Electronic Supplementary Information

Fabrication of Inorganic-Organic Core-Shell Heterostructure: Novel CdS@g-C₃N₄ Nanorod Arrays for Photoelectrochemical Hydrogen Evolution

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Fig. S12 The incident photon to current efficiency (IPCE) was measured based on a monochromator (Zolix Instruments, China) in an aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S (pH=12) at 0.9 V versus RHE. The generated photocurrent signals were collected using a lock-in amplifier (standford instrument SR830 DSP) synchronized with a light chopper (standford instrument SR540). IPCE was calculated according to following equation:¹

$$IPCE(\%) = \left[\frac{1240I(\lambda)}{\lambda J_{light}(\lambda)}\right] \times 100\%$$

where λ is the incident light wavelength, $I(\lambda)$ and $J_{\text{light}}(\lambda)$ are the corresponding measured photocurrent density and the recorded irradiance intensity at the specific wavelength of λ , respectively.

Fig. S13 Photocurrent density versus potential curves for different deposition times of $g-C_3N_4$ onto CdS NRs in an aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S (pH=12) under (100 mW/cm² AM 1.5G) illumination.



Fig. S1 XPS spectrum of the CdS@g-C₃N₄ CSNRs.



Fig. S2 XPS spectra of Cd 3d for pure CdS NRs and the CdS@g-C₃N₄CSNRs.



Fig. S3 EDX spectrum of the CdS@g-C₃N₄CSNRs.



Fig. S4 Photocurrent density versus potential curves for CdS NRs and CdS@g-C₃N₄ CSNRs in a 0.2 M Na₂SO₄ (pH=6.8) aqueous solution under (100 mW/cm² AM 1.5G)



Fig. S5 Photostability measurements of CdS NRs and CdS@g-C₃N₄CSNRs in a 0.2 M Na₂SO₄ (pH=6.8) aqueous solution under continuous (100 mW/cm² AM 1.5G) illumination for one hour at 1.6 V versus RHE.



Fig. S6 Open circuit voltage decay with time for CdS NRs and CdS@g-C₃N₄ CSNRs after illumination interruption.



Fig. S7 Comparison of the lifetime of electrons derived from the given equation as a function of open circuit voltage decay.

Note: Open circuit voltage decay measurements were conducted to further examine effective charge separation and the lifetime of electrons. As revealed in Fig. S11, Analysis of open circuit voltage decay showed that $CdS@g-C_3N_4$ CSNRs heterostructure alleviated open circuit voltage decay compared with pure CdS NRs. Furthermore, we also studied electron lifetime by the following model equation:²

$$\tau = -\frac{K_{B}T}{e} \left(\frac{dV_{OC}}{dt}\right)^{-1}$$

where $k_{\rm B}$ is Boltzmann's constant, *T* is the temperature, V_{oc} is the open circuit voltage, and e is the elementary charge. As presented in **Fig. S12**, the calculated results show that CdS@g-C₃N₄ CSNRs heterostructure exhibit a much higher lifetime of electrons with a lower recombination rate as compared to pure CdS NRs. This phenomenon further demonstrates that efficient charge separation is obtained in the CdS@g-C₃N₄ CSNRs heterostructure.



Fig. S8 Enlarged SEM image of the CdS@g-C₃N₄ CSNRs (g-C₃N₄ sheets are marked by white arrows).



Fig. S9 Enlarged TEM image of the CdS@g-C₃N₄ CSNRs.



Fig. S10 XRD pattern of blank FTO substrate.



Fig. S11 Photocurrent density versus potential curves for pure $g-C_3N_4$ in an aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S (pH=12) under (100 mW/cm² AM 1.5G) illumination.

Note: Pure $g-C_3N_4$ shows a much smaller photocurrent density (the maximum of photocurrent density is 12.3 μ A/cm²).



Fig. S12 Incident photon to current efficiency (IPCE) of CdS NRs and CdS@g-C₃N₄ CSNRs.

Note: Fig. S10 shows IPCE spectra of CdS NRs and CdS@g-C₃N₄ CSNRs. Pure CdS NRs shows rising IPCE from 530 nm in agreement with bandgap. The IPCE of CdS@g-C₃N₄ CSNRs is higher than that of CdS NRs across the visible light

absorption range, which indicates that photogenerated electron-hole pairs are efficiently separated in the $CdS@g-C_3N_4CSNRs$ heterostructure.



Fig. S13 Photocurrent density versus potential curves for different deposition times of $g-C_3N_4$ onto CdS NRs.

Note: Photocurrent density versus potential curves for different deposition times of g- C_3N_4 onto CdS NRs also were measured in an aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S (pH=12) under (100 mW/cm² AM 1.5G) illumination. As shown in **Fig.S13**, as the deposition times increase, the CdS@g-C₃N₄ CSNRs show decreased Photocurrent density, which possibly due to the light-filtering effect and low conductivity of g-C₃N₄.³

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