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Ultrathin Ni (II)-based Coordination Polymer Nanosheets as Co-catalyst for Promoting Photocatalytic H₂-production

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The Ni (II) coordination polymers nanosheets (Ni-CPNS) were prepared via a top-down liquid ultrasonication exfoliation method. For the first time, Ni-CPNS was used as a co-catalyst (Ni-CPNS@CdS) via a mechanic grinding strategy. The optimized Ni-CPNS@CdS catalyst reached a super high visible-light photocatalytic hydrogen production activity of 10210 $\mu\text{mol h}^{-1} \text{g}^{-1}$, exceeding that of bare CdS nanoparticle by 1480%. Our work can open new avenues towards the design of stable and cheap CPNS co-catalyst to replace expensive and rare noble metals for photocatalysis processes.

solar energy driven H₂ production by water splitting has been regarded as an environment-friendly alternative to fossil fuels for solving energy and environmental problems.¹⁻⁴ Exploration of highly efficient and cost-effective H₂-production photocatalysts driven by sunlight has been vastly studied.⁵⁻⁸ Traditional noble-metal like Pt loaded photocatalysts almost keep the best activity and stability.⁹⁻¹⁰ However, noble-metal naturally restricts the commercialization due to extreme scarcity and high cost. Thus, developing stable, cheap and highly active co-catalyst to replace the noble-metal catalysts is of paramount significance for large-scale solar driven H₂ production in the future. Up to now, many earth-abundant co-catalysts were investigated. It is mainly focused on different modification methods like doping various guest and self-assembly nano materials.¹¹⁻¹² Although great progress was made in photocatalytic activities, current co-catalysts still exist intrinsic deficiencies such as insufficient surface functionalities and inefficient interfacial charge transfer.¹³⁻¹⁴ Therefore, it is urgent to search new co-catalyst to overcome these shortcomings.

Except for traditional applications,¹⁵⁻¹⁹ a few metal-organic frameworks (MOFs) are emerging as potential photo/electrocatalysts for hydrogen (H₂) evolution reaction.²⁰⁻²⁵ Compared with bulk MOFs, the two-dimensional (2D) MOF nanosheets showed more excellent

catalytic ability mainly due to more accessible active sites.²⁶ Different from 2D MOFs, one-dimensional (1D) metal-organic coordination polymers (CPs) have rich weak H-bond between layers and simple structure components.²⁷⁻²⁹ These advantages may be easily transferred to the CPs nano-sheets (CPNS). Obviously, CPNS building blocks have the potential to decrease aggregation and exhibit more active sites, contributing to increase the catalytic activity. As a result, exploring advanced functional CPNS as co-catalysts to replace the expensive noble metals for photocatalytic H₂-production are inspired, though it is a great challenge.

Scheme 1. The schematic illustration of the synthesis of Ni-CPNS and Ni-CPNS@CdS heterostructure for photocatalytic H₂-production.

In our previous work, we reported that the Ni-based CPs could be used as an excellent OER electrocatalyst in strong alkaline solutions.³⁰ Herein, taking advantage of the layered supramolecular frameworks, we successfully prepared a few-layer CPs nanosheets (Ni-CPNS) via a top-down liquid ultrasonication exfoliation method. Further, Ni-CPNS were introduced to the CdS nanoparticles forming Ni-CPNS@CdS composites (Scheme 1). Remarkably, the resulting Ni-CPNS@CdS hybrid materials greatly enhanced photocatalytic H₂-production under visible light-driven catalytic system. It is for the first time that single chain CPNS is used as co-catalyst for photocatalysis processes. A best hydrogen production activity of 10210 $\mu\text{mol h}^{-1} \text{g}^{-1}$ was achieved which is almost 14.8 times that of the bare CdS nanoparticles.

As a new member of the 2D nanomaterials family, few coordination polymer nanosheets materials have been reported up to date. The bulk Ni-CPs are constructed from strongly coordination bonded framework layers and connected by weak hydrogen bonds. The weak nature of interactions between the layers is critical for Ni-

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CPs to be delaminated by liquid ultrasonication exfoliation method (for details, see the Experimental Section in ESI†). To confirm the structure and morphology of nanosheets, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to characterize the delaminated Ni-CPNS. The SEM images indicated the overlaps of multilayer nanosheets (Fig. 1a-b). Compared with the bulk Ni-CPs, the color of Ni-CPNS was lighter as pale blue (Figure 1a-b, inset). As can be seen from Fig. 1c, TEM images further confirmed the sheet-like morphology. The colloidal aqueous suspension of Ni-CPs showed the Tyndall effect (Fig. 1d), indicating highly dispersion. The nanosheets have flat surfaces in AFM phase image (Fig. 1e, S1), revealing flaky 2D layers. The height of the nanosheets reached a thickness of ~ 5 nm according to cross-sectional analysis (Fig. 1f), corresponding to ten metal coordination layers or three 4, 4'-bipyridine ligands coordination layers (Fig. S2). In addition, PXRD studies exhibited that the Ni-CPNS kept high crystallinity and the pattern matched well with the bulk Ni-CPs (Fig. S3). As a result, these satisfied characterizations suggested the successful fabrication of the Ni-CPNS.

