Supporting Information for

Metal-Free Carbon Dots toward Bio-Green Hydrogen Evolution via Photocatalysis

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Supplementary Methods

1. Methods

1.1 Electrochemical test

The electrochemical measurements were conducted using a CHI 760 C electrochemical workstation (CH Instrument, Shanghai, China) in a standard three-electrode configuration. A saturated calomel electrode (SCE) served as the reference electrode, while a carbon electrode was used as the counter electrode. The working electrode was prepared using a glassy carbon electrode (GCE). 0.1 M Na_2SO_4 aqueous solution was employed as the electrolyte.

1.2 Photocatalytic performance measurements

The photocatalytic performance of H_2 was evaluated using a multichannel photocatalytic reaction system (CELLAB200E7, 80 mW/cm^2). Unless otherwise specified, 10 mg of photocatalyst was uniformly dispersed in 20 mL of ultrapure water by ultrasonication, without the addition of any sacrificial agent or cocatalyst (The photocatalytic reaction was carried out in a sealed 50 mL container). The photocatalytic reaction was conducted under visible light illumination (420 nm ≤ λ ≤ 700 nm) with continuous stirring. Gas chromatograph (GC-7900T, 5A molecular sieve column, TCD detector) is used to detect the generated H_2.

The H_2 production was calculated by off-line chromatography. The gas in the container was taken by syringe and 1 mL was injected into the gas chromatograph to detect the gas product.

The apparent quantum efficiency (AQE) can be evaluated from following formulas:

$$AQE = \frac{2 \times n_{H_2} \times N_A}{N}$$

n_{H_2} is the number of evolved H_2 molecules respectively, N_A is the Avogadro number (6.02×10^{23}); and N represents the number of incident photons, which can be calculated from equation:

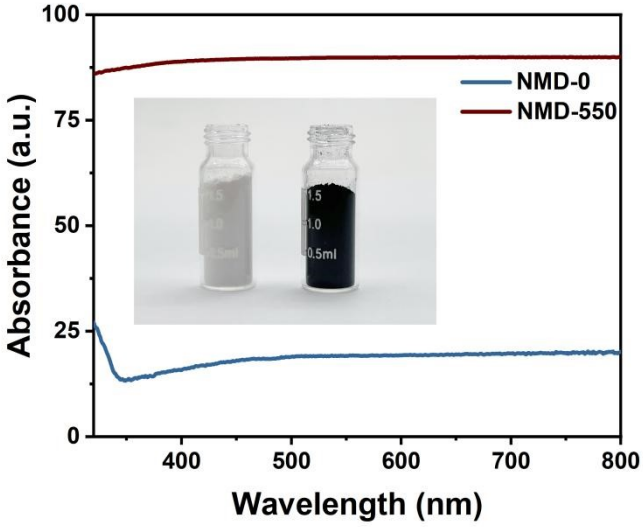
$$N = \frac{\text{light intensity (W cm}^{-2}) \times \text{illumination area (cm}^2)}{\frac{\text{hc}}{\lambda}}$$

where h is the Planck constant (6.626×10^{-34} J·s = 4.136×10^{-15} eV·s), c is the speed of light (3.0×10^{8} m·s^{-1}), and λ is the wavelength of light (365, 420, 500, 590 and 660 nm).

