Supplementary Information

Synergistic Enhancement of Seawater Hydrogen generation via Sulphur vacancy enriched and Phase engineered CQD loaded CdS Photocatalyst

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Characterization

To determine the size of the crystallite and study the structural properties of the synthesized CdS samples, powder XRD analysis was performed using powder diffraction (XRD, PAN Analytical) with Cu Kα radiation (λ = 1.5418 Å) in the 2θ range of 10-60°. The optical properties were studied with absorption spectra, recorded using a UV-1800 Shimadzu, Japan, and Fourier transform infrared (FTIR) spectroscopy recorded using JASCO FT/IR 4200 USA model spectrometer using a KBr pellet with a resolution of 4 cm^{-1}. Fluorescence quenching measurements were performed with the USA F-7000 fluorescence spectrofluorometer. The excitation and emission slit width (each 5 nm) and scan rate (500 nm/ min) were kept constant for all experiments. The surface microstructure and morphology study were done using Scanning electron microscopy (JSM-7610F JEOL Ltd. Tokyo, Japan) and Transmission Electron Microscope (JEOL JEM 2100(HT) 200KV, Japan) and the elemental mapping was performed by energy dispersive X-ray technique (UK Oxford-EDAX). X-ray photoelectron spectroscopy (XPS) was performed on an ESCA Ulvac USA PHI 1600 photoelectron spectrometer from Physical Electronics using Al Kα radiation photon energy of 1486.6 ± 0.2 eV.

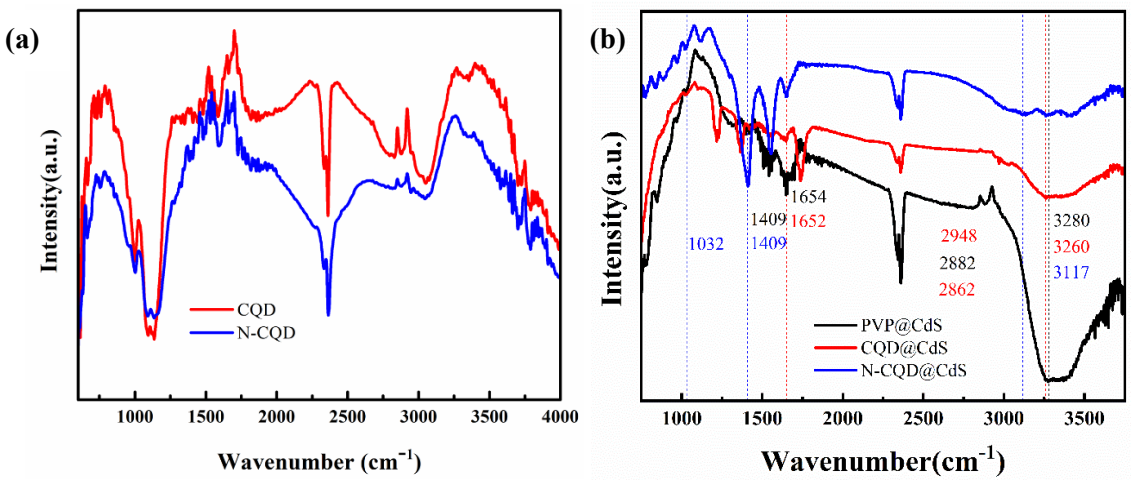
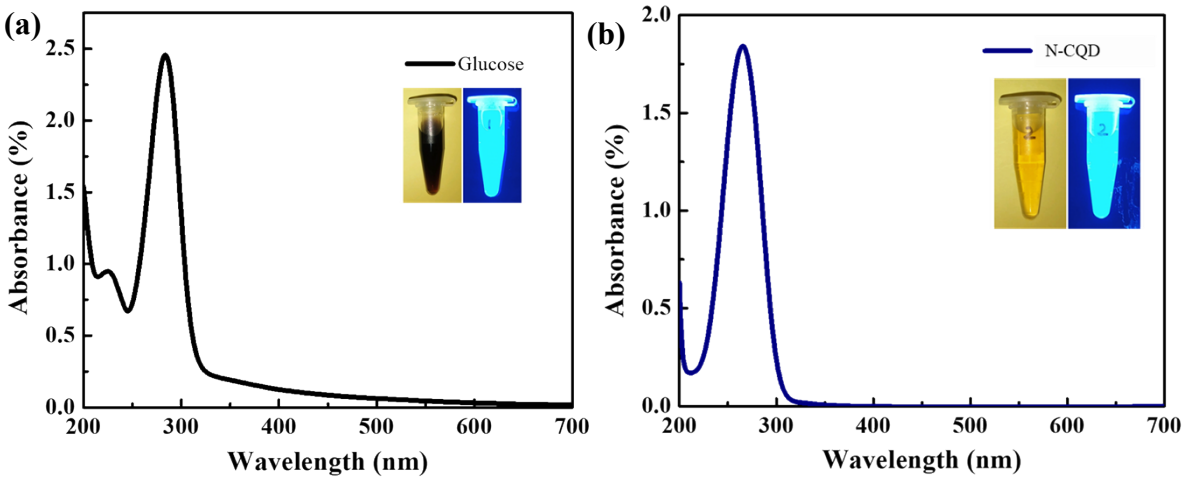


