Nitridation of CoWO₄/CdS Nanocomposite Formed Metal Nitrides Assisting Efficiently Photocatalytic Hydrogen Evolution

Wandi Kuang, Xiangjian Meng, Caihong Wang, Bhusankar Talluri, Tiju Thomas, Chunjie Jiang,* Siqi Liu,* and Minghui Yang*

ABSTRACT: Nitridation of CoWO₄/CdS nanocomposite results in the formation of metal nitrides on the surface of CdS. The high electrical conductivity, appropriate binding energy for hydrogen, and Pt-like properties of the surface nitrides promote the H₂ evolution performance. Therefore, the optimal performance of nitrided CoWO₄/CdS (CoWO₄/CdS-N, 3650 μmol·h⁻¹·g⁻¹) is higher than that of Pt/CdS (2948 μmol·h⁻¹·g⁻¹).

1. INTRODUCTION

The extensive use of fossil fuels and the concomitant environmental pollution are evidently serious challenges. Hydrogen (H₂) is a clean fuel with a high specific enthalpy of combustion. Photocatalytic H₂ production is cost-effective and efficient, which could in fact offer a rather promising approach to solve the energy crisis.

Since the report by Fujishima and Honda, Pt/TiO₂ is considered a champion electrode material for water splitting H₂ production. Thereafter, various semiconductors such as oxides, sulfides, and oxynitrides have been deployed for photocatalytic water splitting.

CdS is a semiconductor with a suitable band gap (2.4 eV), but pure CdS has low performance in practical photocatalytic water splitting due to the fast charge recombination. Loading suitable semiconductor or co-catalyst has been considered a reasonable means to promote the photocatalytic activity of pure CdS. Tungstate-based metal oxides offer advantages associated with ease of synthesis, low cost, low toxicity, chemical stability, and multifunctionality. Among tungstates, cobalt tungstate (CoWO₄) is a semiconductor with an appropriate band gap of 2.8 eV for visible light absorption. Hence, it has gained significant attention in the photocatalytic field. Cui et al. reported that modified CoWO₄ on CdS demonstrated good performance for photocatalytic applications.

Another modification strategy to enhance the activity involves loading suitable co-catalysts. Generally, the best-known co-catalysts in photocatalysis are noble metals. However, the high cost of noble metals reduces their practical applications. Therefore, it is desirable to find alternative solutions to overcome this limitation. One of the solutions is to prepare a noble-metal-based alloy as a co-catalyst to decrease the loading amount. But most of the solutions are still developing cheaper co-catalysts to replace precious metals in photocatalytic H₂ production.

Recently, metal nitrides have emerged as a substitute for noble metals and have attracted increasing attention due to their high electrical conductivity, good corrosion resistance, high chemical stability, and unique Pt-like properties. The relatively high binding energy of hydrogen and the increased density of states on the surface make them suitable as low-cost co-catalysts for replacing noble metals toward photocatalytic H₂ production reactions.

In this work, we prepare a CoWO₄/CdS nanocomposite photocatalyst by the in situ hydrothermal method. Further nitridation of this nanocomposite results in the formation of metal nitrides on the surface of CdS. The resultant photocatalyst exhibits an optimal H₂ production rate of ∼3650 μmol·h⁻¹·g⁻¹ at λ > 400 nm. This is 1.24 times higher than that of Pt/CdS composite (2948 μmol·h⁻¹·g⁻¹) and 2.98 times higher than that of non-nitrided CoWO₄/CdS (1224 μmol·h⁻¹·g⁻¹). This work could offer new insights for the fabrication of low-cost non-noble-metal nanocomposites for efficient artificial photosynthesis.

