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# Highly efficient visible-light-driven photocatalytic hydrogen generation by immobilizing CdSe nanocrystals on ZnCr-layered double hydroxide nanosheets

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## ABSTRACT

Mesoporous CdSe/ZnCr-LDH nanohybrids were synthesized by mixing the suspensions containing cationic ZnCr-LDH nanosheets and anionic CdSe nanosol. It was revealed that the CdSe nanocrystals were immobilized on the ZnCr-layered double hydroxide 2D nanosheets. The strong electronic coupling between the two components in the formed heterostructured nanohybrids remarkably suppressed the photogenerated electron–hole recombination. The as-prepared nanohybrids displayed significantly enhanced photocatalytic activity. When the CdSe content was 30 wt%, the H<sub>2</sub>-evolution rate was 2196 μmol h<sup>-1</sup>·g<sup>-1</sup> with a quantum efficiency of 51.3% under visible-light irradiation, which is far superior to that of its parent ZnCr-LDH (18 μmol h<sup>-1</sup>·g<sup>-1</sup>). The present findings demonstrate that the self-assembly of CdSe-LDHs is quite effective in synthesizing novel LDHs-based visible-light photocatalyst with high performance in hydrogen evolution from water splitting.

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## Introduction

The development of renewable and environmental-friendly energy recourses has attracted extensive attention, reflecting the increasingly serious energy crisis and the environmental pollution caused by the burning of fossil fuels. The photoinduced production of H<sub>2</sub> from water by semiconductor photocatalysts is one of effective approaches to convert solar energy into clean energy [1–3]. Since the ultraviolet light only accounts for about 4% of the solar energy and the visible light

contributes to about 43%, it is important to develop visible-light-driven photocatalysts [1,4,5]. Although bulk CdSe ( $E_g = 1.7$  eV) was not active for photocatalytic hydrogen production, CdSe nanoribbons with an expanded band gap of 2.7 eV were found to photocatalytically produce hydrogen from irradiated Na<sub>2</sub>SO<sub>3</sub>/Na<sub>2</sub>S solution [6]. Osterloh et al. reported the quantitative relationship between the degree of quantum confinement and the photocatalytic water splitting activity [7,8]. To further enhance the photocatalytic activity of nano-CdSe, scientists have explored many approaches, including deposition of noble metals [9,10], decoration of

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carbon nanomaterials [11], and construction of heterojunction composites [12,13]. It was noteworthy that CdSe nanocrystal-graphene composites can efficiently enhance the charge separation and the electron transfer, resulting in improved photocurrent response [11].

Layered double hydroxides (LDHs),  $[M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O]$ , have attracted considerable attention due to their interesting physicochemical properties such as high anion exchange capacity and compositional flexibilities [14–17], and have been widely used as heterogeneous catalysts for base-catalyzed reactions or redox transformations [14,18–20]. Nevertheless, few researchers draw attention to the photocatalytic properties of LDHs [14,21]. Garcia et al. firstly reported the high photocatalytic activity of ZnCr-LDH for  $O_2$  generation [22]. Subsequently, it was found that NiTi-LDH [23], ZnCr-LDH/graphene [24], ZnCr-LDH/layered titanate [2], ZnCr-LDH/polyoxometates [25], and NiTi-LDH/graphene composites [26] have efficient photocatalysis for  $O_2$  evolution. However, there are only a few reports about photocatalytic water splitting into  $H_2$ . Very recently, Parida and Mohapatra reported that the carbonate intercalated ZnCr-LDH [27], and ternary Mg(Al + Fe)- and (Ni + Zn)Cr-LDHs have good photocatalytic activity towards hydrogen evolution from water [21,28].

It is noted that the action of formamide on LDHs can induce their exfoliation into unilamellar nanosheets with a sub-nanometer-level thickness [14,29]. Like graphene, LDH nanosheets have high specific areas and can make a strong electronic coupling with other nanoparticles possible. Coupling with two different semiconductors may construct a heterojunction structure, which will result in a spatial separation of photoinduced electrons and holes, a decrease of their recombination probability, and thus an increase of their lifetime and photocatalytic efficiency [1]. It is expected that strongly coupled hybrid systems can be achieved by intimately combining such a thin thickness of the photocatalytic nanosheets with other semiconductor particles with small crystal sizes [30,31]. The exfoliated LDH nanosheets are positively charged, which suggests the LDH-based nanohybrids can be prepared by electrostatically derived self-assembly in the presence of negatively charged nanoparticles. As mentioned above, the history of LDH-based photocatalysts is very short. LDH-based nanohybrids with photocatalytic activity are underdeveloped [25]. To the best of our knowledge, there is no report regarding the application of CdSe-LDHs on the photocatalytic  $H_2$  production. In this work, we have prepared CdSe/ZnCr-LDH nanohybrids via an electrostatically derived self-assembly of cationic ZnCr-LDH nanosheets with anionic CdSe nanosol. The present heterostructured nanohybrids are mesoporous and exhibit highly visible-light photocatalytic activity for  $H_2$  generation from water splitting.

