Supplementary Information

Constructing hierarchical cadmium sulfide *via* nitrogen-doped carbon dots-mediated interfacial engineering for enhanced hydrogen production †

An-Ran Xue,[a,#] Yang Hao,[a,#] Cun-Wei Kang,[a] Qing Cai,[a] Jia-Shen Li [b], Kun Dong,[b]

Song-Dong Ding,[c] Yuan-Ru Guo,[b,]* and Qing-Jiang Pan[a,]*

[a] *Key Laboratory of Functional Inorganic Material Chemistry (Ministry of Education), School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China. E-mail: panqjitc@163.com*
[b] *Key Laboratory of Bio-based Material Science & Technology (Ministry of Education), College of Material Science and Engineering, Northeast Forestry University, Harbin 150040, China. E-mail: guoyrnefu@163.com*
[c] *College of Chemistry, Sichuan University, Chengdu 610064, China*

[#] These two authors contributed equally to this work.
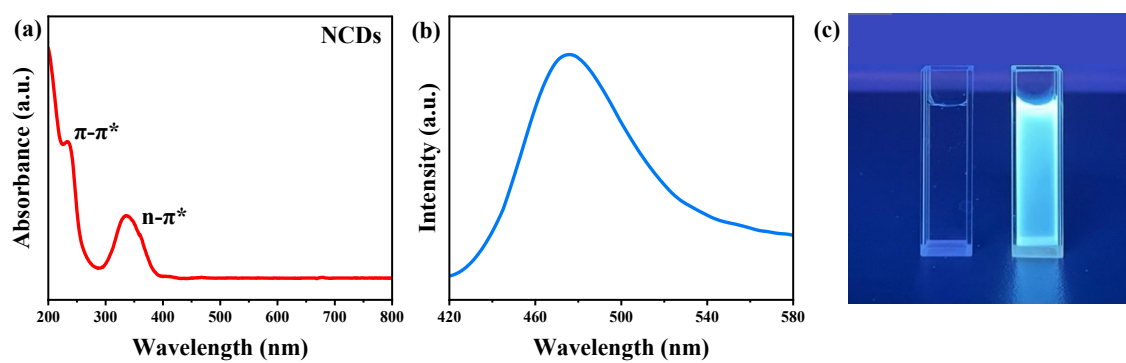* Corresponding authors.

Fig. S1. UV-Vis (a) and fluorescence spectra (b) of NCDs, along with fluorescence images of NCDs solutions under visible and UV light (c).
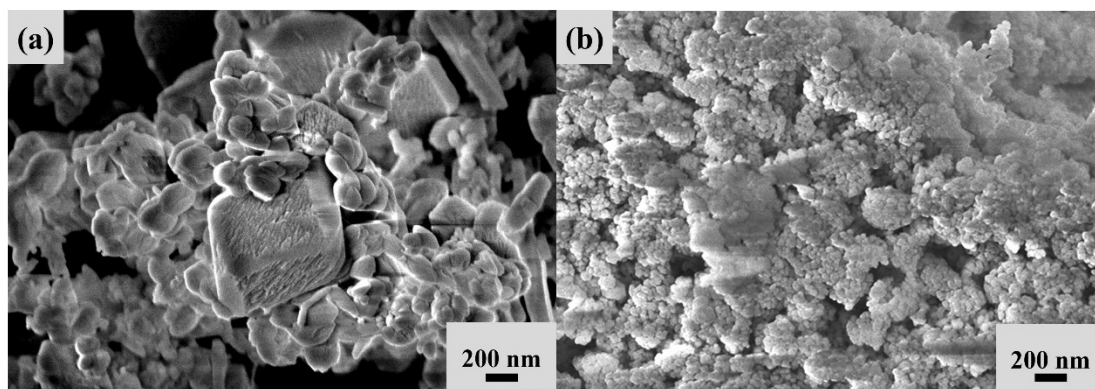

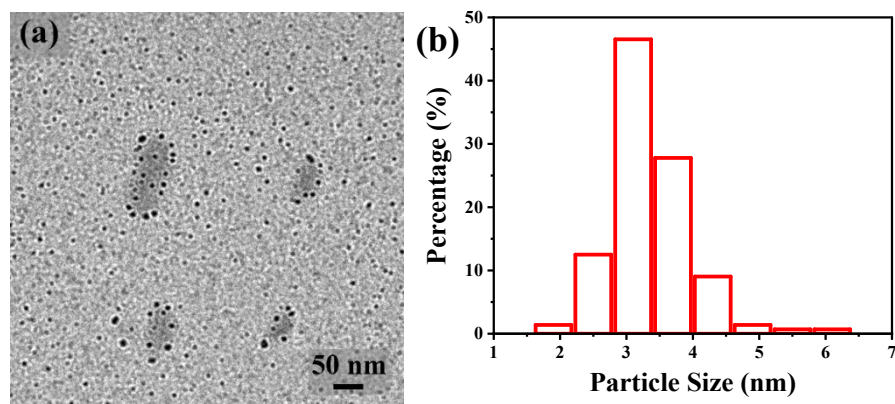**Fig. S2.** SEM images of $CdCO_3$ (a) and $NCDs/CdCO_3$ (b).

