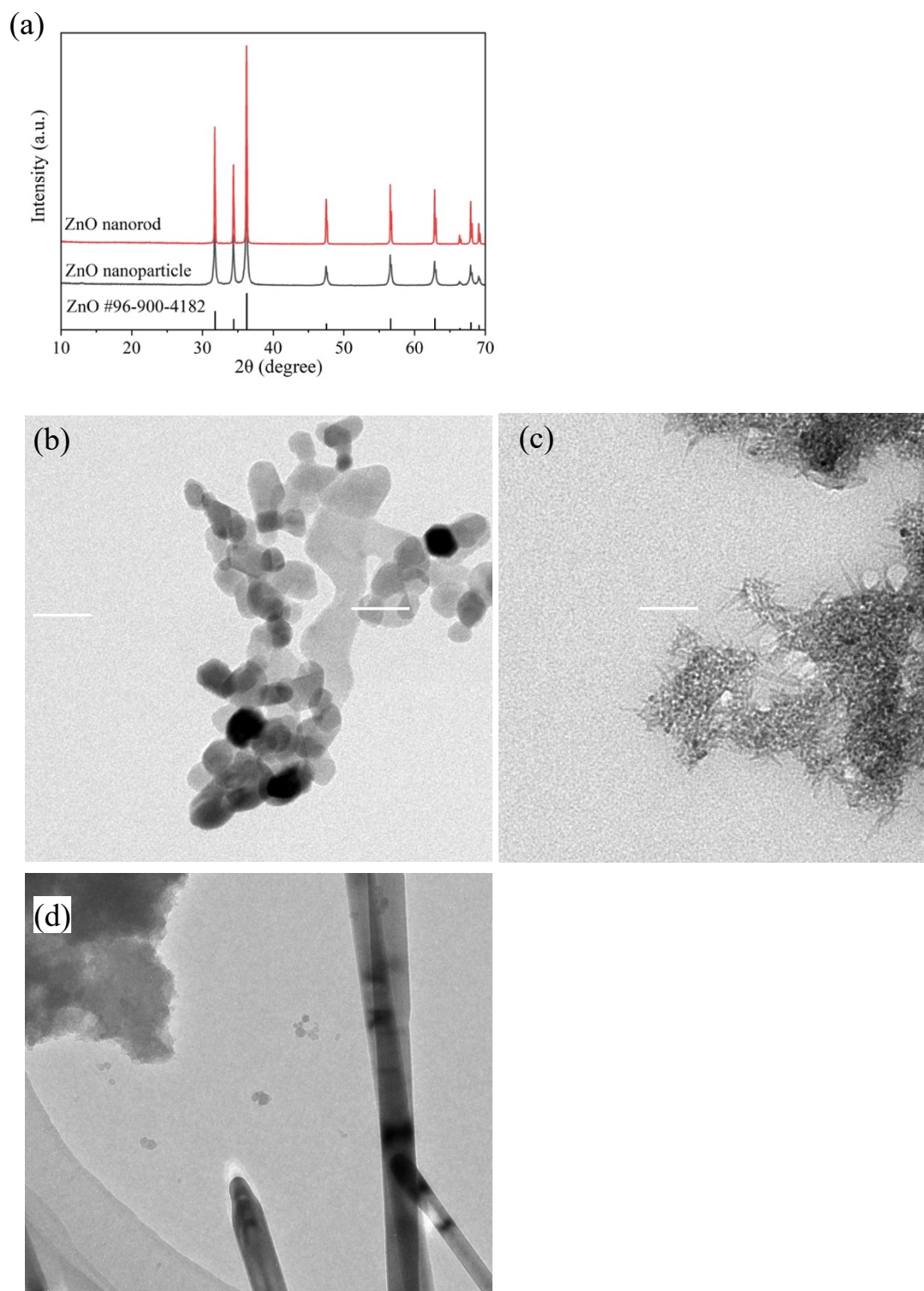


Figure S4 (a) XRD of ZnO nanoparticles and ZnO nanowires. TEM of (b) ZnO nanoparticles, (c) ZnO nanorods and (d) physically mixed ZnO and GDO.