Fig.S1 shows FTIR Spectra of (a) CQD, N-CQD and (b) PVP and CQD loaded CdS samples.



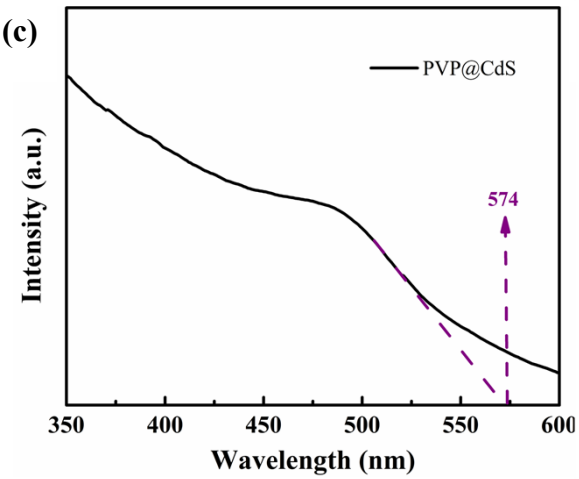


Fig. S2 shows the absorbance of (a) CQD and (b) PVP@CdS

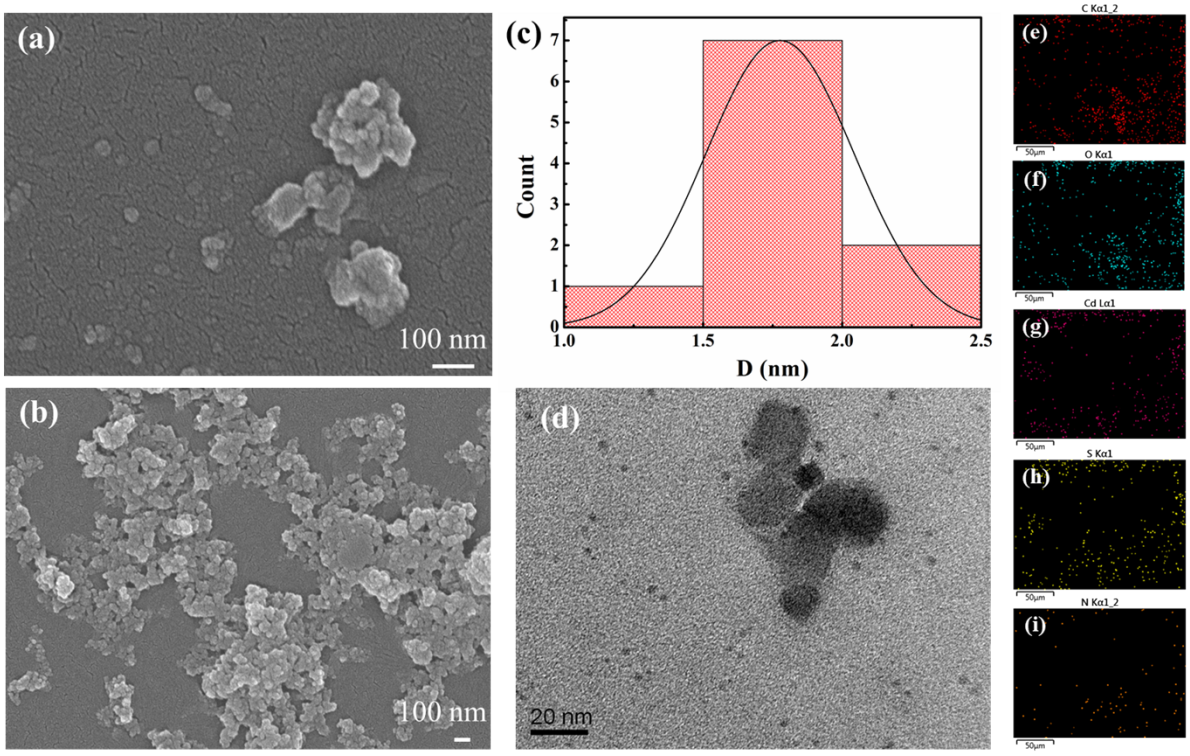
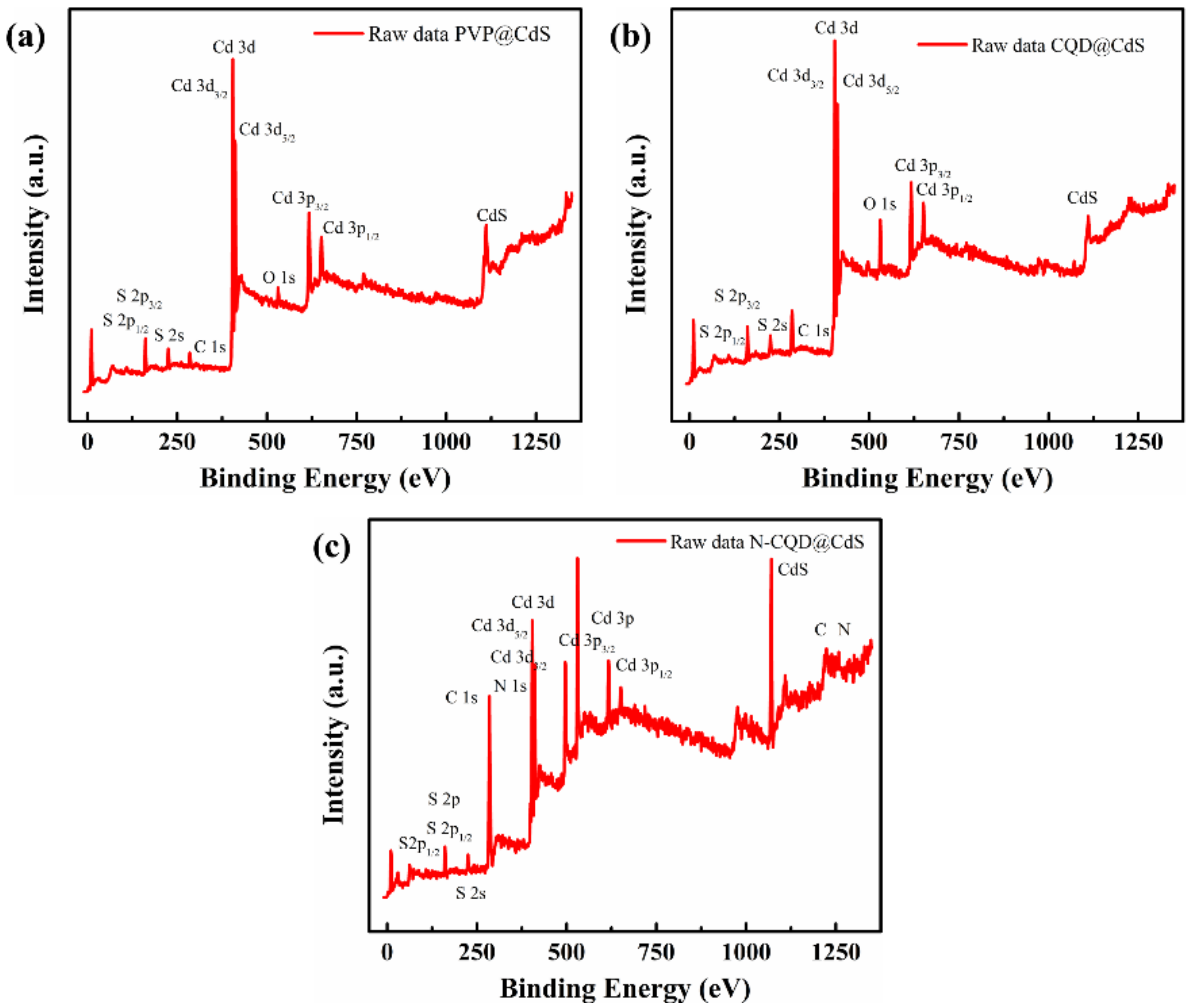