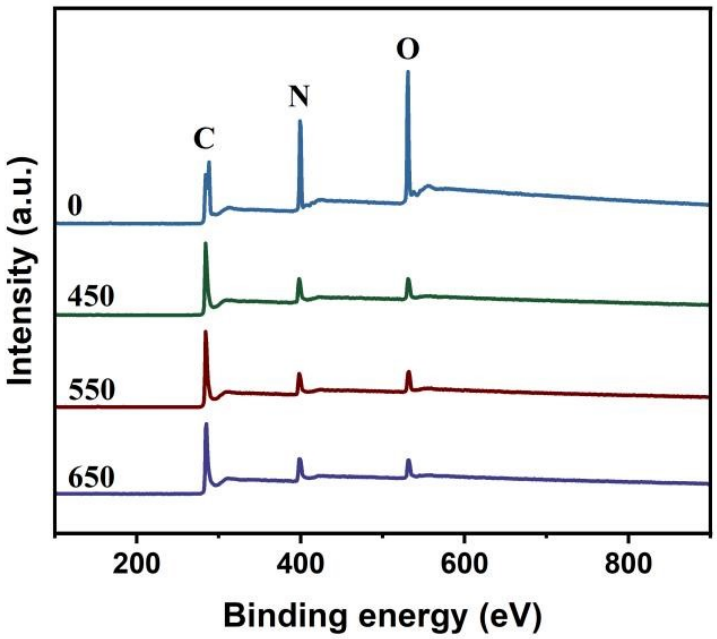
1.3 Transient photovoltage (TPV) test

The time-resolved photovoltage (TPV) system employs a pulsed laser with a wavelength of 355 nm and a pulse duration of 5 ns to detect TPV signals by monitoring variations in output voltage. A critical prerequisite for accurate measurement is that the current in the external circuit must remain approximately zero (<< 1 nA). Under these conditions, changes in output voltage will accurately reflect alterations in the accumulated charge on the photoelectrode, thereby revealing key parameter characteristics of the photoelectrode and the dynamics of charge transfer at the interface. Consequently, through in situ TPV testing, we are able to analyze the processes of photo-generated charge extraction and recombination over a broad time window.

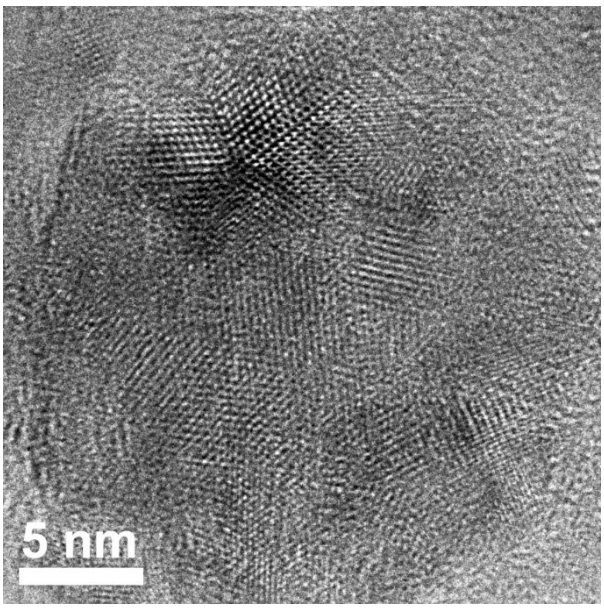
Supplementary Figures



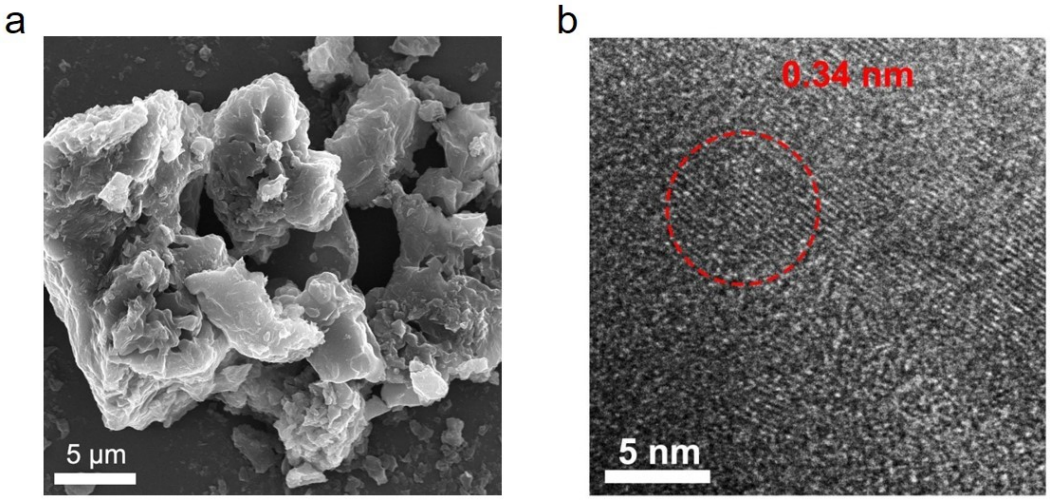
Supplementary Fig. 1 UV-Vis absorption spectra of NMD-0 and NMD-550 with digital photograph inserted (left one is NMD-0 and right one is NMD-550, respectively).



