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Copper Phosphide Modified Cadmium Sulfide Nanorods as a Novel p-n Heterojunction for Highly Efficient Visible-Light-Driven Hydrogen Production in Water

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Developing efficient photocatalysts made of earth-abundant elements for hydrogen (H₂) production from water is considered to be a key pathway for future clean energy supply. Herein we give the first report that p-type copper phosphide (Cu₃P) can be an efficient promoter to improve photocatalytic H₂ production from water when loaded on n-type cadmium sulfide nanorods (CdS NRs). The formation of a p-n junction in Cu₃P/CdS NRs leads to fast charge transfer and enhanced photocatalytic activity under visible light irradiation. Under optimal conditions, the H₂ evolution rate was as high as ~200 μmol h⁻¹ mg⁻¹ (λ > 420 nm) and the apparent quantum yield at λ = 450 nm was ~25% in water.

Due to serious environmental issues and the increasing clean energy demand, developing new energy sources to substitute for fossil fuels is an urgent priority. Hydrogen is considered to be an ideal energy carrier for a future clean energy supply system because of its high energy capacity and environmental friendliness. Since the discovery of hydrogen production by the photoelectrochemical water splitting on TiO₂ in early 1970s, photocatalytic hydrogen production from water over semiconductors has attracted much attention during the past few decades. The main challenge for its commercial application is to produce hydrogen efficiently using photocatalysts that have long-term stability and low cost. To achieve hydrogen production under visible light, the photocatalysts should have a proper band gap for visible light absorption and enough redox potential for water splitting.

Among all the visible-light-responsive photocatalysts, n-type semiconductor CdS appears to be one of the most promising materials for photocatalytic H₂ evolution due to its high activity under visible light (narrow band gap, E_g ~2.4 eV) and sufficiently negative flat-band potential for proton reduction. However, pure CdS is not very stable and exhibits low photocatalytic activity due to its fast electron-hole recombination and photocorrosion. To solve these problems, several approaches have been applied to functionalize CdS semiconductor, such as loading an appropriate cocatalyst. Cocatalysts, which can effectively enhance the transfer of photogenerated charge carriers, play a very important role in promoting the photocatalytic activity. The most common and effective cocatalyst is Pt, and other noble-metal-based materials, such as Ru and Pd, are also studied as cocatalysts owing to the physicochemical properties being similar to Pt. Unfortunately, the high price and scarce supply of noble metals limit their large-scale application. An alternative that has been studied is cocatalysts based on non-noble metals, such as Mo, Co, and Ni. Unluckily, the catalytic performances of these cocatalysts are generally worse than noble metals and therefore, it is necessary to develop more cost-effective and robust catalysts for H₂ production. Another approach to enhance the photocatalytic activity is to construct a p-n junction to retard the electron-hole recombination and improve the charge separation.

Cu₃P, as a p-type semiconductor, was previously reported for application in lithium ion batteries. However, the use of Cu₃P for photocatalytic H₂ production has not received prior investigation. Herein we report the synthesis and evaluation of a novel and low-cost Cu₃P/CdS NRs p-n heterojunction photocatalyst for highly efficient H₂ production from water. Under optimal conditions, the H₂ evolution rate using this Cu₃P semiconductor was as high as ~200 μmol h⁻¹ mg⁻¹ (λ > 420 nm) and the apparent quantum yield was ~25% in water with Na₂S/Na₂SO₃ as the electron donors (λ = 450 nm). Furthermore, a photocatalytic mechanism based on the Cu₃P/CdS NRs p-n junction is proposed and discussed.

Cu₃P/CdS NRs were synthesized by a simple solvothermal method with the content ratio of Cu₃P at 0 % - 2.90 wt %. The as-prepared samples were labeled as CP1, CP2, CP3, and CP4, respectively. The copper ratio in each sample was measured by ICP-AES and the results are shown in Table S1. The Cu₃P ratios were calculated based on the copper contents.

Figure 1a shows the powder XRD patterns of CdS, Cu₃P/CdS, and Cu₃P. The Cu₃P/CdS and CdS samples show the peaks of 2θ at 24.8°, 26.5°, 28.2°, 36.7°, 43.7°, 47.9°, 51.9°, and 66.8°, which were
indexed to the (100), (002), (101), (102), (110), (103), (112), and (203) lattice fringe diffractions of hexagonal CdS (PDF#77-2306), respectively. For comparison, the Cu3P shows peaks located at 36.0°, 39.0°, 41.5°, 45.1°, and 46.2°, which correspond respectively to the (112), (202), (211), (300), and (213) lattice diffractions of hexagonal Cu3P (PDF#71-2261). After loading Cu3P onto CdS, no obvious diffraction peaks belonging to Cu3P were observed and all reflections showed no significant difference from CdS, which might result from the low content of Cu3P in Cu3P/CdS samples and high dispersion of Cu3P nanomaterials deposited on the surface of CdS NRs. To identify the surface chemical composition and valence state of Cu3P/CdS NRs, the XPS spectra were measured (Figure 1b). The survey scan shows the existence of Cd, S, Cu, and P elements. No other elements were observed except C element as the reference and O element from the absorbed gaseous molecules.

