

C₄N Quantum Dots/g-C₃N₄ Nanosheets Organic Homogeneous Structure Self-Assembly for Efficient Charge Separation and Photocatalytic Hydrogen Evolution

1. Materials

Cyclohexane (HKH, Aladdin, 99%), 3,3-diaminobenzidine (BPTA, Aladdin, 99%), methanol (Sinopharm, 99%), methanol (Sinopharm, 99%), Tetrahydrofuran (Macklin, 99%), N-methylpyrrolidone (NMP, Macklin, 99%), Melamine (Aladdin, 99%), Na₂SO₄ (Aladdin, 99%), triethanolamine (Aladdin, 99%), H₂PtCl₆ (Aladdin, 99%), Water was deionized to 18.2 MΩ · cm resistivity using the nanopure system.

2. Experimental section

Synthesis of C₄NQDs: The original synthesis method of C₄N refers to the report in the published literature, and on this basis, C₄NQDs were synthesized by hydrothermal tailoring. First, 41.6 g of cyclohexane Cyclohexane (HKH) and 42.7 g of 3,3-diaminobenzidine (BPTA) were transferred to the lining of 100 mL of polytetrafluoroethylene high-pressure reactor. Then, 25 mL of mixed solution (V_{methanol}: V_{NMP}=1:4) was added. After the reactor was assembled, it was reacted in an oven at 175 °C for 24 h. After cooling to room temperature, the samples were centrifuged. Finally, ethanol, tetrahydrofuran and deionized water were used for Soxhlet extraction for 3 days, and the samples were freeze-dried to obtain the pristine C₄N. Take 10 mg of the pristine C₄N powder prepared and transfer it to the lining of 100 mL polytetrafluoroethylene high-pressure reactor, add 50 mL of deionized water, assemble the reactor and react in an oven at 200 °C for 10h, then filter the sample with 0.22 μm water system filter membrane to obtain the final C₄NQDs.

Synthesis of C₃N₄NSs: Pristine g-C₃N₄ was prepared by the thermal condensation polymerization of melamine. 5 g of melamine powder was put into an aluminum oxide crucible with a cover, heated to 773 K for 4 h at the heating rate of 2 K · min⁻¹. The

yellow product was collected and ground into a powder. 1g pristine g-C₃N₄ powder was transferred to a 90*60*20 mm alumina boat, heated to 793 K for 6 h at a heating rate of 2 K min⁻¹. The final C₃N₄NSs was obtained after cooling to room temperature.

Synthesis of X%C₄NQDs/C₃N₄NSs: C₄N quantum dots of different proportions (the mass ratio of 0.1%, 0.2%, 0.3%, 0.6% and 1.0%) and 25 mg C₃N₄NSs were added to 50 mL deionized water and stirred for 6 h at room temperature. And then stay overnight to the final X%C₄NQDs/C₃N₄NSs.

3. Photocatalytic Test

The photocatalytic activity of the samples was evaluated by water splitting for hydrogen evolution under visible light irradiation. Typically, 25 mg photocatalyst and 10 mL triethanolamine (TEOA) serving as the sacrificial electron donor were added to 90 mL ultrapure water under stirring. Then, H₂PtCl₆ aqueous solution was added as the precursor for the co-catalyst Pt, which was in-situ photo-reduced during the photocatalytic reaction (~3 wt% Pt). Next, the solution was degassed and irradiated by a 300 W Xenon lamp equipped with a 420 nm cutoff filter. The photocatalytic H₂ evolution rate was determined by using a GC-7900 instrument with a thermal conductivity detector (TCD) and high-purity Ar₂ as the carrier gas. The monochromatic light was provided by using 365±15 nm, 420±15 nm, 500±15 nm band pass filter and the average intensity of monochromatic light was determined by CEL-NP 2000 photoradiometer. The Apparent Quantum Yield was calculated by the following Equation:

$$AQY = 1.2 \times 10^8 (v \times k) / (I \times A \times \lambda) \times 100 \%$$

v: reaction rate (mol·s⁻¹), K: Number of reaction transfer electrons, I: Optical power density(W·m⁻²), A: Incident light area (m²), λ: Wavelength of incident light (nm).

