# Supporting Information

# Anisotropic surface modification of GaN:ZnO for photocatalytic water splitting

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## Experimental details

### 1.1 Synthesis of GaN:ZnO

Zn (Sinopharm, 99.99%), $Ga_2O_3$(Aladdin, 99.99%) and $NH_4Cl$ (99.99 %, Aladin) powders were mixed in an agate mortar with the Zn/Ga molar ratio of 3.5, followed with sealing the mixture in an evacuated quartz tube ($\Phi$15 mm, 100 mm in length).[1] The quartz tube was then heated in muffle furnace with temperature programed at 703K, 2h in the first step and 1073K, 6h in the second step. After cooling down naturally, the obtained powder was washed with 1.5 M $HNO_3$ for 2h to remove any remaining Zn. Finally, a post-calcination treatment was conducted by heating the resultant powder at 873K in air for 5h.

### 1.2 Anisotropic surface modification of GaN:ZnO with ZnO

Anisotropic surface modification of GaN:ZnO were achieved by assembling the catalyst particles in a two-dimensional monolayer. Typically, using a mechanical rubbing process,[2] the GaN:ZnO particles were dispersed on a quartz substrate pre-coated with an adhesive polyethyleneimine (PEI) as sticker. In this case, only those particles contacting with the PEI were remained on substrate, namely a monolayer of GaN:ZnO particles were formed on the quartz substrate. Then, the assembly was calcined at 873K to remove residual PEI. For ZnO modification, a calculated amount of $Zn(OAc)_2$ aqueous solution (0.01 $mg \cdot mL^{-1}$) was drop-casted onto the exposed surface of the monolayer. The sample was kept at room temperature for 1 h to reach adsorption equilibrium, dried and aged in an oven at 383K for 24hs. After annealing at 873K for 1h, the decorated particles were recovered by mechanically scraping off the substrate.

ZnO/GaN:ZnO/FTO photoelectrodes were fabricated using an atomic layer deposition (ALD) technique. The assembly of GaN:ZnO monolayer followed identical procedure described above except replacing the quartz substrate with a conductive FTO glass. Subsequently, the ZnO layer was deposited by executing 10 cycles of thermal atomic layer deposition (Savannah, Cambridge NanoTech). The deposition was conducted at 250 °C, where each cycle consisted of alternating pulses of diethylzinc (DEZ) and deionized water ($H_2O$) separated by $N_2$ purges. This sequential surface reaction ensured the self-limiting and layer-by-layer growth of ZnO film. Finally, the as-prepared photoelectrode was annealed at 873K for 1h to enhance crystallinity of the ZnO layer prior to electrochemical evaluation. In contrast, to fabricate a photoelectrode featuring a ZnO underlayer (GaN:ZnO/ZnO/FTO), the preparation sequence of monolayer and ALD was reversed.

Typically, a sample mass of approximately 1 mg/ 5 $cm^2$ was assembled on a single substrate.

### 1.3 Cocatalyst deposition

$IrO_2$ was loaded as an oxidative cocatalyst by solvothermal method. GaN:ZnO/ZnO powder was dispersed in 20 mL of ethylene glycol within a glass vial, followed by adding a calculated quantity of aqueous $IrCl_3$ solution. The mixture was subjected to microwave heating (Monowave 400, Anton Paar Company) at 423 K for 0.5h. The resulting $IrO_2$/GaN:ZnO (1 wt% $IrO_2$ vs. GaN:ZnO) was collected via filtration, thoroughly washed with water, and subsequently dried at 333K before using.

Pt and Rh were loaded on GaN:ZnO/ZnO particles by photodeposition. Catalyst powder and relative amount of precursor solutions ($H_2PtCl_6$ for Pt and $RhCl_3$ for Rh, 1 mg·$mL^{-1}$) were dispersed in 100 mL of L-ascorbic acid solution (10 mM) in reactor cell. Photodeposition of noble metal was carried out under visible light irradiation ($\lambda > 420$ nm) for 2h. Au was loaded with dispersing relative amount of $HAuCl_4$ solution (1 mg·$mL^{-1}$) in 100 mL of aqueous solution containing $Na_2S$-$Na_2SO_3$

(5 mM) in reactor. Photodeposition was carried out under full arc irradiation for 3h.

### 1.4 Photocatalytic reaction

A Pyrex overhead-irradiation vessel reactor connected to a closed gas circulation system was used for reaction trials (Beijing Perfectlight, Labsolar6A). Typically, appropriate amount of catalyst was dispersed in 100 mL of 0.01 M $AgNO_3$ for oxygen evolution reaction, or in 0.01 M L-ascorbic acid for hydrogen evolution reaction. A 300 W Xenon lamp (Eagle engineering CO.LTD, LX300F) with 420 nm cut-off filter (HOYA, L-42) was applied as light source. The system was evacuated to remove air and then introduced with Ar gas to keep the pressure around 5 kPa. Temperature of the reaction suspension was maintained at 288K by circulated cooling water. The amounts of evolved hydrogen and oxygen gases were measured using an online gas chromatograph (SHIMADZU, GC2014C with a TCD detector, JN. 5A columns, and Ar as carrier gas).