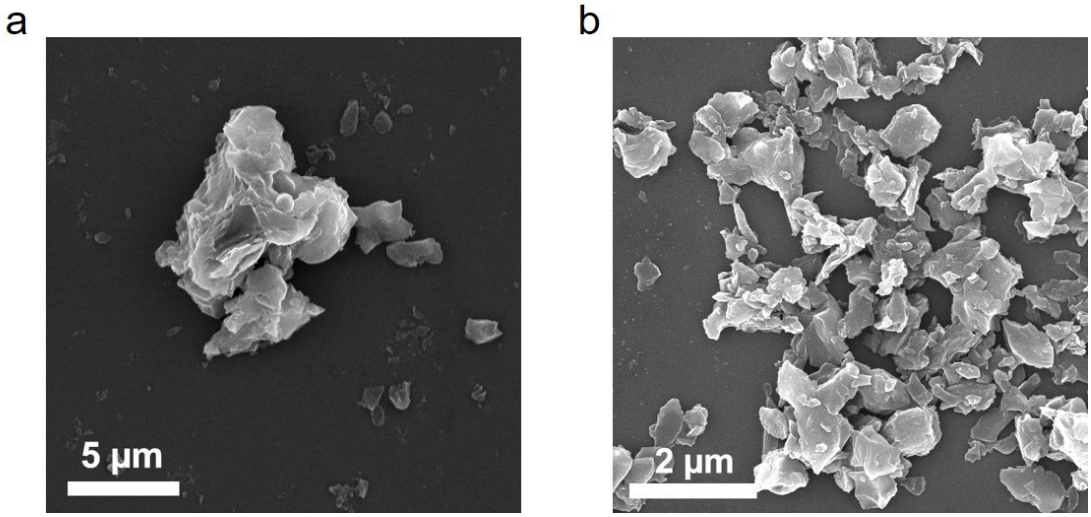
Supplementary Fig. 2 The full XPS spectra of NMD-0, NMD-450, NMD-550 and NMD-650.



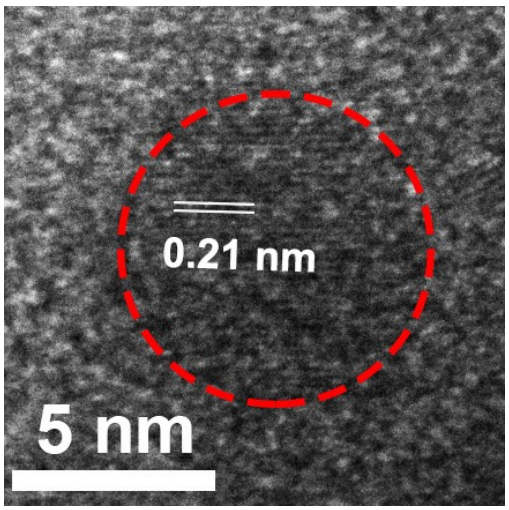
Supplementary Fig. 3 HRTEM image of NMD-0.



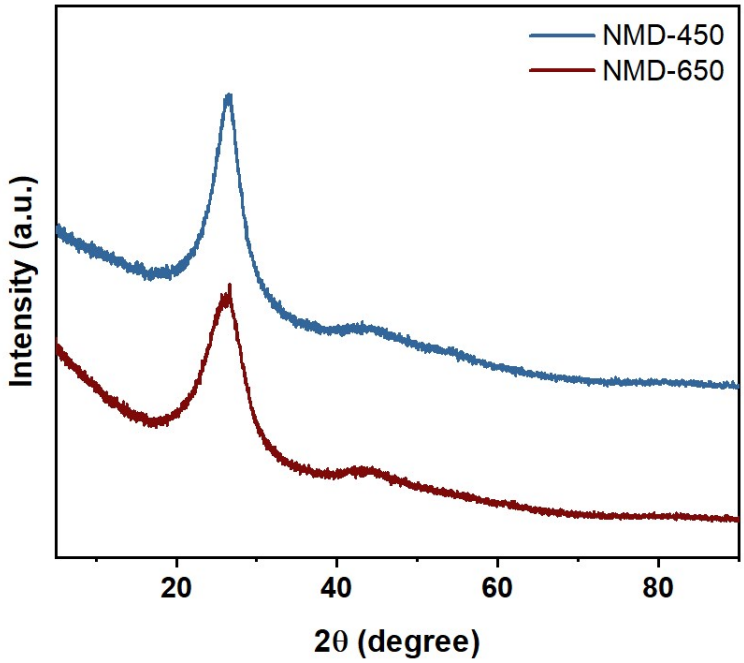
Supplementary Fig. 4 (a) SEM and (b) HRTEM images of NMD-550.