4. X-ray electron spectroscopy

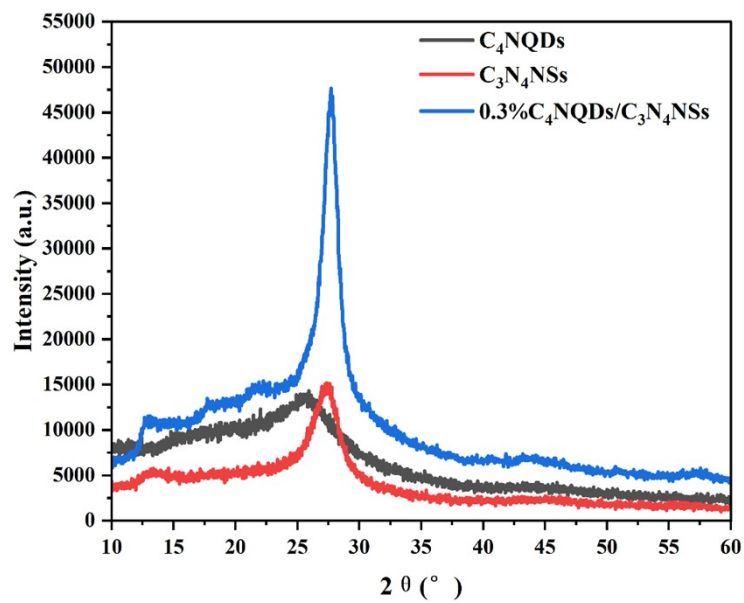


Figure S1 X-ray diffraction spectroscopy of C₄NQDs, C₃N₄NSs and 0.3% C₄NQDs/C₃N₄NSs.

5. The Tauc plots of C₄NQDs and C₃N₄NSs.

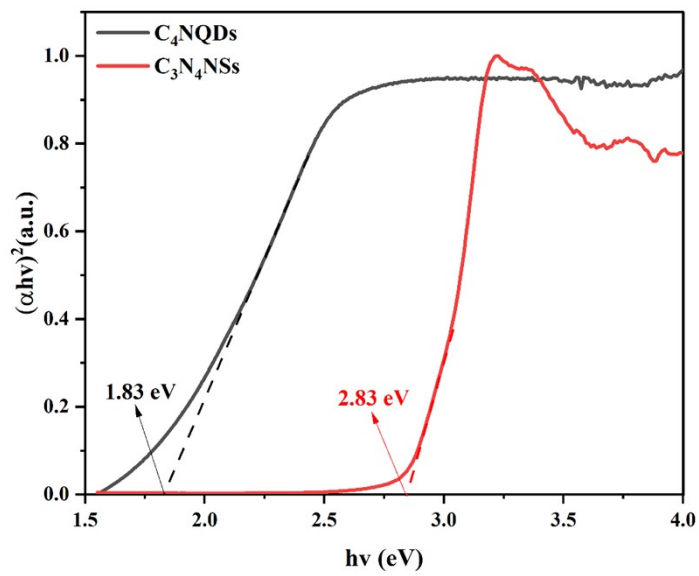


Figure S2 The corresponding Tauc plots of C₄NQDs and C₃N₄NSs.