The EDX spectrum further confirmed the existence of Cd, S, Cu, and P, as shown in Figure 3a. Furthermore, the EDX elemental mapping images clearly show the distribution of Cd, S, Cu, and P elements (Figures 3b-3e). The observed Mo element is from the molybdenum grid substrate. The EDX mapping images of a single nanorod further reveal that both Cu and P elements are uniformly distributed in the whole nanorod. All these results clearly confirm the successful synthesis of core-shell Cu3P/CdS NRs by a facile solvothermal method.

Photocatalytic hydrogen production experiments were carried out using the as-prepared Cu3P/CdS NRs photocatalysts in water under visible light irradiation (λ > 420 nm). The experimental set up is shown in scheme S1. Figure 4a shows the rate of H2 evolution using
Cu3P/CdS samples in the presence of Na2S and Na2SO3 as the electron donors. It was found that an appropriate amount of Cu3P can significantly enhance the photocatalytic activity for H2 production in water. The rate of H2 evolution initially increased and then decreased with increasing amounts of Cu3P. With low content of Cu3P loading (0.03 wt %) on CdS (CP1), the H2 evolution rate was ~96 μmol h⁻¹ mg⁻¹. The highest photocatalytic activity was achieved using CP2, presenting a H2 evolution rate of ~184 μmol h⁻¹ mg⁻¹. This phenomenon can be explained as follows: (1) excess Cu3P covered on the CdS surface probably inhibit the incident light absorption by CdS and then decrease the photogenerated electrons from the CdS NRs; (2) excess Cu3P could decrease the surface active sites of CdS.21, 40-41 For comparison, in the absence of Cu3P, CdS showed very low activity, having a H2 evolution rate of only ~28 μmol h⁻¹ mg⁻¹. Although the mechanical mixture of Cu3P and CdS (0.44 wt % Cu3P) showed a slightly higher rate than CdS (~40 μmol h⁻¹ mg⁻¹), it is still much less than the Cu3P/CdS samples prepared by the solvothermal method. In addition, the Cu3P alone showed no appreciable H2 production with visible light irradiation, revealing that Cu3P is not an active photocatalyst.

The apparent quantum yield (φ) for photocatalytic H2 production using CP2 photocatalyst was measured under 450 nm monochromatic light irradiation (Figure 4b). The result showed that the H2 evolution rate reached ~88 μmol h⁻¹ mg⁻¹ with φ~25% after 8 hours of irradiation. The present efficient quantum yield from visible light energy into chemical energy indicated that Cu3P/CdS NRs is a highly efficient photocatalyst.

![Figure 4](image_url)  
**Figure 4.** (a) Comparison of photocatalytic H2 evolution rates of CdS, CP1, CP2, CP3, CP4, Cu3P, and mixed Cu3P-CdS samples at ambient temperature under visible light (λ > 420 nm). The system contains 1.0 mg photocatalyst, 0.75 M Na2S, and 1.05 M Na2SO3 in 20 mL deionized water. (b) Time courses of H2 production and apparent quantum yield on CP2 under monochromatic 450 nm (±5 nm) light irradiation using 1.0 mg photocatalyst in a 20 mL aqueous solution containing 1.25 M Na2S and 1.75 M Na2SO3. (c) Cycling runs for photocatalytic hydrogen evolution in the presence of 1.0 mg CP2 photocatalyst in a 20 mL aqueous solution containing 1.25 M Na2S and 1.75 M Na2SO3. After every 3 hours, the evolved H2 was evacuated. (d) Long-term evolution of H2 under visible light irradiation (λ > 420 nm) using CP2 photocatalyst. The system contains 1.0 mg photocatalyst, 1.25 M Na2S, and 1.75 M Na2SO3 in 50 mL deionized water.

Besides its high activity, Cu3P/CdS NRs material exhibits good stability during photocatalysis. The reaction system was evacuated to remove the evolved H2 every 3 hours and the process was carried out repeatedly. As shown in Figure 4c, no significant decrease in the activity for photocatalytic H2 production can be observed in 12 hours of cycling tests. Moreover, analysis of the photocatalytic efficiency after long-term operation was also performed, with the results shown in Figure 4d. After 50 hours of irradiation, a total of ~10 mmol H2 was produced with a constant rate of ~200 μmol h⁻¹ mg⁻¹. These results indicate the good stability of Cu3P/CdS NRs for photocatalytic H2 production under visible light. In addition, the SEM image of Cu3P/CdS NRs had no significant change after photocatalysis. Figure S2 shows the SEM image of CP2 sample after 5 hours of irradiation. The image still has a rod-like structure, with nearly the same length and diameter as the sample before illumination, indicating that Cu3P/CdS NRs material is a robust photocatalyst in the present photocatalytic H2 evolution system.