Fig.S3 shows the SEM image of PVP@CdS (a), N-CQD@CdS (b), particle size distribution of CQD (c) elemental mapping of N-CQD@CdS (e-i).



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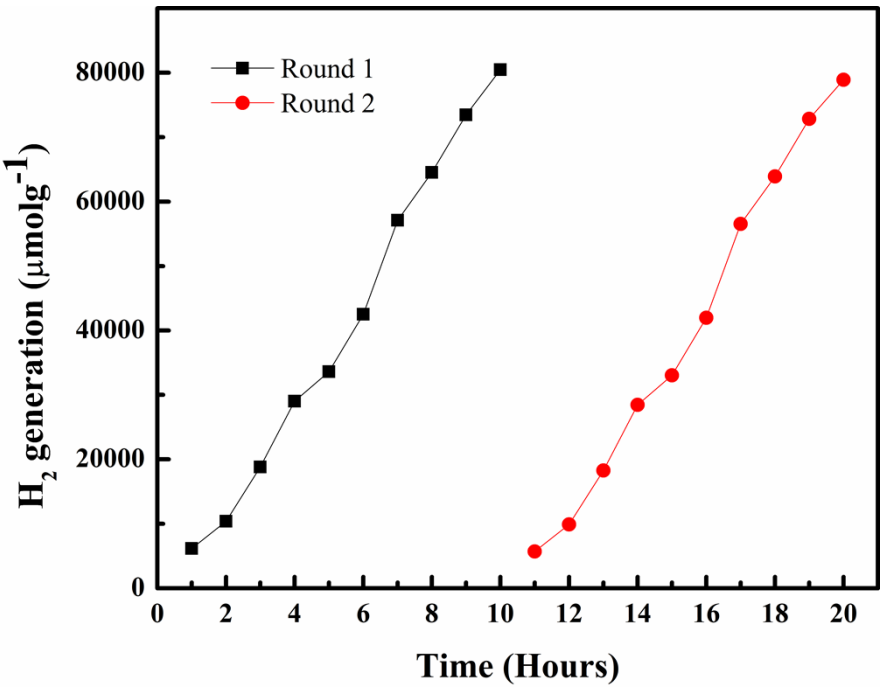
80 Fig.S4 shows the XPS spectra of full survey scan from PVP@CdS, CQD@CdS and N-