2. EXPERIMENTAL SECTION

2.1. Materials. All chemicals used for the synthesis are of analytical grade and obtained from commercial suppliers.
without further purification. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) and sodium tungstate dihydrate (Na$_2$WO$_4$·2H$_2$O) are purchased from Aladdin Chemicals (China). Cadmium chloride (CdCl$_2$), sodium diethyldithiocarbamate trihydrate (C$_{10}$H$_{18}$N$_2$S$_2$·3H$_2$O), ethylenediamine (C$_2$H$_8$N$_2$), absolute ethanol (C$_2$H$_6$O), and lactic acid (C$_3$H$_6$O$_3$) are purchased from Sinopharm, China. Deionized steel autoclave. The autoclave was maintained at 180 °C for 24 h and then allowed to cool to room temperature. A yellowish solid samples are characterized by an X-ray diffractometer. The band gap energy is obtained using the Kubelka−Munk relation, $R/S = (1 - R)^2/2R$, where $R$ is the value of reflectance measurements, and $K$ and $S$ denote the absorption and scattering coefficients of the sample, respectively. Photoluminescence (PL) spectra are recorded on a Horiba Jobin Yvon Fluoromax 4C-L spectrophotometer with an excitation wavelength of 405 nm. Morphologies of the samples are characterized by a field-emission scanning electron microscope (FE-SEM, Hitachi S4800). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images are obtained using a JEOL model JEM 2010 EX instrument at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) is carried out using an AXIS Ultra DLD Shimadzu spectrometer with Al $\text{K}\alpha$ excitation (1486.6 eV).

2.7. Photocatalytic H$_2$ Production Measurements. Photocatalytic experiments are carried out in a Pyrex vessel, which is attached to a closed gas circulation and evacuation system. Photoreduction of H$_2$O to H$_2$ is performed by dispersing 20 mg of photocatalyst in an 80 mL aqueous solution containing 8 mL of lactic acid as the sacrificial agent. In a typical photocatalytic reaction, a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfection Technology Co., Ltd.) with a UV-CUT filter to cut off light of wavelength $< 400$ nm is used as the irradiation source. Continuous magnetic stirring is applied at the bottom of the reactor to keep the photocatalyst in suspension status during the whole experiments. The temperature of the reaction solution is maintained at 278 K by flowing cooling water during the reaction. An online gas chromatograph (Scion GC7900, Ar as carrier gas) with a thermal conductivity detector (TCD) is used for the in situ monitoring of the evolved H$_2$.

3. RESULTS AND DISCUSSION

Scheme 1 explains the synthesis process of nitrided CoWO$_4$/CdS (CoWO$_4$/CdS-N) composites. First, the CoWO$_4$/CdS composites are synthesized by a hydrothermal method at 180 °C for 8 h. Cobalt salt and tungsten salt with a molar ratio of 1:1 are added as a precursor to the CdS NWs suspension with various concentrations (0.2, 0.5, and 0.8 mmol). The corresponding samples are labeled as CoWO$_4$−0.2-CdS, CoWO$_4$−0.5-CdS, and CoWO$_4$−0.8-CdS. Afterward, CoWO$_4$/CdS-N nanocomposites are prepared by further nitridation at 600 °C for 1 h. Similarly, the samples are labeled as CoWO$_4$−0.2-CdS-N$_x$, CoWO$_4$−0.5-CdS-N$_x$, and CoWO$_4$−0.8-CdS-N$_x$, respectively. As shown in Figures 1 and S1, the X-ray diffraction (XRD) patterns of CoWO$_4$/CdS and CoWO$_4$/CdS-N mainly exhibit hexagonal-phase CdS (JCPDS No. 01-075-1545), which is similar to that of blank CdS nanowires (NWs). With increasing precursor amount of CoWO$_4$ to 0.8 mmol, diffraction peaks of monoclinic-phase CoWO$_4$ (JCPDS No. 01-072-0479) and its derived nitride peaks (W$_N$$_4$ phases; JCPDS No. 03-065-4761) can be observed in CoWO$_4$−0.8-CdS and CoWO$_4$−0.8-CdS-N composites, respectively.