6. XPS survey spectra

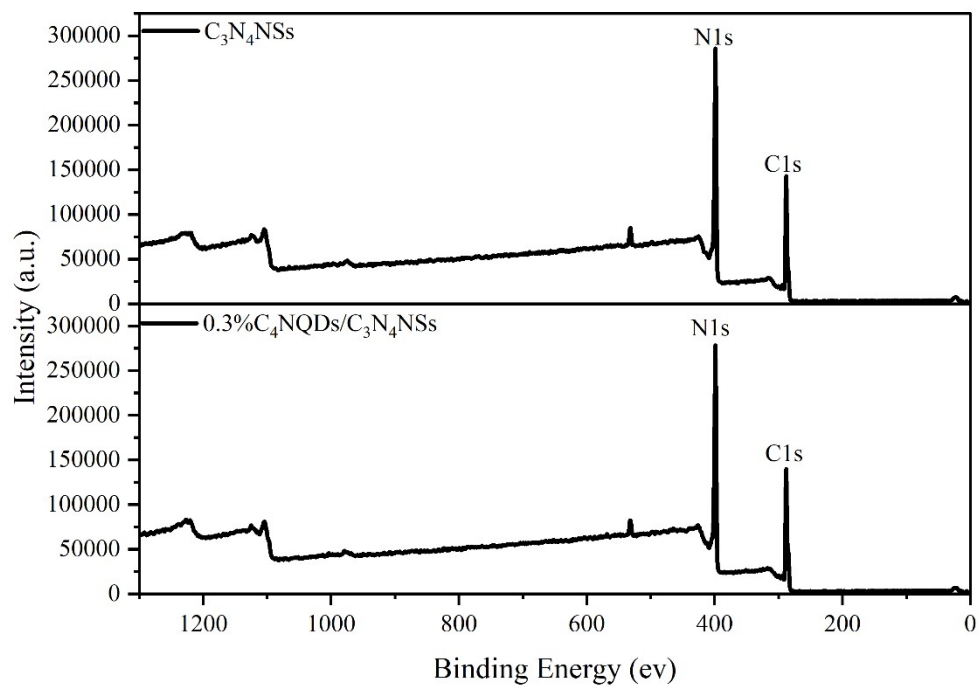


Figure S3 XPS survey spectra of C_3N_4NSs and 0.3% C_4NQDs/C_3N_4NSs .

7. Element content percentage

Table S1 Element content percentage of C₃N₄NSs and 0.3% C₄NQDs/C₃N₄NSs.

