CdS Nanoparticle-Decorated Cd Nanosheets for Efficient Visible Light-Driven Photocatalytic Hydrogen Evolution

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In order to satisfy growing global demand for H₂ in the chemical industry and fuel cell applications, there is an urgent need to develop new and sustainable technologies for H₂ production, distribution, and storage. Industrial H₂ production is currently based on steam methane reforming and the water-gas shift reaction, energy intensive processes that contribute significantly to anthropogenic CO₂ emissions. Water splitting, using sunlight and semiconductor photocatalysts, is widely regarded as a key future technology for hydrogen production, offering the potential of a near limitless H₂ supply with a low to zero carbon footprint. This approach has attracted huge interest since the pioneering work on TiO₂ by Fujishima and Honda in 1972. The valence and conduction band edges of TiO₂ are appropriate for direct water splitting, though the oxide’s wide band gap (E_g = 3.0–3.3 eV depending on the TiO₂ polymorph) means that only UV radiation can be utilized for water splitting reactions. Only 3%–4% of the solar spectrum satisfies this requirement. Other factors, such as rapid electron–hole pair recombination after photoexcitation, and the high overpotential for H₂ production on TiO₂ surfaces, cause H₂ production rates to be too low for practical applications. The performance of TiO₂ for H₂ production from water can be dramatically improved by modifying TiO₂ surfaces with H₂ evolution co-catalysts (e.g., Pd, Pt or Au) or through the use of sacrificial reagents. The inherent limitations of TiO₂ as photocatalyst, especially its wide band gap, motivate the search for alternative, low cost, visible light-driven photocatalysts for water-splitting.

Among the visible light-driven photocatalysts reported to date, CdS is of great interest due to its narrow bandgap (E_g = 2.42 eV) and relatively negative conduction band. CdS displays good rates of photocatalytic H₂ production in the presence of sacrificial reagents. To further improve its performance for photocatalytic H₂ production, various strategies have been adopted, with arguably the most effective strategy being the compositing of CdS nanoparticles (NPs) with conductive supports like carbon nanotube (CNT) or reduce graphene oxide (rGO) to create Schottky junction heterostructures. This reduces the aggregation of the CdS NPs and also facilitates charge separation, since photogenerated electrons in CdS can migrate onto the conductive supports. Gong and co-workers reported that H₂ production rate of a CdS/rGO nanocomposite is about five times higher than that of CdS NPs under visible-light irradiation. However, there are still several issues that limit the development of CNT or graphene-based CdS photocatalysts. For example, the electrical conductivity of most CNT or rGO supports is unsatisfactory (≈5–10 000 S m⁻¹) due to their imperfect structures and further by being black colored they absorb a fraction of the visible light needed by CdS to drive photocatalytic reactions. Improving the conductive and optical properties of the support is a current focus of many research groups, and stimulates the development of novel functional materials and composites.

Cd, a nonnoble metal with metallic luster, not only reflects visible light but possesses an excellent electrical conductivity (1.46 × 10⁷ S m⁻¹). Moreover, Cd is the precursor of important Cd-based semiconductors such as cadmium chalcogenides (CdS, CdSe). Thus, Cd is a strong candidate for the construction of efficient visible light-driven composite photocatalysts with CdS, though minimal work on such systems has been reported in the scientific literature. Wang and Xia prepared a series of Cd and Cd alloy submicron-spheres by bottom-up and top-down approaches in solutions. However, anisotropic Cd nanostructures, such as nanosheets with larger specific surface areas, have only previously been obtained by energy-intensive thermal decomposition methods at temperatures as high as 1000 °C. In this work, we describe the first successful synthesis of Cd nanosheets by a low-temperature, low-cost polyl reduction method. CdS nanoparticle-decorated Cd nanosheets (CdS NP/Cd NSs) were subsequently prepared by a facile oxidation-sulfurization process (Scheme 1). The as-prepared CdS NP/Cd NSs heterostructures exhibited superior photocatalytic H₂ production activity under visible light irradiation compared to unsupported CdS nanoparticles. Moreover, the enhancement in the H₂ production rate achieved using Cd NSs as a support was superior to that realized using CNT or rGO supports, which can be attributed to the superior electrical conductivity and visible light reflectivity of the Cd nanosheets. The promising
results of this study reveal that metallic Cd nanosheets are efficient electron acceptors and conductors, which can be exploited to construct low-cost Schottky junction heterostructure photocatalysts for applications such as solar H₂ production.

