Highly efficient photocatalytic hydrogen generation by incorporating CdS into ZnCr-layered double hydroxide interlayer

Guohua Zhang, Bizhou Lin*, Weiwei Yang, Shaofeng Jiang, Qianru Yao, Yilin Chen and Bifen Gao

Electronic Supplementary Information

Table S1 Parameters obtained from N_2 adsorption–desorption measurements

sample	surface area[a] (m^2/g)	pore volume[b] (cm^3/g)	average pore size[c] (nm)
ZnCr-LDH	33	0.11	3.8
CdS	74	0.14	2.5
CdS/ZnCr-LDH	86	0.17	3.8

[a] BET specific surface area calculated from the linear part of BET plot.
[b] Total pore volume taken from the volume of N_2 adsorbed at $p/p_0 = 0.98$.
[c] Average pore radius was estimated from the Barrett–Joyner–Halenda formula.

Table S2 Binding energies obtained from XPS measurements (eV)

sample	Zn $2p_{3/2}$	Zn $2p_{1/2}$	Cr $2p_{3/2}$	Cr $2p_{1/2}$	Cd $3d_{5/2}$	Cd $3d_{3/2}$	S $2p_{3/2}$
ZnCr-LDH	1021.7	1044.8	577.3	587.1	–	–	–
CdS	–	–	–	–	404.0	410.8	161.7
CdS/ZnCr-LDH	1021.4	1044.4	577.1	586.9	404.8	411.6	162.4

Table S3 Photocatalytic performances of photocatalysts*

irradiation	UV-visible			visible		
sample	ZnCr-LDH	CdS	CdS/ZnCr-LDH	ZnCr-LDH	CdS	CdS/ZnCr-LDH
R_i (quanta/sec)	3.71×10^{18}	3.71×10^{18}	3.71×10^{18}	1.91×10^{18}	1.91×10^{18}	1.91×10^{18}
R_a (quanta/sec)	2.16×10^{16}	2.65×10^{17}	1.50×10^{17}	1.04×10^{16}	7.95×10^{16}	3.19×10^{16}
R_{H2} (μmol h^{-1})	12.8	96.6	216.4	0.7	21.6	37.4
QE (%)	19.8	12.1	48.2	2.4	9.1	42.6

* The calculation of quantum efficiency (QE) was conducted using the same procedure reported in literature (R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269–271.

$$QE = R_r/R_a = 2R_{H2}/R_a,$$

where R_r is the reaction rate of photons involved in hydrogen generation, R_{H2} is the H_2 evolution rate, and R_a is the absorption rate of incident photons.

Take CdS/ZnCr-LDH sample for example. Under the UV-visible light irradiation, the wavelength of UV-Visible light is from 300 to 2500 nm, and the light intensity is 113 mW/cm^2. The irradiating area is 7.1 cm^2. The rate of incident photons (R_i) was determined to be 3.71×10^{18} quanta·sec^{-1}. The absorption rate of incident photons (R_a) was determined to 1.50×10^{17} quanta·sec^{-1}, using the following equation:

$$R_a = \int_{300}^{2500} S \times \alpha \times \rho(\lambda) d\lambda$$

where S is the area of the sample, α is the light absorption and $\rho(\lambda)$ is the light intensity density at wavelength λ. The H_2 evolution rate (R_{H2}) of CdS/ZnCr-LDH is 214.6 μmol·h^{-1} under UV-visible light irradiation. Therefore, the quantum efficiency (QE) can be estimated as

$$QE = 2\times(216.4\times10^{-6}/3.6\times10^{3})mol\cdot sec^{-1}\times6.02\times10^{23}quanta\cdot mol^{-1}/1.50\times10^{17}\,quanta\cdot sec^{-1}\times100\% = 48.2\%$$

Under the visible light irradiation, the wavelength of visible light is from 420 to 2500 nm, and the light intensity is 67 mW/cm^2, $R_i = 1.91\times10^{18}$ quanta·sec^{-1}. The absorption rate of incident photons (R_a) for CdS/ZnCr-LDH was determined to 3.19×10^{16} quanta·sec^{-1}. Based on $R_{H2} = 37.4$ μmol·h^{-1} under visible light irradiation. Hence,

$$QE = 2\times(37.4\times10^{-6}/3.6\times10^{3})mol\cdot sec^{-1}\times6.02\times10^{23}quanta\cdot mol^{-1}/3.19\times10^{16}\,quanta\cdot sec^{-1}\times100\% = 42.6\%$$