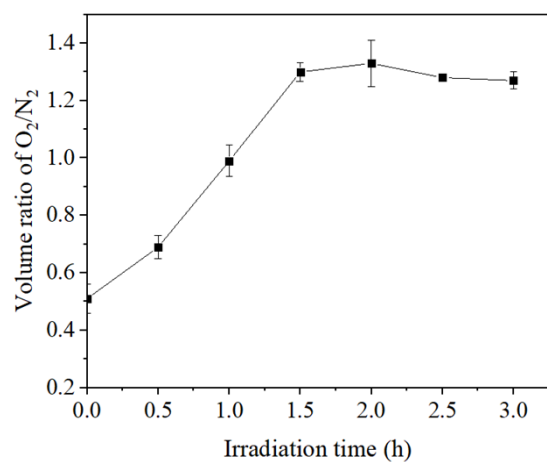


Figure S5. Time dependence of the volumetric ratio of O₂/N₂ during photocatalytic reaction on 3%ZGDO

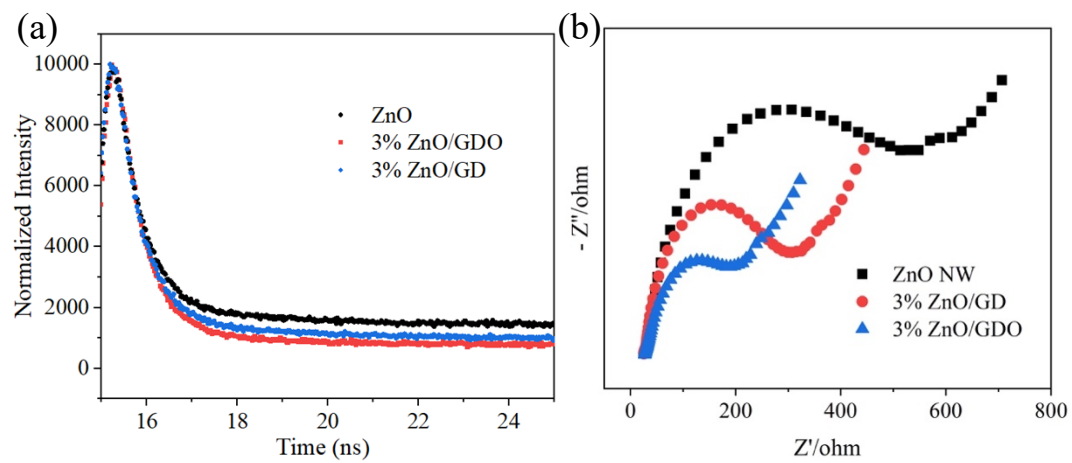


Figure S6 (a) Transient state fluorescence spectra, and (b) Electrochemical Impedance Spectroscopy

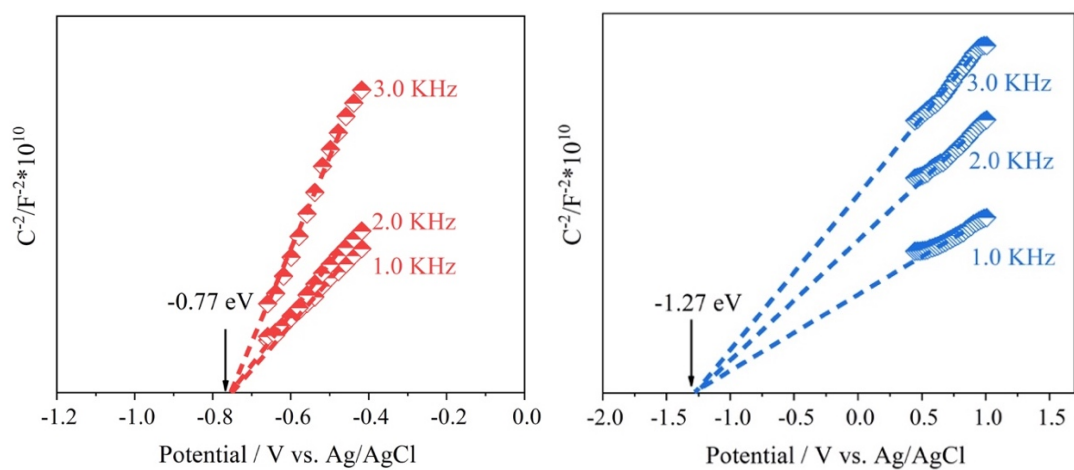


Figure S7 Mott-Schottky plots of ZnO NW and GDO.