The morphology and structure of Cd NSs were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). From Figure 1a–c, it can be seen that as-prepared NSs sample consists of hexagonal platelets with an edge length of 1–3 µm and a thickness of 30–50 nm. The mean thickness of the Cd NSs was determined to be ≈42 nm by AFM, which is consistent with the SEM results (Figure S1, Supporting Information). From the representative high-resolution TEM (HRTEM) image in Figure 1d, clear lattice fringes were found with an interplanar lattice spacing of 0.26 nm, corresponding to the (100) face of the hexagonal Cd nanosheets. The selected area electron diffraction (SAED) pattern (inset of Figure 1e) can be indexed as [001] zone axis, indicating that the as-prepared Cd NSs grow along the [001] direction within the (002) facet. [18,19] And as shown in Figure 1e, the XRD pattern of the as-prepared Cd NSs can be indexed to hexagonal phase with the lattice constants of a = 0.30 nm and c = 0.56 nm (JCPDS Card 50-0674). The strongest peak in the XRD pattern can be attributed to the (002) facet, whilst the strongest peak in JCPDS card which presumably is for a randomly oriented powder is for (101) reflection. Both the SAED and XRD results agree well with the oriented-growth sheet-like structure of the Cd NSs seen by SEM and TEM. From the above, we can conclude that hexagonal Cd NSs with highly exposed (002) facets were successfully prepared by the high-temperature pyrolysis of Cd(Ac)₂ in DEG.

In order to fabricate CdS NP/Cd NSs, as-prepared Cd NSs were first exposed to air to form an oxide shell. The presence of the oxide shell was confirmed by XRD and TEM analyzes. Figure S2 (Supporting Information) shows XRD peaks characteristic of the Cd NSs, and additional peaks which are readily assigned to Cd(OH)₂ (JCPDS Card 31-0228). From the TEM images in Figure S3 (Supporting Information), a large number of NPs with size ≈7 nm were formed on the surface of the nanosheets. A lattice fringe spacing of 0.236 nm determined from the HRTEM image can be attributed to (002) facet of Cd(OH)₂, which supports the XRD data. The oxidized samples were subsequently sulfurred by immersion in an aqueous Na₂S solution. The resulting CdS NP/Cd NSs heterostructures were then characterized by XRD and electron microscopics. As shown in Figure 2a, the obtained XRD pattern contains features due to Cd NSs, as well as a new diffraction peak at 26.5° that can readily be assigned to the (111) face of cubic CdS. The full width at half maximum (FWHM) of the (111) reflection is very broad, indicating that the CdS is nanocrystalline. In the HRTEM image of CdS NP/Cd NSs (Figure 2a), a CdS NP can be seen with a lattice fringe spacing of 0.34 nm. This spacing is typical for the (111) facet of cubic CdS,[13] confirming the XRD result. Energy dispersive spectrometry (EDS) analyzes for CdS NP/Cd NSs (Figure S4, Supporting Information) gave a Cd:S molar ratio of ≈8:5, indicating that the as-prepared heterostructures are composed of metallic Cd and CdS in a molar ratio of ≈3:5. The detailed morphology of CdS NP/Cd NSs was characterized further by SEM and TEM. Figure 2b,c confirms that the CdS NP/Cd NSs complexes still retain the hexagonal structure of the Cd NSs support; while a large number of NPs with size ≈7–9 nm are seen on the surface of CdS NP/Cd NSs (Figure 2d). The SEM, TEM, EDS, and XRD analyzes confirm the successful fabrication of CdS NP-decorated Cd NSs through the oxidation–sulfurization process.