For overall water splitting reaction, 30 mg of $IrO_2$-loaded GaN:ZnO/ZnO were dispersed in 100mL water ( pH=7) containing $Na_3RhCl_6$ and $K_2CrO_4$ (1 wt% Rh and 1.5 wt% Cr vs. GaN:ZnO powder) .

### 1.5 AQY Measurement

The apparent quantum yield (AQY) of the photocatalytic reaction was calculated using

$$AQY(\%) = (nR/I) \times 100$$

where R and I represented the amounts of evolved gas and photons in the incident monochromatic light per unit time, respectively, and n was the coefficient corresponding to the number of electrons needed to generate one molecule of $H_2$ (2).

### 1.6 Photoelectrochemical Measurements

GaN:ZnO and other photoelectrodes were fabricated via a mechanical rubbing method, as reported elsewhere.[2] The Mott−Schottky curves were measured in the dark with an AC amplitude of 10 mV using 0.1 M of $Na_2B_4O_7$ solution (pH 9.3) as the electrolyte, with Pt sheet as a counter electrode and 3 M Ag| AgCl as a reference electrode. A solar simulator (AM 1.5G, SAN-EI, XES-40S3-TT) was employed as the light source. Intensity-modulated photocurrent spectroscopy (IMPS) measurements were conducted in 0.1 M AA with KPi solution (pH 4.0) coupled with the Zahner Zennium Pro potentiostat that allowed the superimposition of sinusoidal modulation (~20%) on a AC illumination level (365 nm LED, 10 mW $cm^{-2}$).

### 1.7 Characterization of materials

Scanning electron microscopy (SEM) images were obtained on a JSM-IT-500-HR microscope with a 10 kV acceleration voltage. X-ray diffraction (XRD) was conducted on a Bruker D2 Phaser XRD using Cu Kα radiation operated at 40 kV and 40 mA. The transmission electron microscope (TEM) and high resolution TEM (HRTEM) were taken from a JEM-F200 (JEOL) system with 200 kV accelerating voltage. UV–vis diffuse reflectance spectroscopy (DRS) spectra were acquired using an Agilent Cary 5000 UV spectrometer with an integrating sphere annex. X-ray photoelectron spectroscopy (XPS) was probed by ESCALAB 250Xi spectroscopy using a monochromatic Al Kα source (hν = 1468.2 eV). Time-Resolved Photoluminescence (TRPL) were performed with HORIBA Scientific DeltaFlex-011x spectrofluorometer. The binding energies were corrected with reference to the C 1s peak (284.8 eV). The contact potential difference (CPD) of the samples was quantified using Kelvin Probe Force Microscopy (KPFM) in lift mode. In this mode, both topographical and CPD signals were simultaneously recorded.

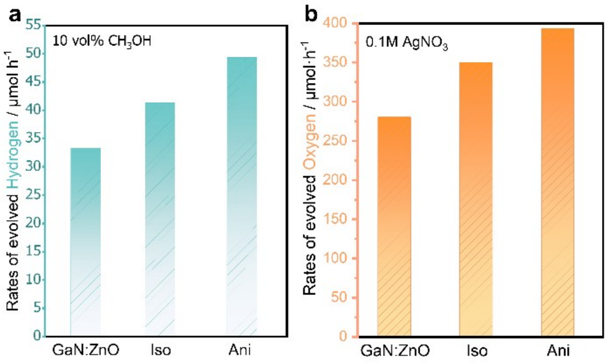

**Figure S1** Photocatalytic (a) hydrogen evolution rates assisted by using methanol as a hole scavenger and (b) oxygen evolution rates in presence of $AgNO_3$ on the bare GaN:ZnO, isotropic (iso) ZnO, and anisotropic (ani) ZnO particles loaded with 0.75 wt% $IrO_2$.

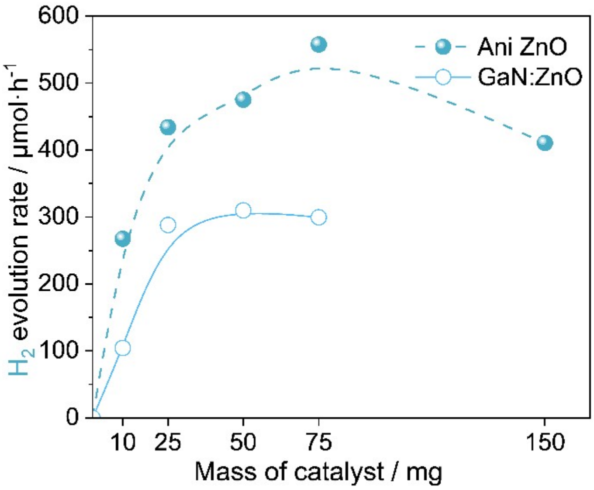

**Figure S2** Dependence of $H_2$ evolution rate on mass of photocatalyst. Reaction conditions: catalyst, bare or anisotropic GaN:ZnO/ZnO powders photo-deposited with Rh(1 wt%); reaction solution, 100 mL of aqueous solution containing 0.1 M AA; light source, 300 W xenon lamp with a cut-off filter ($\lambda$ > 420 nm).