81 CQD@CdS samples



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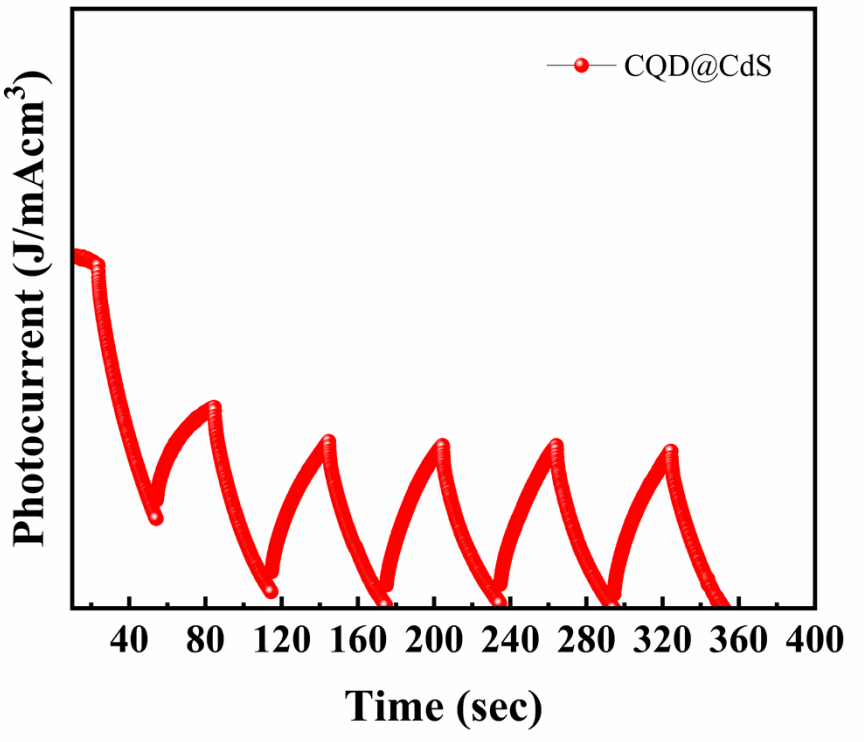
83 Fig S5 shows the recyclability of CQD@CdS photocatalyst for consecutive two rounds



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85 Fig S6 shows stability of photocurrent vs time for CQD@CdS samples

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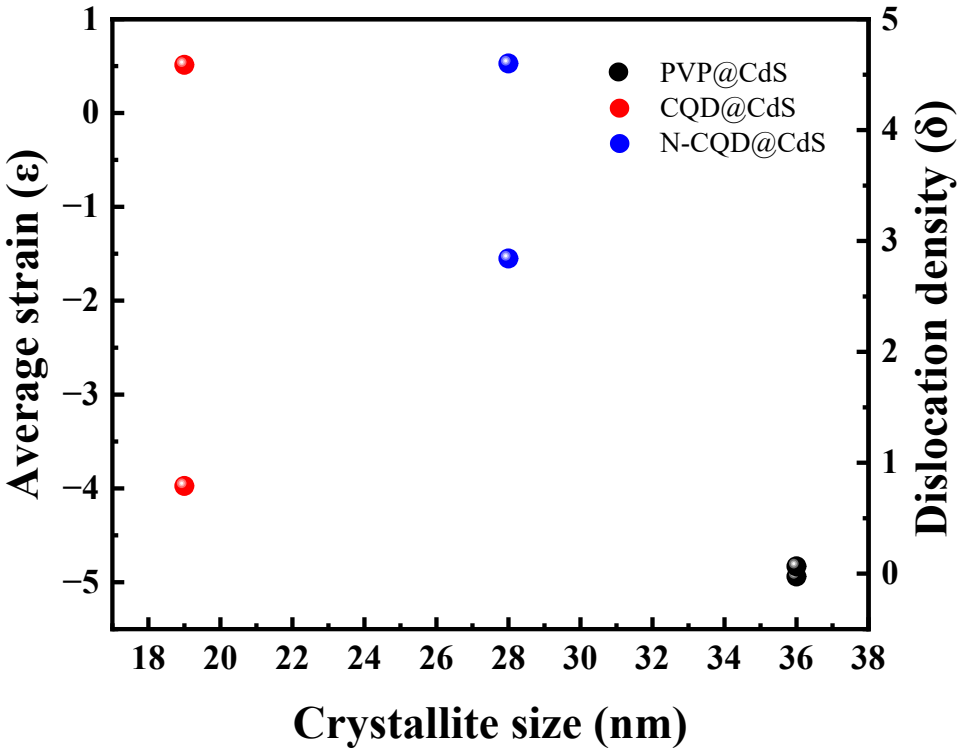