Sample	C%	N%
C ₃ N ₄ NSs	46.3	53.7
0.3% C ₄ NQDs/C ₃ N ₄ NSs	47.2	52.8

8. FTIR and XPS of 0.3% C_4 NQD/ C_3N_4 NS before and after reaction

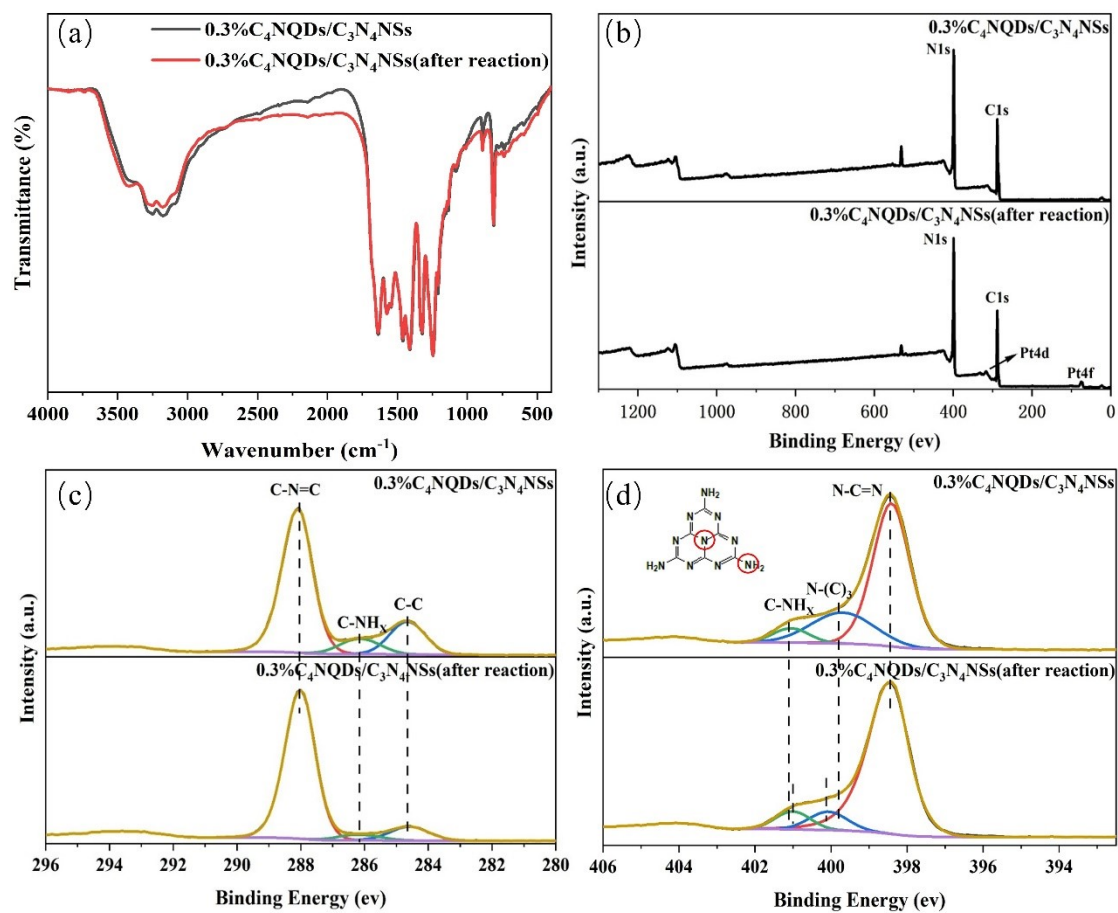


Figure S4 (a)The FTIR spectra and (b) XPS survey spectra and (c) the C1s fine spectra and (d) the N1s fine spectra of 0.3% C_4 NQD/ C_3N_4 NS before and after reaction.

9. XRD of 0.3% C_4N_4 QD/ C_3N_4 NS before and after reaction

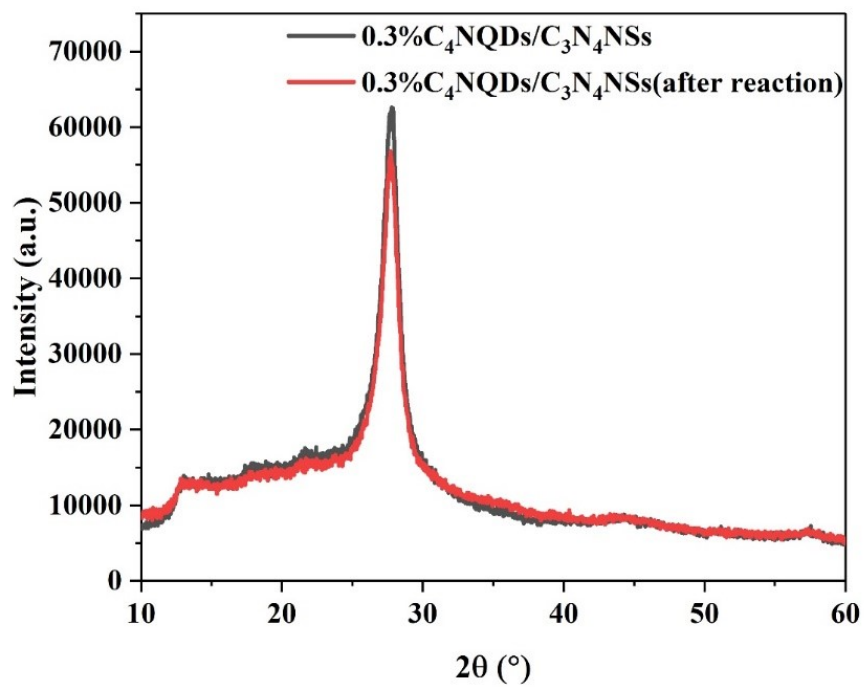


Figure S5 The XRD patterns of samples before and after reaction.