The morphologies of the as-prepared composites are investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure S2a,b, the length of CdS NWs lies in the range of 3−10 μm with an average diameter of 40−70 nm. Pure CoWO$_4$ NPs show quasi-spherical morphology and size in the range of 50−
CdS-N composites. The sizes of NPs on the NW surface in CoWO4/CdS-N samples are similar to those of pure CoWO4 NPs. Interestingly, the sizes of NPs on the CdS NWs become smaller, in the range of 30–60 nm after nitridation. This may be due to the formation of new nitrides. The CoWO4−0.5-CdS and CoWO4−0.5-CdS-N samples are then investigated by TEM and high-resolution TEM (HRTEM), which are shown in Figure 2c−f. The morphologies of the two samples in the TEM images are consistent with the SEM images. In addition, the HRTEM image indicates lattice fringes of dimensions 0.361 and 0.316 nm, which correspond to the (110) plane of monoclinic CoWO4 and the (101) plane of hexagonal CdS phase. After nitridation, it is observed that the lattice spacings of 0.179, 0.218, and 0.238 nm correspond to the (200) plane of cubic Co4N, the (100) plane of cubic Co, and the (102) plane of hexagonal W5N4. These results clearly indicate that the nitridation process has transformed CoWO4 into metal nitrides and metal.

Surface compositions and chemical states are recorded using X-ray photoelectron spectroscopy (XPS). As shown in Figure 3a,b, all of the phases in the composites evidently have Cd2+ and S2− ions.32−34 Notably, both Cd 3d and S 2p peaks in CoWO4/CdS-N exhibit a shift of about 0.2 eV toward higher binding energies compared to CoWO4/CdS. This is attributed to the strong interaction between the nitrides formed on the surface and CdS.35−37 Hence, there is electronic coupling between the nitrides, metal, and CdS NWs. In the Co 2p spectra (Figure 3c), the two peaks observed in CoWO4/CdS are assigned to Co2+ in CoWO4.38,39 The Co 2p spectrum in CoWO4/CdS-N has multiple peaks, indicating more than one chemical state of Co. The peaks located at 778.26 and 793.31 eV are assigned to Co−Co, while the peaks centered at 780.77 and 796.17 eV correspond to Co−N bonds.40,41 Afterward, for the W 4f spectra (Figure 3d), the two peaks in CoWO4/CdS are assigned to W6+ in CoWO4.42 CoWO4/CdS-N displays three species, and the binding energies of 32.46 and 34.61 eV are attributed to the valence state between W5+ and W6+. This species is denoted by Wm−n+, where 0 < n < 4. Considering that 33.10 and 35.25 eV correspond to Wm−n+, these two species indicate the presence of the W−N bond.43,44 Besides, the broad peaks at 36.03 and 38.18 eV are attributed to the W−O bond, a typical phenomenon in nitrides.40 The N 1s spectrum shown in Figure S3 also reveals that N species exist as metal−N bonds, further confirming the existence of nitrides on the surface of CdS.40 Based on the above, it could be indicated that the CoWO4 in CoWO4/CdS samples has been destroyed in the nitridation process and Co2+ and W6+ are reduced to low valence states (Co2+ and W3+) with the formation of new nitrides on the CdS NWs, which is consistent with the TEM results.

As shown in Figure S4, the UV−vis DRS spectra of CdS and CoWO4−0.5-CdS composites exhibit absorption edges rising at around 516 nm, and the corresponding band gap is found to be 2.40 eV. This is consistent with the reported spectra.12,29 CdS-N shows a marginal red shift compared to pure CdS, and the band gap shifts from 2.40 to 2.35 eV, which may be due to the structural defects caused by nitridation (Figure S4b).45,46 The UV−vis DRS spectra of CdS in CoWO4/CdS-N samples are shown in Figure S4c−d. CoWO4−0.5-CdS shows a distinct red shift in the absorption edge, and the band gap shifts from 2.35 to 2.17 eV. It could come from the interfacial interactions between CdS NWs and the surface metal nitrides (other proportions are shown in Figure S4e−f). Moreover, CoWO4−0.5-CdS-N shows a better light absorption intensity than CoWO4−0.5-CdS and pure CdS in visible light regions, which is attributed to the intrinsic optical properties of metal nitrides.47