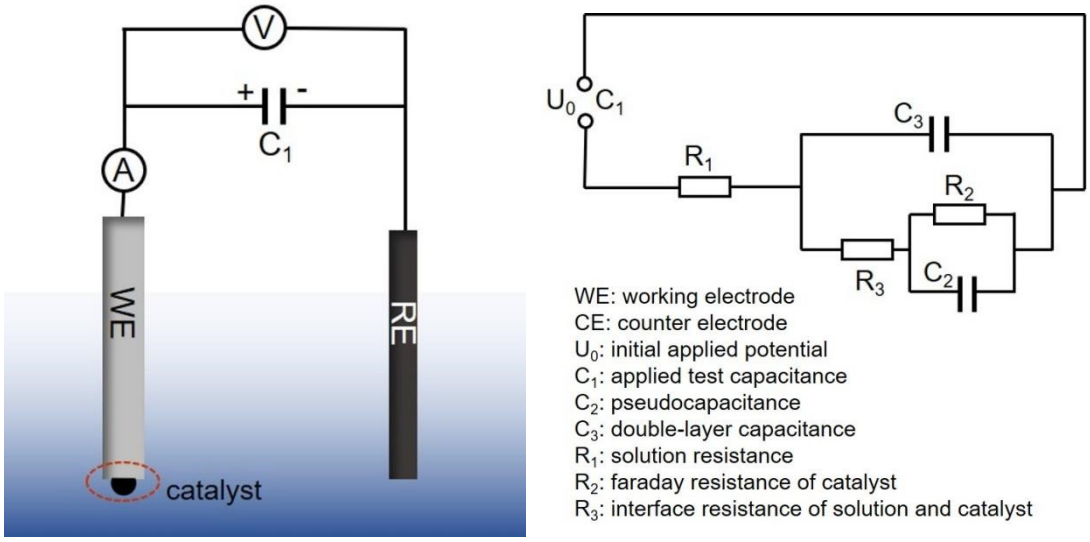
Supplementary Fig. 5 SEM images of (a) NMD-450 and (b) NMD-650.



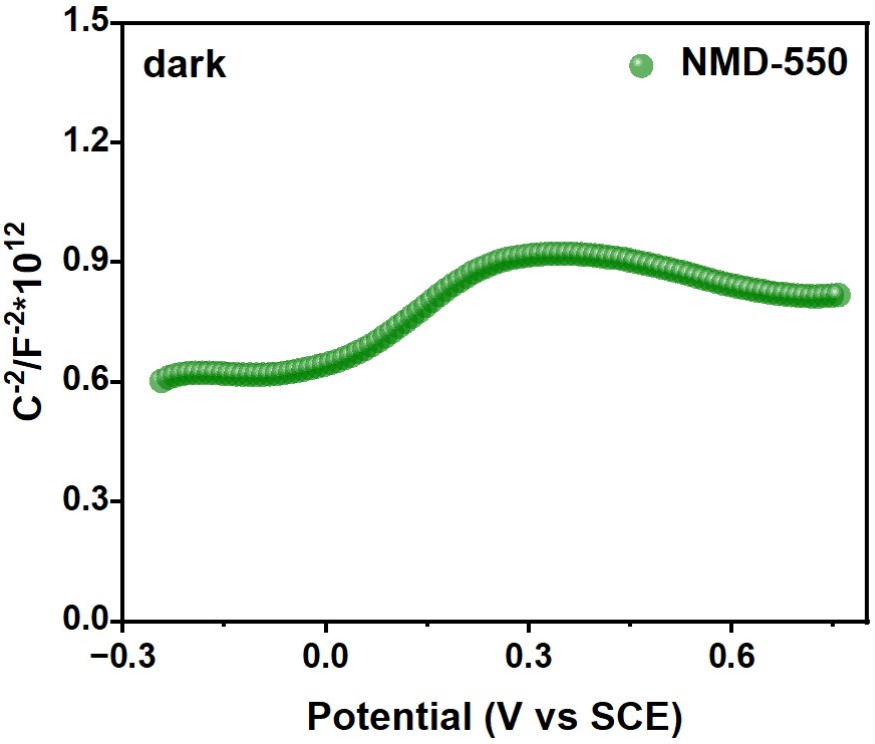
Supplementary Fig. 6 HRTEM image of CDs.