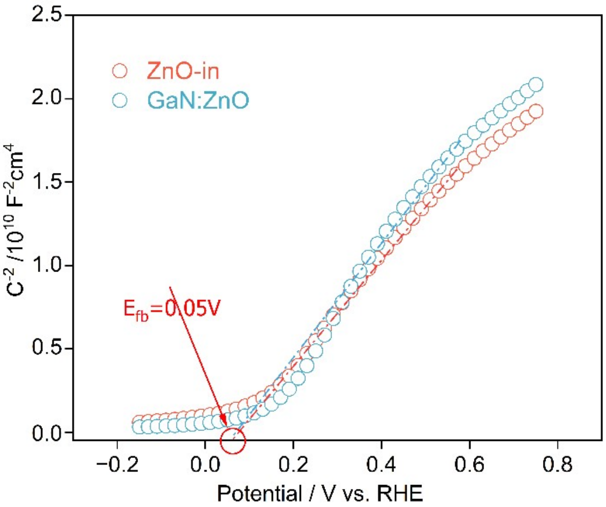

**Figure S3** Mott-Schottky plots of bare GaN:ZnO and ZnO-in electrodes.

To investigate the thermodynamic stability of the electronic structure, Mott-Schottky analysis was performed. Both the bare GaN:ZnO and the ZnO-in electrodes exhibit the same flat-band potential $E_{fb}$ of 0.05 V vs. RHE. This unchanged $E_{fb}$ demonstrates that the Fermi level of the GaN:ZnO host remains constant after surface modification. Therefore, the improved charge separation is substantially driven by the artificially built-in electric field at the interface.

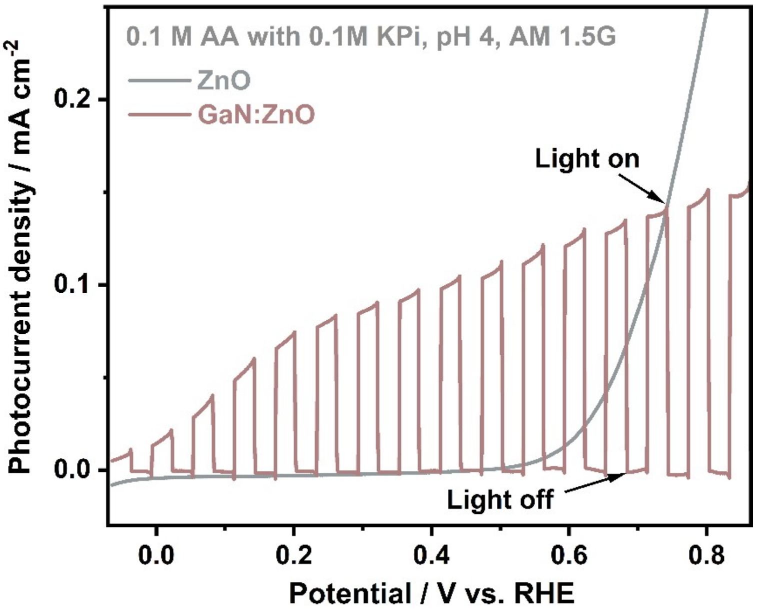

**Figure S4** Photocurrent density-potential curves of the pure ZnO and bare GaN:ZnO electrodes.

The ZnO thin film, as an electrode, was deposited on FTO by ALD with 10 cycles of gas charge and evacuation. The GaN:ZnO electrode was fabricated by a rubbing method using FTO as substrate. The measurements were conducted in a 0.1 M ascorbic acid (AA) aqueous solution containing 0.1 M potassium phosphate (KPi) buffer (pH = 4.0). A solar simulator (AM 1.5G equipped with a 420 nm cut-off filter, $\lambda > 420$ nm) was employed as the light source, and the "Light on" and "Light off" labels denote the periodic illumination cycles. As observed, the pure ZnO exhibits negligible photoresponse, which is in stark contrast to the distinct photocurrent steps of GaN:ZnO. This confirms that pure ZnO cannot be excited under the evaluated visible-light conditions and has no intrinsic photocatalytic contribution to the overall reaction.

## REFERENCES

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2 W. Lin, B. Zhang, K. Liu, J. Zhang, J. Wang and G. Ma, *Chemistry – A European Journal*, 2022, **28**, e202201169.