## Experimental

### Synthesis of photocatalysts

All the reagents were of analytical-grade and were used as received without further purification. ZnCr-LDH in the nitrate form was prepared, similar to the reported procedure [32].

Under the protection of  $N_2$  atmosphere, a mixture of  $Zn(NO_3)_2 \cdot 6H_2O$ ,  $Cr(NO_3)_3 \cdot 9H_2O$  and  $NaNO_3$  with a Zn/Cr/ $NO_3$  molar ratio of 2:1:1 was dissolved in 100 mL of decarbonated deionized water ( $[Zn^{2+}] + [Cr^{3+}] + [NO_3^-] = 0.2 M$ ). The mixed solution was then titrated with 1.0 M NaOH up to pH 9.0 with vigorous stirring at room temperature. After 15 min, the resulting slurry was hydrothermally treated at 90 °C for 13 h, followed by separated by centrifugation, washed and vacuum-dried at 60 °C for 24 h. The exfoliation of ZnCr-LDH was completed by vigorous shaking LDH in formamide (1 g  $L^{-1}$ ) under  $N_2$  bubbling to avoid carbonate contamination, as reported previously [2].

The anionic CdSe nanosol was prepared as reported [33]. Under the protection of  $N_2$  atmosphere and constant stirring, a mixture of 2 mmol  $Cd(NO_3)_2 \cdot 4H_2O$  and 2 mmol mercaptoacetic acid were dissolved into 2000 mL deionized water, and the pH of the solution was then adjusted to 11.0 by the dropwise addition of 0.1 M NaOH. After 30 min, 200 mL of 0.01 M  $Na_2Se$  solution (0.222 g  $SeO_2$  dispersed in deionized water was reduced with 0.25 g  $NaBH_4$  until a clear, transparent solution was obtained under anaerobic conditions) was slowly injected into the above solution. The resulting suspension was kept stirring overnight under  $N_2$  environment before using. The whole preparation process required strictly anaerobic conditions to prevent  $Se^{2-}$  from oxidation. For comparison, the CdSe precipitates were obtained by adding methanol into the solution.

The nanohybrid CdSe/ZnCr-LDH was prepared by the dropwise addition of the above-mentioned CdSe nanosol ( $2.0 \times 10^{-4} M$ ) into the formamide suspension of ZnCr-LDH nanosheets ( $2.0 \times 10^{-4} M$ ) at room temperature. After stirring for 24 h, the mixed suspension was aged at 60 °C for 24 h. The resulting product was separated by centrifugation, washed with absolute ethanol and distilled water, and vacuum-dried at 60 °C for 24 h. To prevent the contamination of the LDHs materials from carbonate ions, the preparation processes throughout were carried out with decarbonated water under  $CO_2$ -free  $N_2$  atmosphere. The different products prepared at CdSe content of 20, 30, 40 and 45 wt% are designated as CZC-1, CZC-2, CZC-3 and CZC-4, respectively.

### Characterization

Powder X-ray diffraction (XRD) patterns were collected at room temperature on a Rigaku SmartLab 3 KW diffractometer using  $Cu K\alpha$  radiation ( $\lambda = 0.15418 nm$ ). High-resolution transmission electron microscope (HRTEM) images using a JEOL JEM-2100 with an accelerating voltage of 300 kV. The samples were suspended in ethanol and sonicated over 10 min. Subsequently, a drop of the supernatant dispersion was placed onto a carbon film supported by a copper grid. UV–vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-2550 spectrophotometer equipped with a 60-mm integrating sphere using  $BaSO_4$  as the reference. Specific surface area and porosity measurements were carried out on a Nova 1200e instrument at liquid-nitrogen temperature using ultrapure nitrogen gas as the adsorbate, in which all samples were degassed at 150 °C for 2 h in flowing  $N_2$  prior to the measurements. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Escalab MK II

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