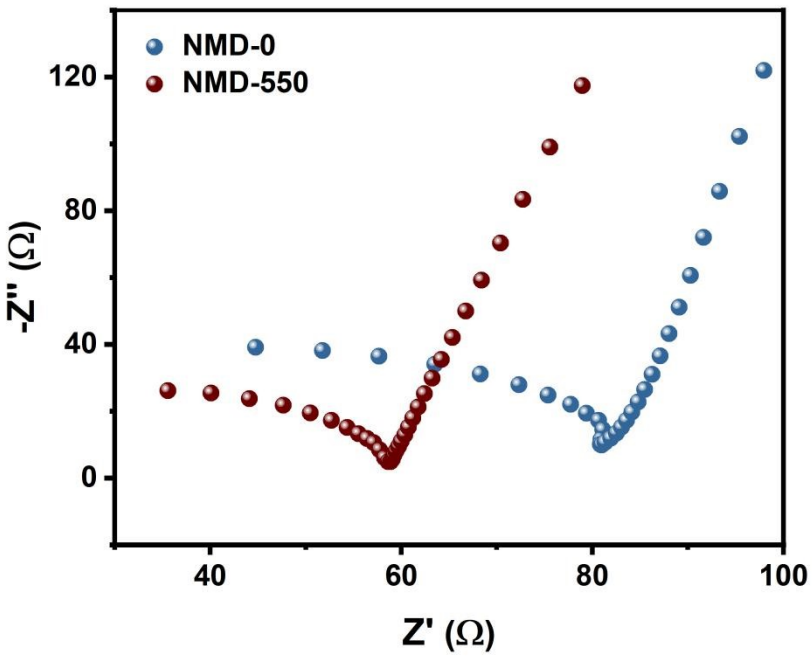
Supplementary Fig. 7 XRD patterns of (a) NMD-450 and (b) NMD-650.



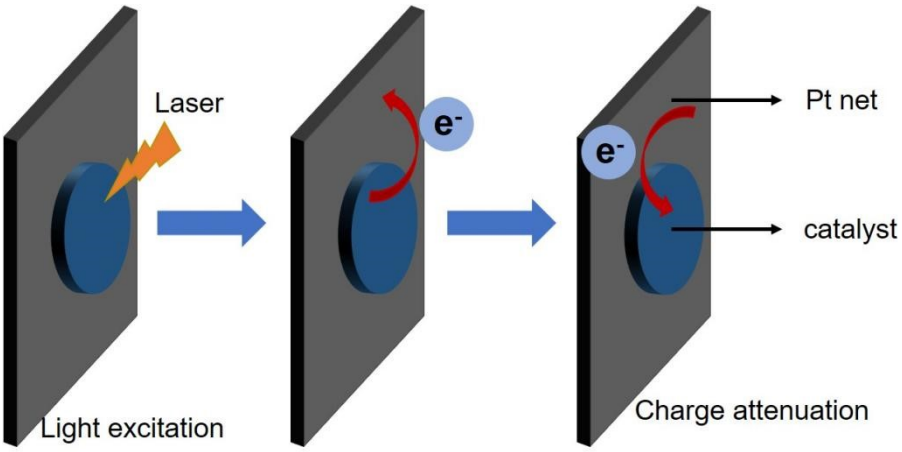
Supplementary Fig. 8 Circuit diagram of TPS test.



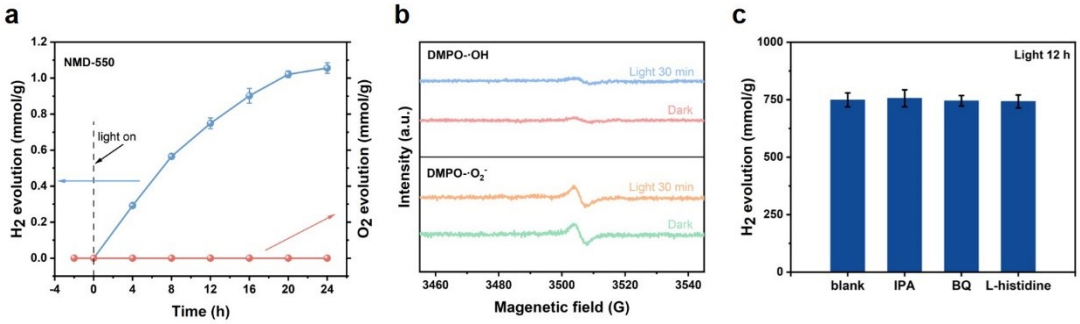
Supplementary Fig. 9 Mott-Schottky plots of NMD-550 measured at a frequency of 1000 Hz.