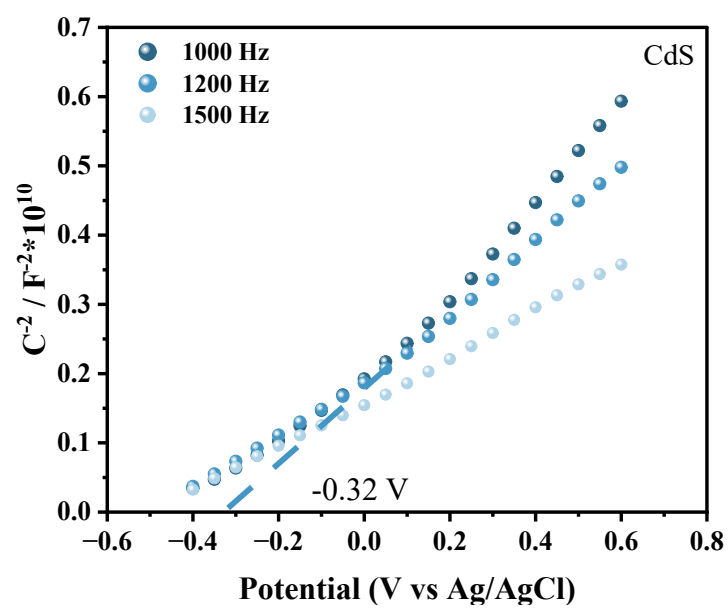**Fig. S3.** TEM image (a) and size distributions (b) of NCDs.
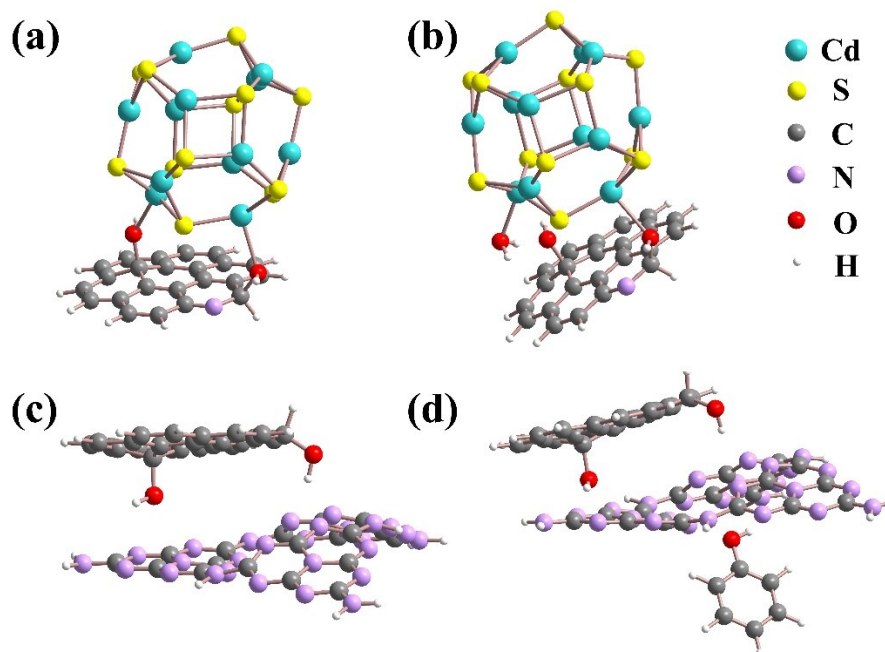

Fig. S4. The Mott-Schottky curves of CdS.

Fig. S5. Optimized structures of NCDs/CdS (a), NCDs/CdS-H_2O (b), CDs/g-C_3N_4 (c) and CDs/g-C_3N_4-PhOH (d).
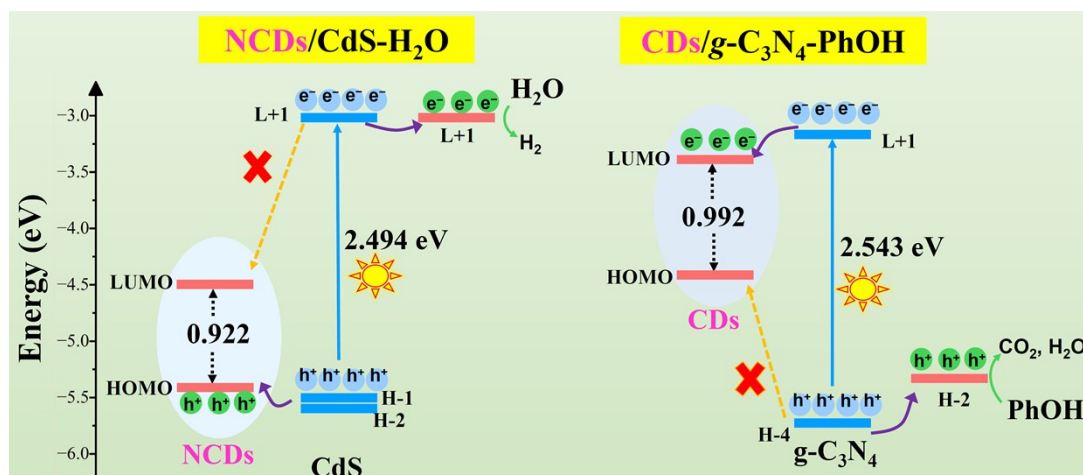

