Supplementary Information

Rational Design of Hollow Multilayer Heterogeneous Organic Framework for Photochemical Applications

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Figure S1. Schematic for the synthesis of hollow BPQD/g-C3N4@PDA organic framework nanosphere



Figure S2. The TEM image of PS, PDA@PS, and hollow PDA nanospheres (a-b). The Zeta potentials of PS and PDA@PS (f). The synthesis process of hollow PDA nanospheres (e).

The TEM image in Figure. S2 shows that the PS, PDA@PS, and hollow PDA nanospheres, which maintain a well-preserved spherical morphology after the template removal process. As shown in Figure 1(d-e), the zeta potentials of PS and PDA@PS were -34 mV and +8.4 mV, respectively. During the polymerization process, large amounts of amidogen and phenolic hydroxyl groups are preserved, so the PDA@PS is positively charged.



Figure S3. The TEM image of g-C3N4, PDA@PS, and hollow g-C3N4@PDA nanospheres (a-c). The Zeta potentials of PDA@PS and g-C3N4 nanosheets (f). The synthesis of hollow g-C3N4@PDA nanospheres (e-f)

When we added the protonated PDA and deprotonated g-C3N4, the PDA and g-C3N4 could not selfassembled to form a composite structure. The electrostatic repulsion is much stronger than the interaction between the PDA and g-C3N4. To further investigate which kind of g-C3N4 nanosheets can self-assemble onto the PDA, we designed different kinds of protonated PDA: the PH value ranged from 3 to 7. Although the total charge of the PDA is increased gradually, it still cannot bind to the g-C3N4. The lack of a self-polymerization phenomenon might be attributed to the intramolecular tension and steric effect. The g-C3N4 molecule was unable to bring the negative charges into adjacent positions, which ultimately weakened the interaction between the PDA and g-C3N4. The TEM image in Figure. S3(a-c) shows that the sample has g-C3N4 nanosheets, PDA@PS, and hollow PDA@g-C3N4 nanospheres. Figure 2d shows that the zeta potential of PDA was shifted from +8.72 to +37.6 mV, and the zeta potential of g-C3N4 nanosheets was -31.3 mV. Interestingly, Figure 2c shows that the g-C3N4 nanosheets with a negative charge and PDA with a positive could not effectively self-assembled to form PDA@g-C3N4 organic frameworks. Fig. S3(e-f) shows the process of protonation, deprotonation, and preparation of the PDA@g-C3N4. The amino groups of PDA and H+ can bond, producing positively charged PDA. In contrast, the terminal amino groups of g-C3N4 tend to lose protons, leading to the carbon nitride becoming negatively charged. The directionality of the charge increases the steric hindrance between the molecules, therefor, the PDA@g-C3N4 organic framework cannot fabricated by the electrostatic interactions.



Figure S4. The Zeta potentials of the g-C3N4 (a) and the PDA (b), the synthesize process of hollow PDA@ g-C3N4 nanospheres (c), Synthesis route of PDA@g-C3N4 via polymerization (d)

The protonation procedure promotes the formation of terminal amino groups by sacrificing a certain amount of the original quaternary amine of g-C3N4, and the terminal amino groups and H+ can bond to produce positively charged g-C3N4. Figure. S4a show that the zeta potential of g-C3N4 nanosheets was shifted from -31.3 mV to + 48 mV, and the zeta potential of PDA was shifted from +8.3 mV to -54.6 mV. Figure. S4b show that the PDA with a negative charge, which is attributed to the phenolic hydroxyl group of PDA losing electrons and the direction of the charge is from the inside out. The charged g-C3N4 nanosheets can effectively self-assemble on the surface of PDA to construct hollow PDA@g-C3N4 nanospheres by electrostatic attraction.



Figure S5. The SEM images of PDA@g-C3N4.

Sample	C/N atomic	SBET (m²/g)	Prove Volume (cm ³ /g)
g-C3N4	0.73	7.93	0.11
PDA	7.10	19.69	0.15
PDA@g-C3N4-9	1.23	22.43	0.14
PDA@g-C3N4-10	1.52	27.88	0.17
PDA@g-C3N4-11	1.98	35.29	0.15
PDA@g-C3N4-12	2.21	37.13	0.16



Figure S6. The EIS Nyquist plots of the bulk g-C3N4, PDA, and the series of hollow PDA@g-C3N4.



Figure S7. The Stability test of the PDA@g-C3N4-11 photocatalyst.



Figure S8. The Stability test of the PDA@g-C3N4/BPQD photocatalyst.



Figure S9. The TEM image of the PDA@g-C3N4/BPQD-11 and mapping of C, N and P after four cycling



Figure S10. The H₂ production rate of different samples loading on different co-catalyst under visible light irradiation (λ >420 nm)



Figure S11. Wavelength dependence of hydrogen evolution rate onPDA@g-C3N4/BPQD photocatalyst with visible light irradiation



Figure S12. Wavelength dependence of AQY on PDA@g-C3N4/BPQD photocatalyst with visible light irradiation



Figure S13. The H₂ production rate of different samples under near-infrared light irradiation (λ >620 nm)



Figure S14. Polarization curves of PDA@g-C3N4/BPQD electrode, together with PDA, g-C3N4 and PDA@g-C3N4 as reference in a 0.2 M Na₂SO₄ aqueous solution.



Figure S15. The fluorescence spectra of DCFH incubated with PDA@g-C3N4/BPQD at elevated concentrations (50, 100, 150, 200, 250, 300 μ g/mL) under irradiation (660 nm, 30 mW cm⁻² 15min).