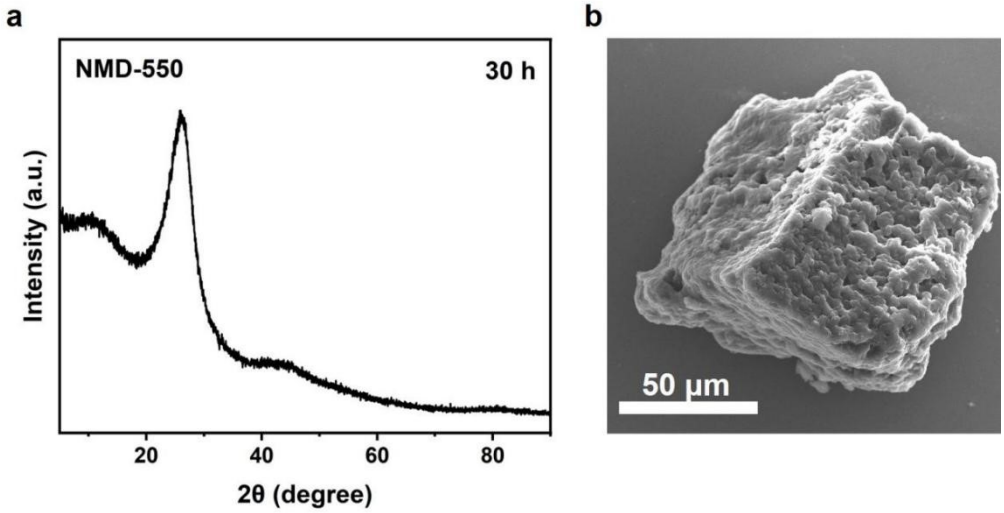
Supplementary Fig. 10 Nyquist plots for the EIS spectra of NMD-0 and NMD-550.



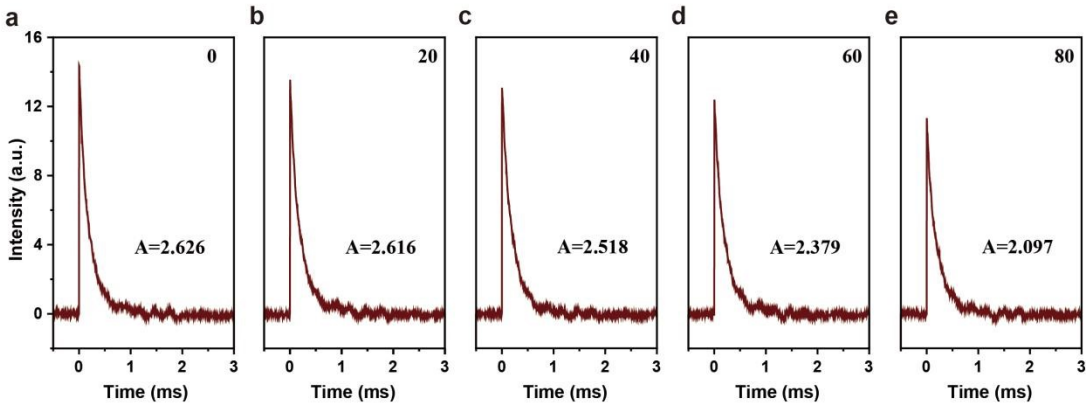
Supplementary Fig. 11 Circuit diagram of TPV test.