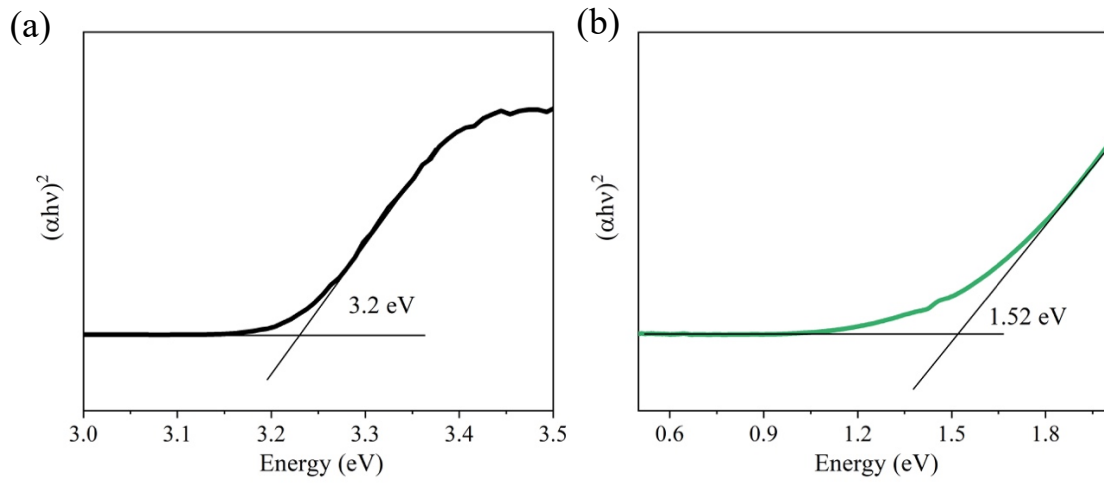


Figure S8 Tauc plot of (a) ZnO NW and (b) GDO.

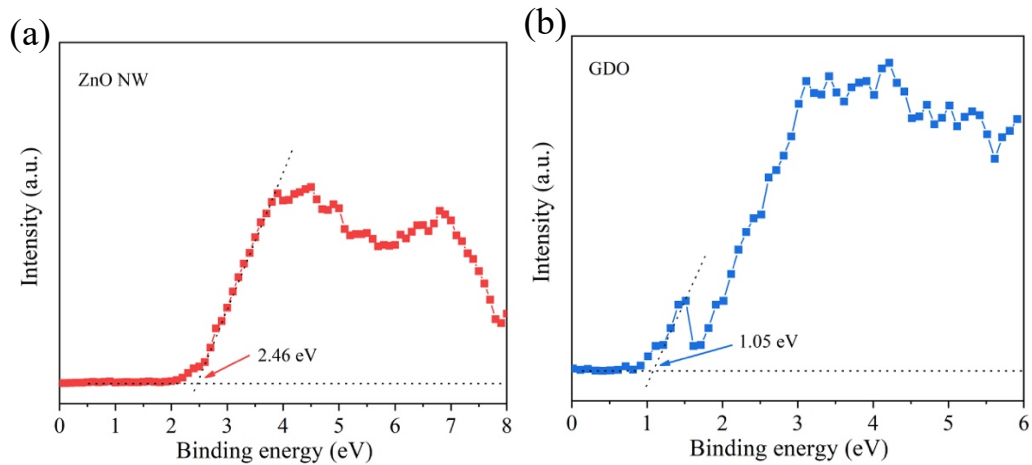


Figure S9 XPS valence-band spectrum of (a) ZnO NW and (b) GDO

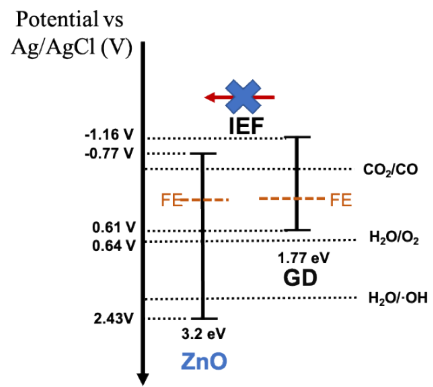


Figure S10 The band structures of ZnO nanowire and GDO

Table S1 Brunauer–Emmett–Teller (BET) surface areas of samples.

Sample	BET (m ³ /g)	Average pore size (nm)	Pore volume (cm ³ /g)
ZnO NW	106.4	6.7	0.2
ZnO/GD	153	5.1	0.16
ZnO/GDO	160	5.0	0.17