Fig. 1 SEM images of bulk Ni-CPs (a) and ultra-thin Ni-CPNS (b) (The inset displays different color before and after exfoliation). (c) TEM images of ultra-thin Ni-CPNS. (c) and its cross-sectional analysis (d). AFM image of ultra-thin Ni-CPNS (e) and the corresponding height profiles (f).

The rich active atoms such as Ni and N in Ni-CPNS encourage us to do further photocatalytic H_2 -production studies. By environment friendly mechanical grinding strategy, the as-synthesized Ni-CPNS and CdS nanoparticles (NPs) can be combined to prepare new hybrids photocatalysts. Ni-CPNS were used to integrate CdS NPs via mechanical-mixing under Argon environment until the final products became fine powder (see the ESI† for details). The successful preparation of the CdS nanoparticles (NPs) was demonstrated by TEM and PXRD analyses (Fig. S4-5).

The resulting products (Ni-CPNS@CdS) were thoroughly investigated. First, SEM, TEM, and energy dispersive X-ray (EDX) and EDX elemental mapping images (Fig. 2a-c) of the Ni-CPNS@CdS suggested that Ni-CPNS is successfully covered by CdS NPs. Then the elemental composition of Ni-CPNS@CdS were tested by X-ray photoelectron spectroscopy (XPS) (Fig. 2d-e, S6-7). In the XPS spectrum of Ni 2p region, two strong peaks at 873.9 and 856.3 eV can be assigned to Ni 2p_{1/2} and 2p_{3/2}, respectively, implying the presence of Ni in a divalent state. Compared to CdS, the Cd 3d and S 2p peaks in Ni-CPNS@CdS showed slightly right-shift of ca. 0.19 eV,

0.20 eV, respectively, confirming the electronic coupling between Ni-CPNS and CdS after their combination (Fig. 2b-c). To estimate the impact of Ni-CPNS on the CdS nanoparticles, we further studied the Zeta potential (ZP) and particles size distribution (PSD) of the CdS and Ni-CPNS@CdS (Fig. S8-9). The latter ZP value exhibited a slightly more negative potential than that of CdS NPs. Meanwhile, we also found the PSD of Ni-CPNS@CdS decreased. These measurements suggested that there was interaction force between Ni-CPNS and CdS particles' surface. Moreover, the synchrotron-based X-ray absorption near edge structure (XANES) characterization was tested to analyse whether the intimate electronic interaction exists in Ni-CPNS and CdS. As shown in Fig. 2f, the S L edge for Ni-CPNS@CdS shows a left-shift in contrast with CdS NPs, indicating the electron transfer from Ni-CPNS to the CdS NPs. Such strong electronic interaction is supposed to arise from the weak electronic push-pull effect between the CdS and Ni-CPNS. Unfortunately, the CdS and Ni-CPNS may be separated during the course of ultrasonication Ni-CPNS@CdS when preparing the AFM samples. We failed to obtain the perfect Ni-CPNS@CdS AFM characterizations (Fig. S10). However, we tried to mix the bulk Ni-CPs with CdS for grinding, SEM distinguished from the Ni-CPNS@CdS (Fig. S11). Especially, the XRD of CdS remains unchanged after mixed with Ni-CPNS (Fig. S5), indicating that the crystal structure of CdS still keeps stability after combination. Based on these results, Ni-CPNS and CdS NPs should form homogeneous hybrids materials of Ni-CPNS@CdS.

Fig. 2 (a) SEM image of Ni-CPNS@CdS. (b) TEM image of Ni-CPNS@CdS. (c) EDX spectrum of Ni-CPNS@CdS (inset: elemental mapping images). XPS spectra of (d) Cd 3d and (e) S 2p of CdS and Ni-CPNS@CdS. (f) S L edge XANES of CdS and Ni-CPNS@CdS.

Under a 300 W Xenon light, the photocatalytic H_2 -production reactions were performed using Ni-CPNS as a co-catalyst, along with triethanolamine (TEOA 17 vol.%) as a sacrificial electron donor. Remarkably, the coupling of Ni-CPNS with CdS indeed leads to an