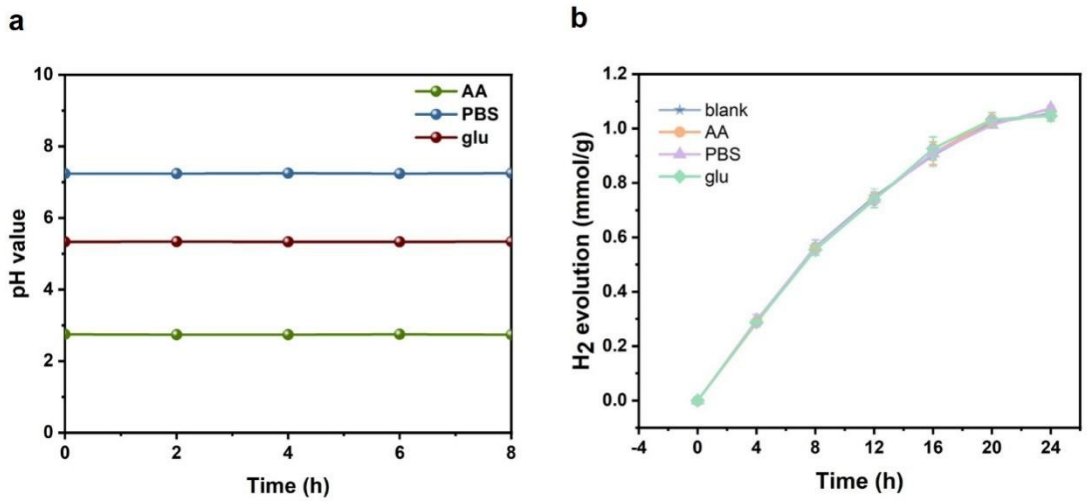
Supplementary Fig. 12 (a) Photocatalytic H_2 and O_2 evolution performance of NMD-550. (b) *In-situ* EPR spectra of the NMD-550 photocatalytic system under dark and after 30 min of visible light irradiation. (c) Photocatalytic H_2 production in ultra-pure water with different sacrificial agents.



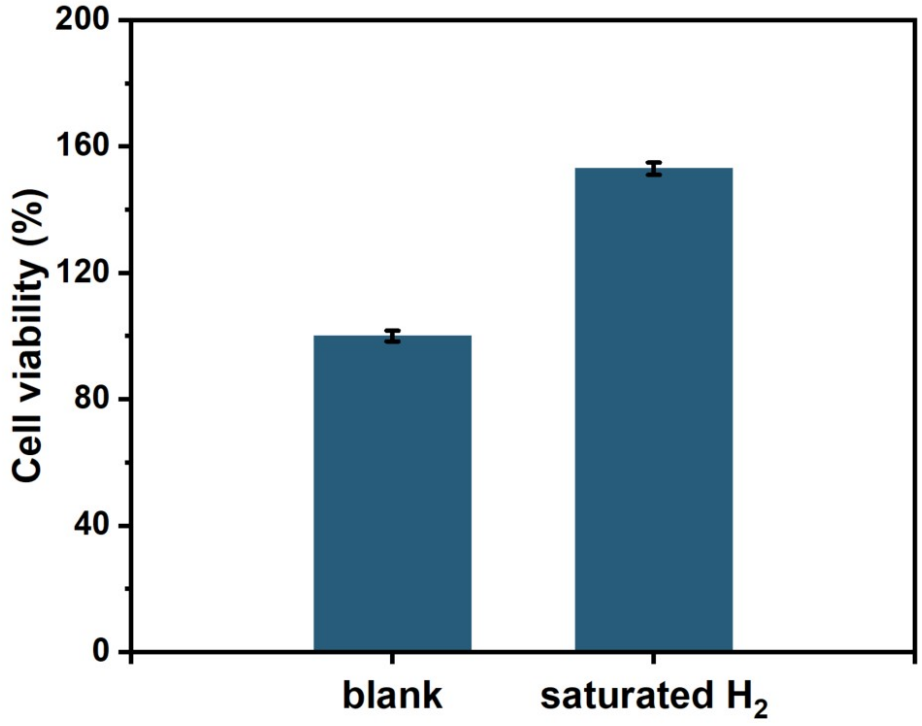
Supplementary Fig. 13 (a) XRD pattern and (b) SEM image of NMD-550 after 30 h photocatalytic experiment.