Fig. S6. Energetic levels of frontier molecular orbitals of NCDs/CdS-H_2O and CDs/g-C_3N_4-PhOH. It is illustrated that NCDs serve as acceptors of photogenerated holes and CDs act as acceptors of photogenerated electrons. Notably, it is kinetically unfavored for NCDs accepting photogenerated electrons and CDs accepting holes.
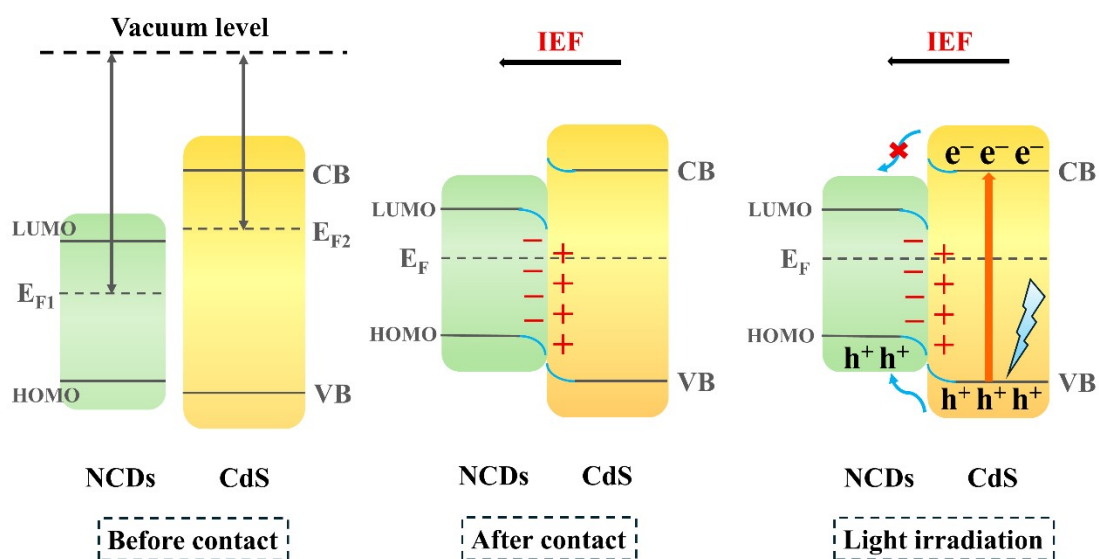
Fig. S7. Schematic charge-transfer process in NCDs/CdS: the energetic band structures and Fermi level (E_F) of NCDs and CdS before contact (a), the internal electric field (IEF) and band edge bending at the interface of NCDs/CdS after contact, and the photogenerated charge transfer under light irradiation.

Computational details and mechanism discussion:

Full structural optimizations were performed with Priroda code.[1] The scalar relativistic four-component Hamiltonian was used, along with the PBE functional and the all-electron correlation-consistent Gaussian basis sets. At the structures, we conducted frequency calculations. No imaginary frequency values confirmed the minimum point on the potential energy surfaces. Electronic structure calculations were carried out by ADF2014 program.[2, 3] The integration parameter of 6.0*6.0*6.0 was applied, along with the ZORA scalar relativistic Hamiltonian, PBE functional and Slater-type TZP basis sets. It is worth noting that the GGA-PBE is naturally underestimating the HOMO-LUMO gap of the calculated system relative to the experimental value. It will be enlarged when using MetaGGA and hybrid functionals like M06L, B3LYP and PBE0. Additionally, other factors like computational model and code, Hamiltonian, basis sets and environmental effects also have effect on these calculations.

NCDs/CdS and water-adsorbed complex were studied by DFT calculations. And the optimized structures are presented in Fig. S5. One can note that the catalyst composite can catch water *via* hydrogen bonds and dative bonds. The composite CDs/g-C_3N_4 was computationally investigated for photocatalytically degrading phenol in our previous work.[4] It was found that the photoelectrons were easily moved out from g-C_3N_4 to the energy-matching unoccupied orbital of CDs, while the remained holes jumped up to phenol and degraded it by oxidization (Fig. S6). CDs provided a suitable photoelectron-accepted unoccupied orbital and successfully hampered the fast electron-hole recombination. In contrast, NCDs in our composite NCDs/CdS contribute to hole-accepted occupied orbital. Therefore, the difference originates from different electronic structures of NCDs and CDs, which are caused by the nitrogen doping.

In brief, photogenerated electrons of NCDs/CdS are efficiently applied in splitting water for H_2 production; and left holes are rapidly transferred from CdS to NCDs, greatly inhibiting the photocorrosion of CdS and raising chemical stability of the composite catalyst.

References:

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