10. TEM images of 0.3% C_4N_4QD/C_3N_4NS after reaction

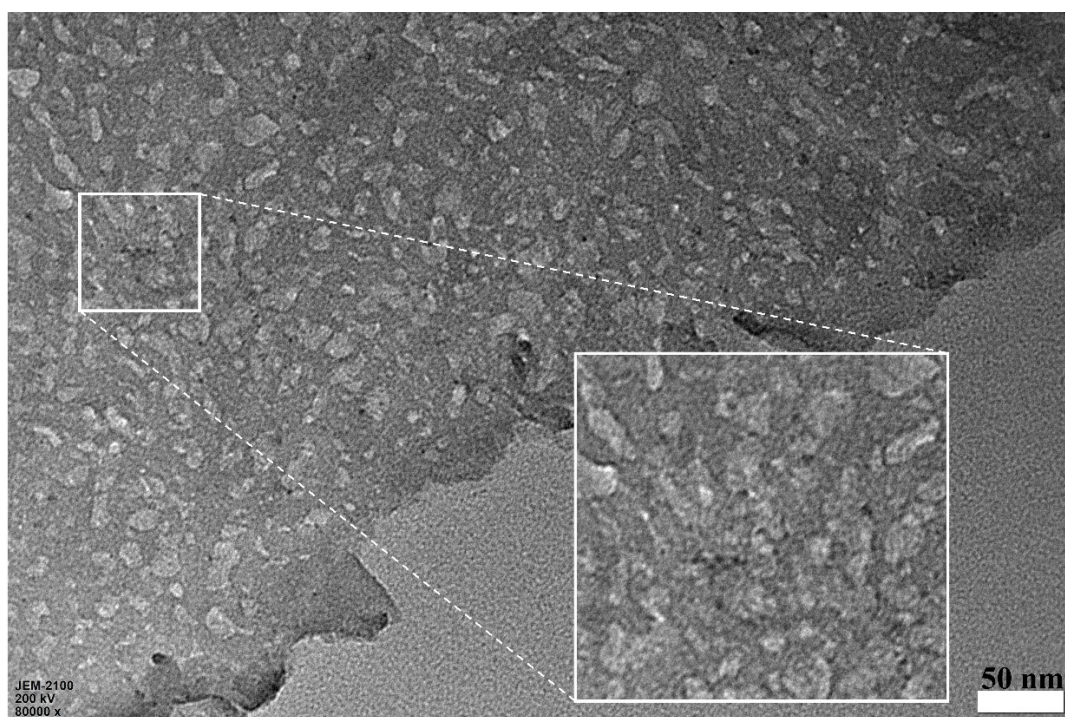


Figure S6 The TEM images of samples after reaction.

11. PL spectra

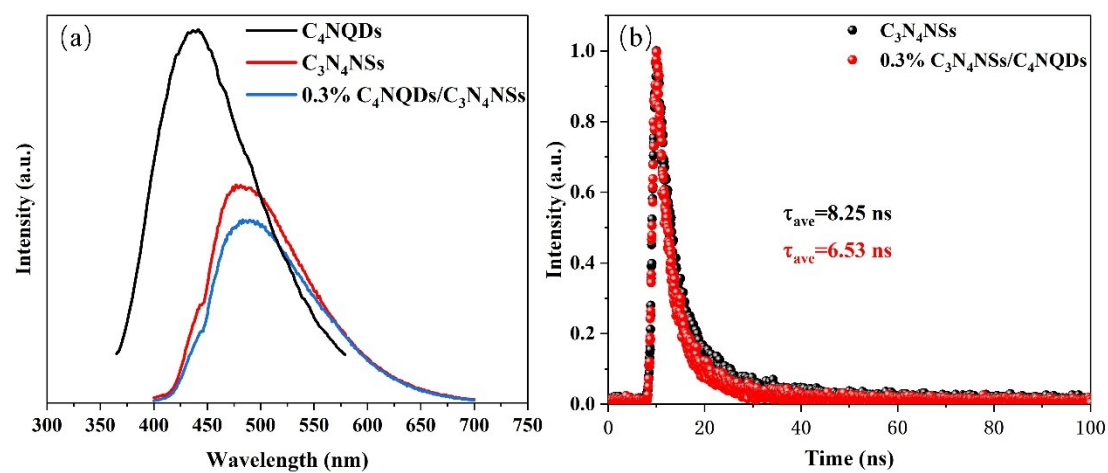


Figure S7 (a) The PL spectra of C₄NQDs, C₃N₄NSs and 0.3% C₄NQDs/C₃N₄NSs, (b) The transient state PL spectra of C₃N₄NSs and 0.3% C₄NQDs/C₃N₄NSs.