The absorption edge of CdS NP/Cd NSs is at 530 nm, compared to 420 nm for the Cd NSs (Figure S5, Supporting Information). The band gap energy of CdS NP/Cd NSs was determined to be 2.36 eV from a plot of (ahv)² versus photon energy (α = absorption coefficient) (inset of Figure S5, Supporting Information). Both the new optical absorption edge and the band gap values are characteristics of nanocrystalline CdS, suggesting that CdS NP/Cd NSs should be suitable for visible light-driven photocatalysis. Subsequently, the photocatalytic H₂ production activities of CdS NP/Cd NSs were evaluated under visible light irradiation (λ > 420 nm) with an aqueous solution containing Na₂SO₃ and Na₂S as sacrificial reagents. For comparison, the Cd NSs in CdS NP/Cd NSs were removed completely by immersion in dilute HNO₃ (denoted as CdS NP/Cd NSs-HNO₃) and then used as a control sample along with two other efficient CdS photocatalysts with the same crystal structure (Figure S6, Supporting Information), 6 nm CdS NPs and 50 nm CdS mesoporous hollow nanosheets (MHNSs) with a wall thickness of 4 nm (Figures S7 and S8, Supporting Information). As shown in Figure 3a, the photocatalytic H₂ evolution rate of CdS NP/Cd NSs (0.037 mmol h⁻¹) is 7.4, 2.8, and 4.6 times higher than that of CdS NPs (0.005 mmol h⁻¹), CdS MHNSs (0.013 mmol h⁻¹), and CdS NP/Cd NSs-HNO₃ (0.008 mmol h⁻¹), respectively. Results confirm that CdS NP/Cd NSs demonstrate excellent photocatalytic H₂ evolution efficiency compared to the corresponding structure without a Cd NS core or other commonly used CdS photocatalysts.

Decoration of semiconductor photocatalysts with Pt is an effective strategy for enhancing H₂ production by suppressing electron–hole pair recombination and reducing the overpotential of reduction/oxidation reactions.[21] Pt NPs were difficult to load on the surface of CdS NP or CdS HMNS using a conventional photodeposition method.[22] No Pt NPs could be identified by TEM (Figures S9a,b, Supporting Information) on the surface of CdS NPs and CdS HMNSs. Pt 4f X-ray photoelectron spectroscopy (XPS) analyzes (Figure S10, Supporting Information) revealed peaks located at 72.5–72.6 eV (Pt 4f⁷/₂) and 75.5–75.6 eV (Pt 4f⁵/₂), indicating that surface Pt species on the CdS NP or CdS HMNS photocatalysts were in the divalent Pt²⁺ state, in agreement with previous reports.[22] In contrast, thanks to the strong reducing ability of the Cd NSs, PtCl₆²⁻ can be easily chemically reduced to Pt⁰ on the surface of CdS NP/Cd NSs via