Figure 4a and SS display the photocatalytic H2 evolution performance of as-prepared samples under visible light irradiation (λ > 400 nm). Pure CdS and CoWO4 samples show low photocatalytic activities of 35 and 82 μmol·g−1·h−1, respectively. Before the nitridation treatment, CoWO4−0.5-CdS exhibits a H2 evolution rate of 1224 μmol·g−1·h−1, which is 35 times higher than that of pure CdS and 15 times higher than that of pure CoWO4. After nitridation, CoWO4−0.5-CdS-N shows the best photocatalytic hydrogen production activity (3650 μmol·g−1·h−1); this is 104 times higher than pure CdS, 298 times higher than CoWO4−0.5-CdS, and 1.24 times higher than CdS−1%Pt (2948 μmol·g−1·h−1). The CoWO4/CdS-N samples show evidently higher H2 production activity
than the non-nitrided composites; this is attributed to the presence of metal nitrides on the surface. The presence of nitrides on the CdS surface evidently correlates with an enhanced H₂ evolution rate. Through a rough comparison to the other CdS-based photocatalysts in Table S1, the metal nitrides formed from CoWO₄-N have been proved to be excellent co-catalysts to improve the H₂ evolution rate. In addition, the H₂ evolution rates for as-prepared catalysts are carried out in ultrapure water (Figure S6). Pure CdS and CoWO₄₋₀.₅-CdS both exhibit trace hydrogen production due to the fast recombination of the photoinduced carriers. Moreover, CoWO₄₋₀.₅-CdS-N still exhibits a photoactivity of 0.₁₁₈ μmol·g⁻¹·h⁻¹ even without adding a sacrificial reagent, which indicates that metal nitrides could increase the separation rate of photoinduced carriers. Recycling experiments of the CoWO₄₋₀.₅-CdS-N photocatalyst shown in Figure S7 exhibit no significant decrease of hydrogen production after five consecutive runs, indicating that CoWO₄₋₀.₅-CdS-N has good photocatalytic stability. Besides, the corresponding XRD pattern and SEM image of the sample after the long-term reactions are similar to those of the fresh photocatalyst (Figure S8), further certifying the photocatalytic stability of CoWO₄₋₀.₅-CdS-N. Photoluminescence (PL) emission spectra are used to study the charge carrier recombination and electronic transition behavior of the as-prepared photocatalysts under light irradiation with an excitation wavelength of 405 nm. As observed in Figure S9, pure CdS NWs show the highest PL intensity compared to the other two samples, which proves the rapid recombination of photogenerated electron–hole pairs. After nitridation, the CoWO₄₋₀.₅-CdS-N composite exhibits the weakest peak intensity, indicating that the formation of metal nitrides can greatly suppress the recombination of photogenerated carriers, which could facilitate effective charge transfer and improve the photocatalytic performance of CdS for hydrogen production.⁴⁸,⁴⁹

Photocatalytic experiments are further performed to demonstrate the efficient transfer of charge carriers in the nanocomposite photocatalysts under visible light irradiation. The transient photocurrent response (I–t) curves of as-prepared samples is recorded for several visible lights on–off cycles. As shown in Figure 4b, the CoWO₄₋₀.₅-CdS-N sample exhibits a much higher photocurrent intensity than CoWO₄₋₀.₅-CdS and pure CdS under the same condition, suggesting that a higher separation efficiency of the photogenerated electron–hole pairs is achieved after loading metal nitrides on the surface of CdS NWs. Therefore, more photogenerated electrons could be created and transferred to produce hydrogen. The above results further demonstrate that the metal nitrides on the surface of CdS NWs could dramatically promote the photocatalytic activity by increasing the charge transfer and separation efficiency.⁵₀,⁵¹ Another electrochemical characterization of EIS spectra is shown in Figure 4c. The CoWO₄₋₀.₅-CdS-N sample has the smallest radius of the arc, which is an indication of the charge transfer resistance being low in this case. This indicates that the CoWO₄₋₀.₅-CdS-N sample has optimal charge separation and transfer efficiency.⁵² This proves that nitrides on the CdS surface can indeed improve the charge transfer properties and the photocatalytic performance.