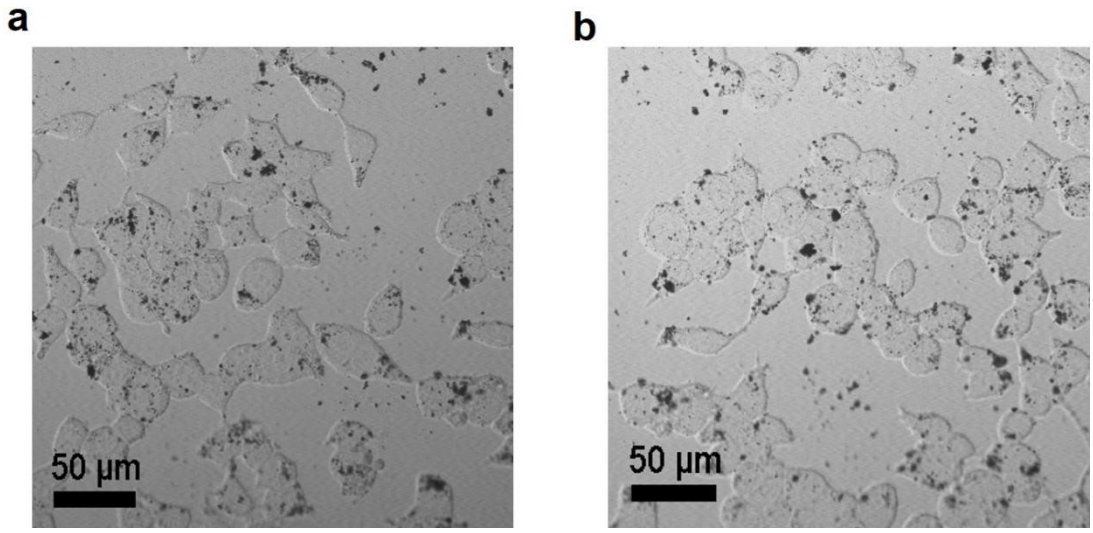
Supplementary Fig. 14 *In-situ* TPV curves of NMD-550 with different content of H_2O in acetonitrile to form the liquid film and spray it onto the surface of the catalyst (0, 20, 40, 60, 80 μL H_2O in 50 mL acetonitrile).



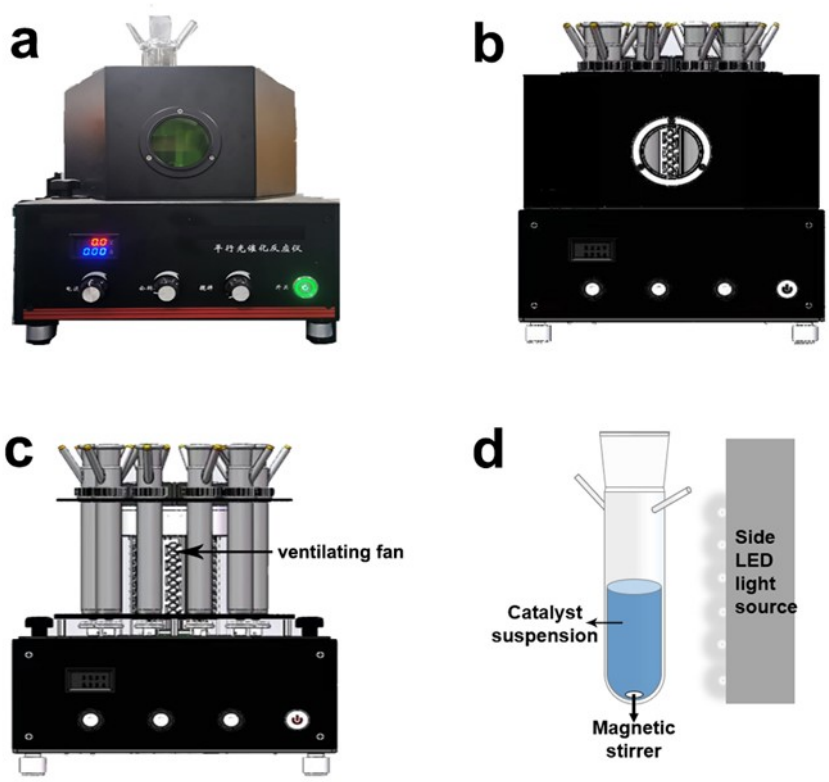
Supplementary Fig. 15 (a) The pH value of AA, PBS and glucose (glu) solutions after adding NMD-550. (b) H_2 evolution of NMD-550 in simulated biological solution (AA, PBS and glucose solution).



Supplementary Fig. 16 Cell viability of 293T with and without saturated H_2.



Supplementary Fig. 17 Confocal microscopy images of 293T cells (a) before and (b) after irradiation with NMD-550 added.



Supplementary Fig. 18 (a) The photo of light reaction device. Photo catalytic reaction device (b) external (c) internal model diagram. (d) Photocatalytic reaction model diagram[1].

Reference:

1. T. He, J. Wu, Y. Li, K. Wei, Y. Liu, H. Huang, Y. Liu, Z. Kang, *Chem. Eng. J.*, 2023, 4**51**, 138551.