obvious enhancement in the photocatalytic activity. As displayed in Fig. 3a, pristine CdS showed a very low photocatalytic activity of $690 \mu\text{mol h}^{-1} \text{g}^{-1}$. When a tiny amount of Ni-CPNS (1.5 wt.%) was loaded, the photocatalytic activity was greatly enhanced to $1228 \mu\text{mol h}^{-1} \text{g}^{-1}$. With the increasing amount of Ni-CPNS, the photocatalytic activity of Ni-CPNS@CdS is gradually enhanced. Surprisingly, with the optimal loading of 13 wt.% Ni-CPNS, Ni-CPNS@CdS shows the highest photocatalytic H_2 -production rate of $10210 \mu\text{mol h}^{-1} \text{g}^{-1}$, exceeding activity by 3.5 times for the bulk Ni-CPNS@CdS (Fig. S12) and more than 14 times for bare CdS (Fig. 3a). The photocatalytic activities Ni-CPNS@CdS is also comparable to or even better than most co-catalysts (Table S1). In this case, the superior activity of Ni-CPNS@CdS could be ascribed to the much stronger combination between CdS and Ni-CPNS, which greatly facilitates the rapid interfacial charge transfer. However, further increase in the loading of Ni-CPNS leads to the obvious decrease of photocatalytic activity due to Ni-CPNS overlapping on surface active sites and impeding the light absorption of CdS. These results indicated that Ni-CPNS@CdS can efficiently photocatalyze H_2 evolution, consequently, improving the HER performance of Ni-CPNS@CdS over CdS. Although Ni-CPNS and Ni-CPs displayed no activity toward H_2 production under the same environment (Fig. S12), Ni-CPNS has proven to be an efficient co-catalyst of CdS. In addition, after three runs (Fig. S13), the XRD, SEM and TEM as well as photocatalytic activity show no obvious change (Fig. S4, S14-15). It was noted that the Ni-CPNS@CdS still kept photocatalytic performance even after 20 hours test under visible light-driven catalytic processes (Fig. S16), indicating high catalytic stability.

Fig. 3 Photocatalytic performance and spectroscopy characterization. (a) A comparison of the photocatalytic H_2 -production activities of CdS and Ni-CPNS@CdS based co-catalysts (a: CdS, different Ni-CPNS loaded on CdS, b: 1.5 wt.%; c: 5.7 wt.%; d: 13 wt.%; e: 18 wt.%; f: 22 wt.%). (b) Ultraviolet-visible diffuse reflectance spectra of CdS, Ni-CPNS and Ni-CPNS@CdS. (c) Time-resolved PL spectra and (d) steady-state PL emission spectra of CdS and Ni-CPNS@CdS.

To understand photocatalytic H_2 -production reactions of Ni-CPNS based co-catalysts, firstly, the light harvesting capability of Ni-

CPNS@CdS was tested by the ultraviolet visible diffuse reflectance spectra. The absorption edge of Ni-CPNS@CdS showed no obvious shift compared to CdS (Fig. 3b), indicating that electron-rich elements such as N and O are not doped into the crystal structure of CdS. The strong electronic interaction played an important role on the rapid interfacial charge transfer between Ni-CPNS and CdS. Such an intimate interaction is further confirmed by the efficient interfacial charge transfer between Ni-CPNS and CdS, as proven by the steady-state photoluminescence (PL) spectra, transient-state PL spectra, transient photocurrent (TPC) and electrochemical impedance spectra (EIS) spectra. Compared with CdS NP, Ni-CPNS@CdS exhibits an increased long charge-carrier lifetime ($\tau_1 = 0.024 \text{ ns}$, $\tau_2 = 6.4 \text{ ns}$) and average charge-carrier lifetime ($\tau_{\text{av}} = 1.65 \text{ ns}$), suggesting that the coupling of Ni-CPNS cocatalyst with CdS can greatly elongate the charge-carrier lifetime (Fig. 3c). Obviously, Ni-CPNS@CdS shows a decreased peak intensity in steady-state PL spectra (Fig. 3d) than CdS NP, suggesting the effective separation of photoexcited electrons in Ni-CPNS@CdS. Moreover, TPC was obviously increased after loading Ni-CPNS (Fig. S17), meaning efficiency of charge separation was greatly improved. The satisfied test indicated that upon light irradiation photo-excited electrons are spatially separated and holes will be achieved in Ni-CPNS@CdS system. Especially, as compared with pure CdS and Ni-CPNS, Ni-CPNS@CdS was possessed of a smaller semicircle in electrochemical impedance spectroscopy (Fig. S18). In addition, the slope of Mott Schottky was evidently changed along the dopant of Ni-CPNS, indicating the charge-carrier density of Ni-CPNS@CdS is increased and the photogenerated hole is thermodynamically feasible (Fig. S19). Those results indicated the Ni-CPNS@CdS owned unique advantage as a photocatalytic catalyst for hydrogen evolution reaction under visible light.

Finally, from the point of crystal engineering, the Ni-CPNS possessed much richer six-membered ring than that of bulk Ni-CPNS, which more benefited interfacial charge separation and transfer in Ni-CPNS@CdS system due to the enhanced π -conjugated effect. Hence, upon light illumination, the photo-excited electrons can rapidly move to its abundant active sites, where the protons are adsorbed and reduced to evolve H_2 .

In conclusion, the ultrathin Ni(II)-based coordination polymer nanosheets were successfully obtained via the simple liquid ultrasonication exfoliation method, which is rarely reported for metal coordination polymers nano-sheets preparation. The resulting Ni-CPNS was employed as co-catalyst of CdS by an environment-friendly mechanical mixing method, showing greatly enhanced photocatalytic H_2 -production activity under visible light. This work not only opens a new window for designing the stable CPs co-catalyst photocatalytic H_2 -production, but also highlights huge potential of CPNS to replace noble metal in hetero-structures towards the development of sustainable energy.

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