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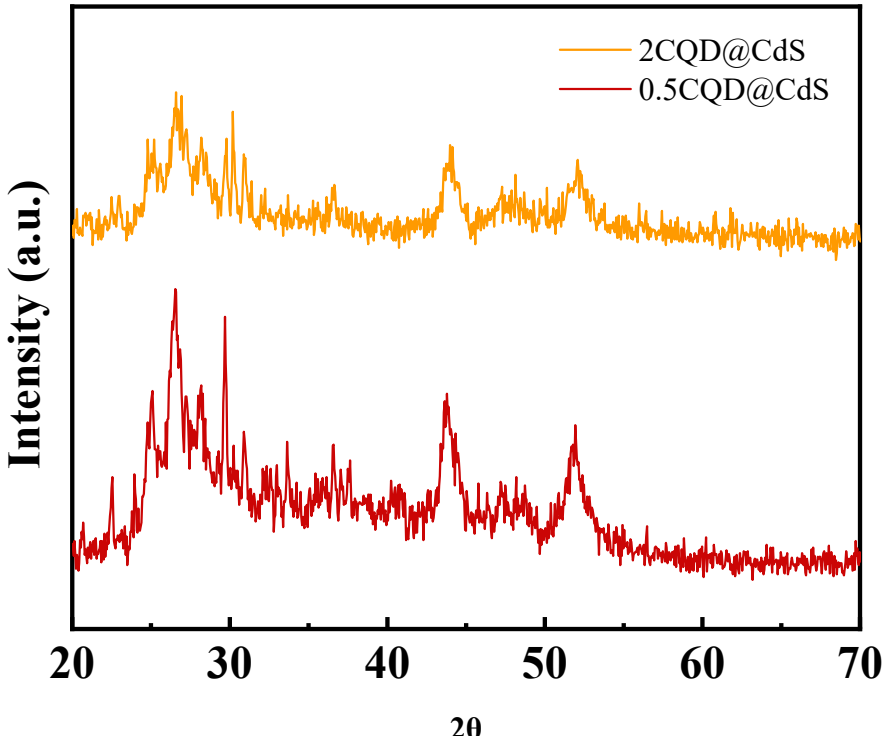
88 Fig S7 shows average strain, crystallite size and dislocation density for CdS samples.



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90 Fig S8 shows the diffraction pattern for different ratios of CQD loaded CdS samples.