**Scheme 1.** Preparation of CdS NP/Cd NSs via a two-step process involving (1) Cd⁰ reduction in DEC to obtain Cd NSs, and (2) oxidation–sulfurization of Cd NSs.
a facile replacement reaction. The TEM images in Figure S9c (Supporting Information) show Pt NPs with sizes ranging from 10 to 200 nm on the surface of the CdS NP/Cd NSs support. The interplanar lattice spacing of 0.227 nm measured from Figure S9d (Supporting Information) agrees well with the lattice parameter of the Pt(111) plane. It is well documented that the activity of Pt$^0$ as a co-catalyst for photocatalytic H$_2$ production is much higher than that of Pt$^{2+}$. To probe the function of the Cd NSs in promoting photocatalytic H$_2$ production, Pt loaded CdS NP/Cd NSs-HNO$_3$ photocatalysts were also prepared and tested (Figure S9e, Supporting Information). Figure 3a shows that the H$_2$ evolution rate of Pt loaded CdS NP/Cd NSs (0.820 mmol h$^{-1}$) was 16.7, 6.4, and 7.1 times higher than that of Pt loaded CdS NPs (0.049 mmol h$^{-1}$), Pt loaded CdS MHNSs (0.129 mmol h$^{-1}$),
and Pt loaded CdS NP/Cd NSs-HNO$_3$ (0.115 mmol h$^{-1}$), respectively. Considering the mass fraction of CdS in the CdS NP/Cd NSs ($\approx 68.0$ wt% CdS determined by EDS), the weighted H$_2$ evolution rate of Pt loaded CdS NP/Cd NSs (1.21 mmol h$^{-1}$ g$_{\text{CdS}}$$^{-1}$) is actually even higher, around 10.4 times higher than that of Pt loaded CdS NP/Cd NSs-HNO$_3$ (0.115 mmol h$^{-1}$ g$_{\text{CdS}}$$^{-1}$). Further, it should be noted that the rate enhancement factor of photocatalytic H$_2$ production caused by the presence of the Cd NS supports is much larger than enhancements achieved for CdS photocatalysts composited with CNT or graphene derivative supports (typical enhancements $\approx1.5$–$5$ times, Table S1, Supporting Information).\cite{13,23–36} Furthermore, we found that the H$_2$ evolution rate of CdS NP/Cd NSs can be further improved by adjustment of Pt loading. Figure 3b shows that a H$_2$ evolution rate of 1.68 mmol h$^{-1}$ was achieved at a Pt loading of 4 wt%, which appears to be the optimum loading under the photocatalytic test conditions used here, with the quantum efficiency of the photocatalytic H$_2$ evolution determined to be $\approx33.0\%$ at 420 nm.

The catalytic stability of 1.0 wt% Pt loaded CdS NP/Cd NSs was evaluated using repeated cycle experiments (Figure S12, Supporting Information). For each new cycle, the H$_2$ gas evolved in the previous cycle was removed, then the H$_2$ production activity under visible light was monitored over a 4 h period. The time course plots of H$_2$ evolution show that the photocatalyst maintains excellent activity over six successive test cycles. The slight decrease in the H$_2$ evolution rate in each successive run can be attributed to the progressive consumption of sacrificial reagents (SO$_3$$^2$ and S$^2$). The high stability of the photocatalyst is encouraging for practical applications.

In order to understand the remarkable enhancement of the photocatalytic performance realized in the CdS NP/Cd NSs system, the texture and charge separation/recombination characteristics of the CdS-based photocatalysts were examined. Specific surface area is an important parameter, since photocatalytic activities often correlate with active surface area.\cite{37} N$_2$ adsorption–desorption isotherms presented in Figure S13 (Supporting Information) for CdS NP, CdS MHNSs, and CdS NP/Cd NSs are type IV, indicating the existence of meso-sized pore structures. Specific surface areas obtained from the adsorption isotherms by the Brunauer–Emmett–Teller (BET) method are 150, 115, and 25 m$^2$ g$^{-1}$ for CdS NPs, CdS MHNSs, and CdS NP/Cd NSs, respectively. Interestingly, the specific surface area of CdS NP/Cd NSs is the lowest amongst the three samples. It can, therefore, be concluded that factors other than specific surface area are important to achieving high H$_2$ production rates in the CdS NP/Cd NSs system.
Compared with the other three photocatalysts which contain a single CdS phase, the CdS NP/Cd NSs contain intrinsic Schottky junctions, which are expected to strongly enhance the separation efficiency of photogenerated carriers.\(^{24,38}\) Electron–hole pair recombination in semiconductors following photoexcitation gives rise to photoluminescence (PL), the monitoring of which allows the efficiency of charge carrier separation in semiconductor photocatalysts to be gauged.