Cyclic voltammetry (CV) measurement results are shown in Figure 4d. It is clearly seen that CoWO₄₋₀.₅-CdS-N exhibits a larger anodic current density than pure CdS and CoWO₄₋₀.₅-CdS. This indicates a remarkably increased electron transfer rate associated with the CoWO₄₋₀.₅-CdS-N, which is attributed to the introduction of nitrides with a high electrical conductivity.⁵₃ The H₂ evolution kinetics of the three samples is displayed by the polarization curves in Figure 4e. It can be seen that the sample under nitridation shows the lowest electrocatalytic H₂ generation overpotential and enhances the current density. The superior activity of the metal nitride could be explained by the high binding energy of hydrogen, which

![Figure 3. XPS spectra of (a) Cd 3d; (b) S 2p for CdS, CoWO₄/CdS, and CoWO₄/CdS-N composite; (c) Co 2p; and (d) W 4f for CoWO₄/CdS and CoWO₄/CdS-N composites.](image-url)
results in higher hydrogen adsorption to the metal nitride surface. Meanwhile, the presence of nitrogen strongly influences the electronic properties of the metal by increasing the density of electrons on the surface.\textsuperscript{54−56} Therefore, the metal nitrides formed on the surface of CdS could serve as excellent co-catalysts and provide more active sites to improve the separation efficiency of photogenerated charge carriers, promote the H\textsubscript{2} generation kinetics, and enhance the photocatalytic performance of semiconductors.\textsuperscript{57−60}

Based on the above, a possible mechanism of the H\textsubscript{2} production performance of the CoWO\textsubscript{4}/CdS-N composite is proposed (Figure 4f). Under visible light irradiation, CdS NWs are excited to produce photoinduced electrons and holes. Pure metal nitrides are not active for H\textsubscript{2} production and cannot absorb visible light to produce electron−hole pairs according to previous reports.\textsuperscript{61,62} Therefore, benefiting from the high electrical conductivity and Pt-like properties of the metal nitrides, the photogenerated electrons in the conduction band of CdS can quickly get transferred to the surface nitrides and be captured, which would improve the separation rate of photogenerated electrons and holes and further enhance the H\textsubscript{2} evolution rate of the pure CdS. Meanwhile, the holes in the valence band of CdS are trapped by the sacrificial agent lactic acid. The metal nitride co-catalysts on the CdS surface accelerate the H\textsubscript{2}-generation kinetics. Therefore, the CoWO\textsubscript{4}/CdS-N composites display improved photocatalytic H\textsubscript{2} evolution efficiency compared to pure CdS and CoWO\textsubscript{4}/CdS composites.

4. CONCLUSIONS

In summary, CoWO\textsubscript{4}/CdS-N nanocomposites are successfully synthesized. The nitridation process causes the formation of metal nitrides on the CdS NWs. The surface nitrides which act as co-catalysts not only help with enhanced absorption and improve the separation efficiency of photogenerated charge carrier pairs but also accelerate the H\textsubscript{2}-production kinetics. The optimal sample exhibits a H\textsubscript{2} production rate of 3650 μmol·g\textsuperscript{−1}·h\textsuperscript{−1}, which is 104 times higher than that of pure CdS, 2.98 times higher than that of CoWO\textsubscript{4}/CdS, and 1.24 times higher than that of Pt/CdS. This work provides fresh insights into the use of metal nitride co-catalysts for enhancing the photocatalytic hydrogen production rate.

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00288.

Photoelectrochemical measurements, XRD patterns, SEM images, XPS spectra, UV−vis DRS spectra,
photocatalytic hydrogen production rates of photocatalysts, photoluminescence spectra, and a table of photocatalytic activity for photocatalysts (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Chunjie Jiang — School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P. R. China; Email: jiangcj@lnnu.edu.cn

Siqi Liu — Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China; Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China; Email: liusiqi@nimte.ac.cn

Minghui Yang — Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China; Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China; Email: myang@nimte.ac.cn

**Authors**

Wandi Kuang — School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P. R. China

Xiangian Meng — Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China; Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Caihong Wang — Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China; Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Bhusankar Talluri — Department of Metallurgical and Materials Engineering, DST Solar Energy Harnessing Center, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

Tiju Thomas — Department of Metallurgical and Materials Engineering, DST Solar Energy Harnessing Center, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India; orcid.org/0000-0001-8322-6387

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00288

**Notes**

The authors declare no competing financial interest.

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