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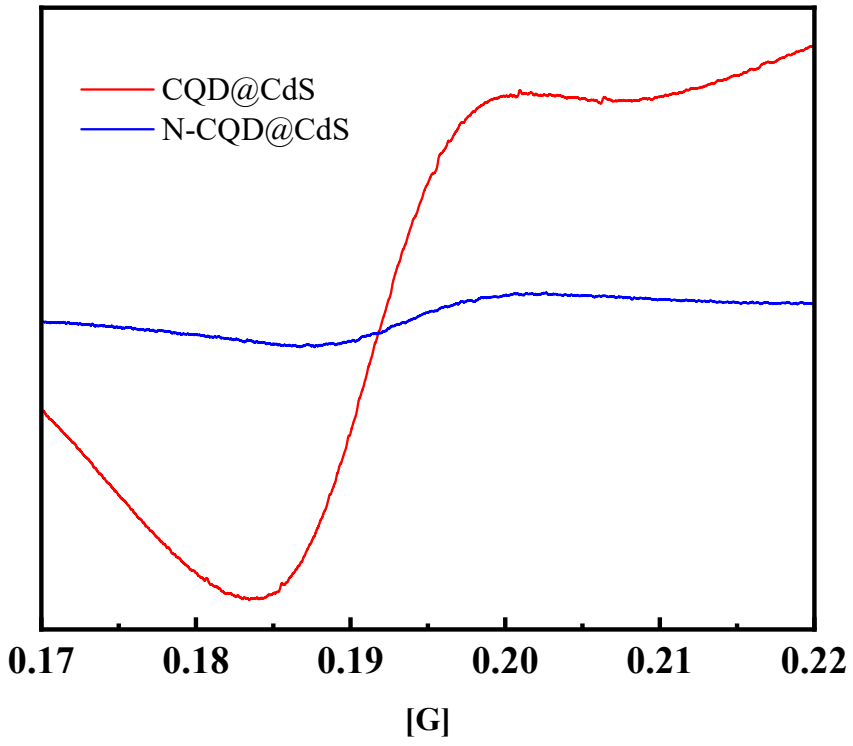

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93 **Fig S9** shows the EPR spectra of CQD@CdS and N-CQD@CdS.

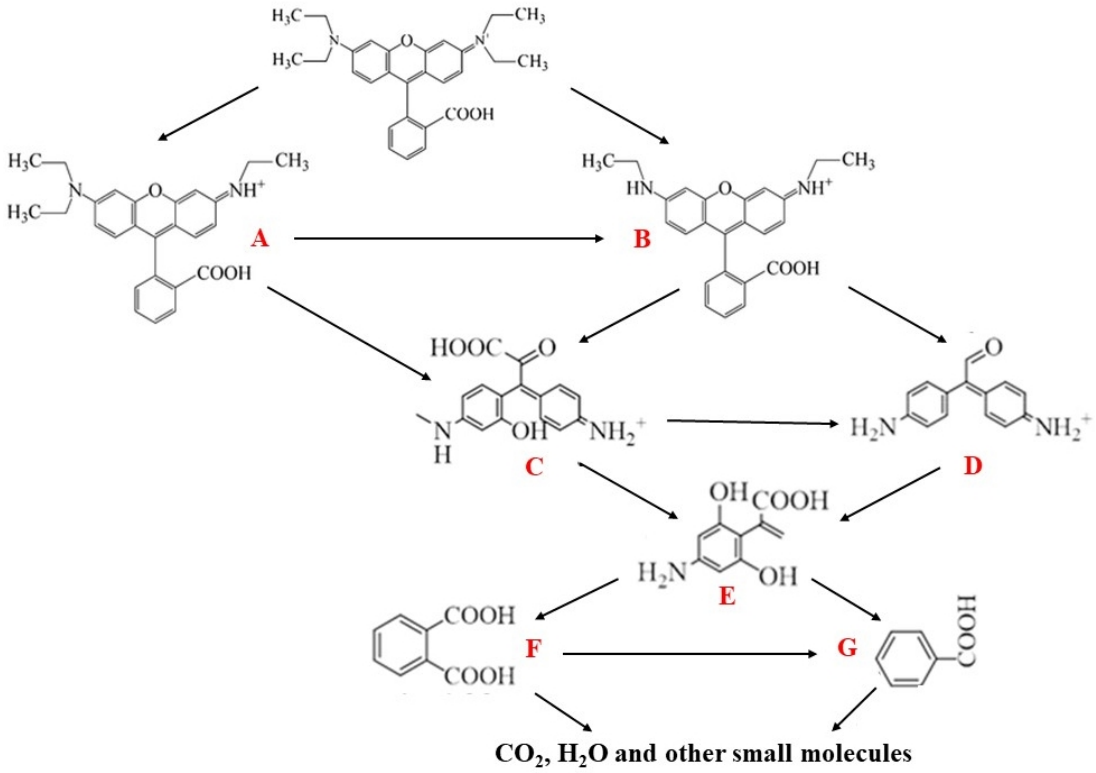

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Fig S10 Proposed possible N-deethylation degradation pathways of RhB by photocatalytic system.