**Figure 4**a shows the room-temperature PL spectra of CdS NPs, CdS MHNSs, CdS NP/Cd NSs, and CdS NP/Cd NSs-HNO\(_3\). The CdS NPs, CdS MHNSs, and CdS NP/Cd NSs-HNO\(_3\) show intense and broad emission peaks at 588 nm, which can be attributed to the radiative recombination of electron–hole pairs in CdS, and include contributions from surface defect states.\(^{39}\) In contrast, the PL spectrum of CdS NP/Cd NSs does not show a broad feature at 588 nm, indicating a low recombination rate. It is concluded that the presence of Cd metal suppressed the recombination of photogenerated charge carriers, presumably by accepting electron photoexcited in CdS, which in turn greatly promoted the photocatalytic performance of CdS NP/Cd NSs. The photogenerated electron transfer process can also be followed by monitoring the emission decays of the excited CdS photocatalysts at room temperature. Rapid charge transport in CdS NP/Cd NSs was confirmed by electrochemical impedance spectra (EIS). The CdS NPs and CdS MHNSs photocatalysts give near identical EIS Nyquist plots (Figure 4b), indicating that charge transfer processes in these materials are similar. For CdS NP/Cd NSs, the semicircle size of the Nyquist plot is much smaller, reflecting an acceleration of charge transfer process in presence of Cd NSs.\(^{40}\) Therefore, Cd NSs increase both charge separation and the kinetics of charge transfer in the composite.

Based on the results and discussion above, a probable mechanism for the improved photocatalytic activity of CdS NP/Cd NSs can be proposed, based on the formation of Schottky junctions (Scheme 2). Under visible light irradiation, electrons are excited from the valence band (VB) to the conduction band (CB) of CdS NPs, and are then rapidly transferred to Cd NSs via the Schottky junction, finally migrating onto the Pt co-catalyst quickly due to the excellent electrical conductivity of Cd NSs to react with H\(^+\). Holes in the VB of the CdS NPs react with reducing agents (electron donors) at the surface of CdS. Through these processes, electron–hole recombination in the Cd NPs is effectively suppressed, particularly when compared with the pure CdS systems. The silvery Cd NSs (as shown in Figure S14, Supporting Information) likely act both as a support reducing the aggregation of the CdS NPs and micro-mirrors for light, allowing enhanced light absorption by CdS.
Scheme 2. Schematic showing charge separation and transfer processes in CdS NP/Cd NSs under visible light.

NPs and improving overall light utilization efficiency. It is conceivable, therefore, that Cd NSs enhance the photocatalytic performance of the CdS NPs in four ways: (1) reducing the aggregation of the CdS NPs; (2) facilitating charge separation; (3) accelerating charge transfer; and (4) enhancing light absorption by reflecting more light to the active surfaces of the CdS absorber. 

In summary, metal Cd NSs with thicknesses ranging from 30–50 nm were synthesized for the first time by the polyl reduction method and transformed into CdS NP-decorated Cd NSs heterostructured photocatalysts by an oxidation–sulfurization process. CdS NP/Cd NSs photocatalysts showed significantly enhanced activity in visible light-driven photocatalytic H₂ production compared with conventional unsupported CdS photocatalysts. The dramatically enhanced photocatalytic performance of CdS NP/Cd NSs can be attributed to the electrical conductivity and high optical reflectivity of Cd NSs, which results in very efficient charge carrier separation across the rectifying Schottky junctions formed between the CdS NP absorbers and Cd NSs. This novel study demonstrates the potential of non Noble metal Cd NSs as supports for the construction of low-cost Schottky junction heterostructure photocatalysts with an excellent activity. The Cd NSs technology reported here is expected to be transferable to other heterojunction photocatalyst systems, thus enabling the development of many new and improved solar energy conversion systems.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors are grateful for the financial support from the Ministry of Science and Technology of China (2013CB834505, 2014CB239402), the Key Research Programme of the Chinese Academy of Sciences (KGZD-EW-T05), the National Natural Science Foundation of China (51322213, 21401206, 21401207, 21301183, 51172245, 91127005), the Beijing Natural Science Foundation (2152033, 2122054, 2154058), and the National Program for Support of Top-notch Young Professionals.

Received: June 24, 2015
Revised: September 15, 2015
Published online: November 9, 2015

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