12. Electrochemical impedance spectroscopy

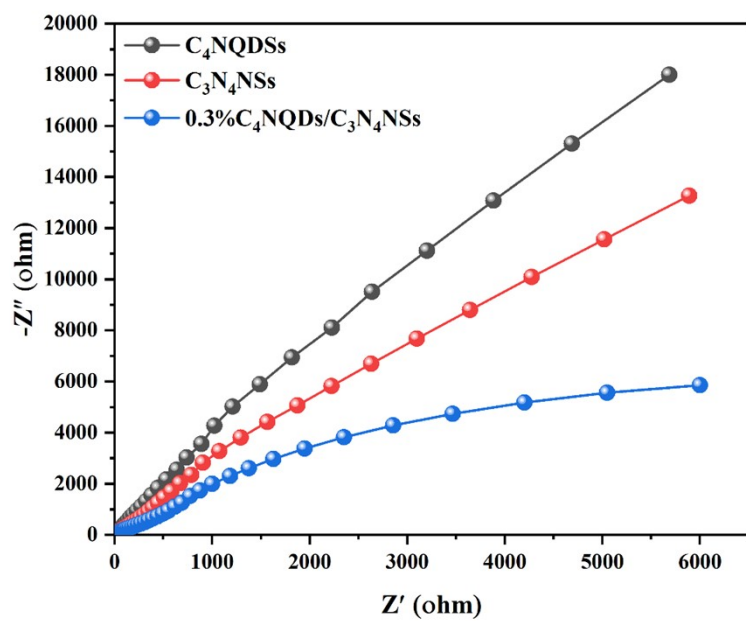


Figure S8 Electrochemical impedance spectroscopy of C_4NQDS , C_3N_4NSs and 0.3% C_4NQDs/C_3N_4NSs .

13. Mott-Schottky curve

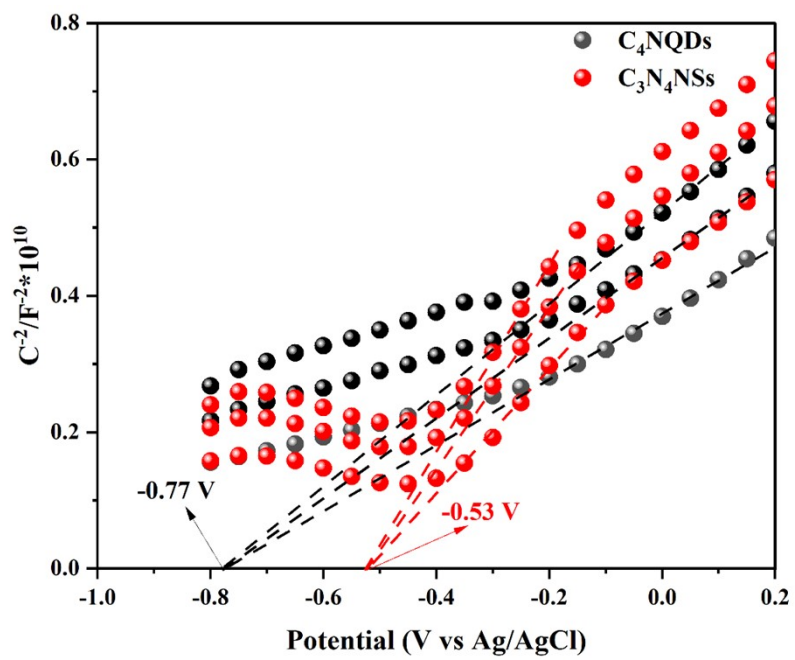


Figure S9 Mott-Schottky curve of C_4NQDs and C_3N_4NSs