According to the previous reports [1–3], the possible degradation pathway of RhB was proposed in Figure. The N-deethylation occurred on the nitrogen atoms of RhB molecules due to the attacks of h^+ and $\cdot O_2^-$, resulting in two main intermediates of A and B. The chromophore structures of these deethylated products were destroyed through cleavage of the conjugated xanthene structure, leading to the intermediates with low molecular weights including products C, D, and E. The benzene ring structures of the above intermediates were attacked continuously and converted to products F and G. Ultimately, the products were mineralized to CO_2, H_2O and small molecules.

Table S1 shows Functional groups of PVP@CdS, CQD@CdS and N-CQD@CdS samples with respective to their wavenumber from FTIR spectroscopy.

Material	**Wavelength (cm^{-1})**	**Assigned Functional Group**
PVP_CdS	1409, 2882 3280	-C-H bonding (due to PVP) -OH bond
CQD@CdS	2862- 2948 3260 1652	-CH bonding -OH bond -C=O stretching modes
N-CQD@CdS	1409 1032 3117	-C=C -C=N $-NH_2$

Table S2 Comparison of different dye degradation obtained in this study with literatures.

Sample Name	**Dye name**	**Dye (ppm/ml)**	**Photocatalyst (mg)**	**Degradation Efficiency (%)**	**Time (min)**	**Reference**
$AC_{80}CdS$	Rhodamine 6G	50/100	-	98%	295	[4]
CdS@Y-CQDs	Rhodamine 6G	10/100	10	98%	45	[5]
gC3N4-CdS	Rhodamine 6G	10/100	100	88.2%	90	[6]
Carbon@CdS	Rhodamine 6G	40/100	40	94%	120	[7]
Carbon	Rhodamine 6G	3/100	80	97.8	40	[8]

@CdS						
Carbon@ CdS Petals	Rhodamine 6G	5/100	20	95	40	[9]
rGO/CuI/PANI	Rhodamine 6G	9.5/50	50	96	50	[10]
PANI@ graphene	Rhodamine 6G	10/100	10	100	100	[11]
CQDd@ CdS	Rhodamine B	**50/100**	**25**	**45**	**97**	**This work**

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123 **Table S3** Comparison of H_2 production rate obtained in this study with literatures.

Photocatalyst	**Amount of photocatalyst (mg)**	**H_2 generation ($\mu molg^{-1}$)**	**Lifetime**	**Sacrificial reagents**	**References**
CQD/CdS@MIL	50	0.49	10	Lactic acid	[12]
Bi-CQDs/CdS	50	1.77	35	Na_2SO_3 + Na_2S	[13]
CDs-CdS	50	0.05	20	No SR	[14]
CdS/MoS_2	20	1.36	25	Lactic acid	[15]
ReS_2/CdS	25	24.36 137.5	16	Na_2S+Na_2SO_3 Lactic acid	[16]
Pt/CdS	25	16.26	20	Lactic acid	[17]
$rGO/CdS/MoS_2$	50	1.98	20	Lactic acid	[18]
Ni_2O_3/CdS	50	4.45	10	Methanol	[19]
CQD@CdS	**25**	**80450**	**30 hours**	**Methanol and Triethylamine**	**This work**

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Table S4 shows the atomic percentage of Cadmium and Sulphur and their atomic ratio in all samples.

Sample	Cd 3d%	S 2p%	Cd/S ratio
PVP@CdS	83.80	16.20	5.17
N-CQD@CdS	85.37	14.63	5.83
CQD@CdS	88	11.18	7.45

Table S5 shows the ICP-MS data of PVP@CdS and CQD@CdS after photocatalytic hydrogen generation.

Sample	Concentration (ppm) Cd^{2+} after Photocatalysis
PVP@CdS	80.60 ppm
CQD@CdS	38.37 ppm

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