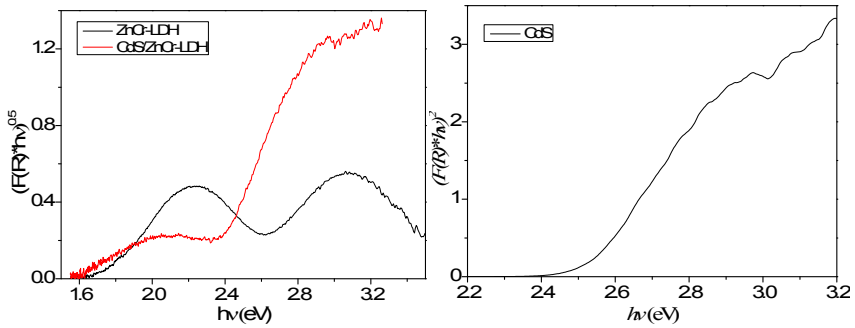

Fig. S1. The relationships between $(F(R)*hv)^{\alpha}$ and photon energy (hv).

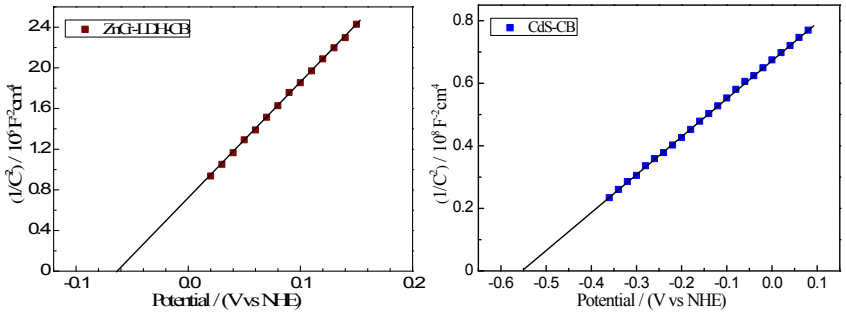

Fig. S2. Mott-Schottky plots of ZnCr-LDH and CdS.

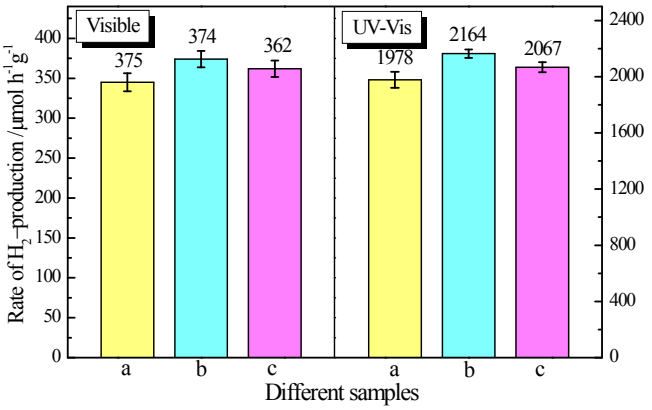

Fig. S3. Comparison of hydrogen evolution activity of the different CdS/ZnCr-LDH nanohybrids prepared from the molar ratio of CdS:ZnCr-LDH being 1:2 (a), 1:1 (b) and 2:1 (c).

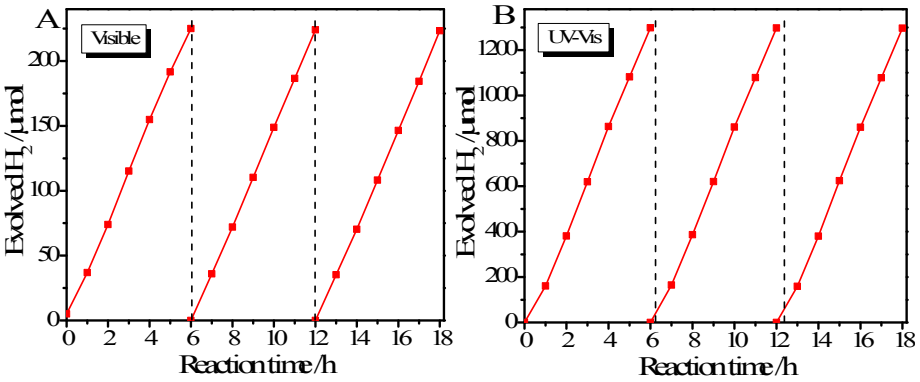

Fig. S4. Recyclability of photocatalytic hydrogen evolution over CdS/ZnCr-LDH under visible (A) and UV-visible (B) irradiation.