The optical properties of the pure CdS, Cu3P/CdS, and pure Cu3P were measured by using a UV-vis-NIR spectrophotometer. Figure 5a shows the UV-vis absorption spectra for all samples. The spectrum of pure CdS displayed a sharp edge at around 530 nm. The optical band gap energy (Eg) is estimated to be about 2.4 eV by the Tauc plot (Figure 5b),42 which agrees well with the reported value.14, 43-44 The absorption onset of Cu3P/CdS is also located at around 530 nm, probably originating from the absorption of CdS in Cu3P/CdS heterojunction photocatalysts. The same absorption edges of pure CdS and Cu3P/CdS indicated that copper did not dope into the CdS lattice in Cu3P/CdS. The increased absorption features of Cu3P/CdS, CP2, and P/CdS samples in the presence of Na2S and Na2SO3 might be explained as follows: (1) excess Cu3P covered on the CdS surface probably inhibit the incident light absorption by CdS and then decrease the photogenerated electrons from the CdS NRs; (2) excess Cu3P could decrease the surface active sites of CdS.21, 40-41 For comparison, in the absence of Cu3P, CdS showed very low activity, having a H2 evolution rate of only ~28 μmol h⁻¹ mg⁻¹. Although the mechanical mixture of Cu3P and CdS (0.44 wt % Cu3P) showed a slightly higher rate than CdS (~40 μmol h⁻¹ mg⁻¹), it is still much less than the Cu3P/CdS samples prepared by the solvothermal method. In addition, the Cu3P alone showed no appreciable H2 production with visible light irradiation, revealing that Cu3P is not an active photocatalyst.

The apparent quantum yield (φ) for photocatalytic H2 production using CP2 photocatalyst was measured under 450 nm monochromatic light irradiation (Figure 4b). The result showed that the H2 evolution rate reached ~88 μmol h⁻¹ mg⁻¹ with φ~25% after 8 hours of irradiation. The present efficient quantum yield from visible light energy into chemical energy indicated that Cu3P/CdS NRs is a highly efficient photocatalyst.

![Figure 5](image_url)  
**Figure 5.** (a) The UV-vis diffuse reflectance spectra of and (b) the estimated band gap of the CdS, CP2, and Cu3P. (c) The steady-state photoluminescence (PL) spectra of the CdS and CP2. (d) The transient photocurrent responses of blank FTO, CdS, and CP2.

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In order to study the migration, transfer, and recombination processes of the photogenerated charge carriers over Cu3P/CdS, the photoluminescence (PL) spectra were examined. Figure 5c shows the PL spectra of CdS and Cu3P/CdS under excitation at 405 nm. It was observed that the as-prepared CdS displayed two distinct emission band at ~511 nm and ~713 nm, which is in agreement with previous studies. The broad photoluminescence spectrum centered at ~713 nm.
nm should be the trapped emission, which was mainly due to the surface defects. Such surface defects would act as recombination centers for electron-hole pairs to lower the photocatalytic activity. The PL spectrum of Cu$_3$P/CdS was similar to that of CdS. However, the emission intensity was much weaker than that of CdS, indicating the transfer of photogenerated charge carriers in Cu$_3$P/CdS by forming p-n interfacial junctions.

To further investigate the photocatalytic H$_2$ production mechanism over Cu$_3$P/CdS, photocurrent tests were performed. As shown in Figure 5d, the Cu$_3$P/CdS photocatalyst exhibits much higher photocurrent response than CdS NRs, revealing that the charge transfer process in Cu$_3$P/CdS is more effective than pure CdS. The fast transfer of charge carriers can highly enhance photocatalytic activity for H$_2$ production according to the literature.

Based on above results, a possible reaction mechanism for photocatalytic H$_2$ evolution using Cu$_3$P/CdS heterojunction is proposed and the schematic diagram is illustrated in Scheme 1. Both Cu$_3$P and CdS can absorb visible light to produce photoinduced electron-hole pairs. Since Cu$_3$P is a p-type semiconductor and CdS is an n-type material, a large number of nanoscale p-n junctions could be generated when two such types of semiconductor materials are closely attached. It has been reported that the conduction band (CB) position of CdS (~3.98 eV vs. A V S) is lower than that of Cu$_3$P (~3.8 eV vs. A V S). Therefore, the photoinduced electrons on the CB of Cu$_3$P can directly transfer to the CB of CdS. The electrons, together with the electrons excited from the VB of CdS, would transfer to the surface of CdS to reduce H$^+$ for H$_2$ production. For the valence band (VB), the corresponding VB position of CdS (~6.38 eV vs. A V S) is also lower than that of Cu$_3$P (~5.1 eV vs. A V S). As a result, the photogenerated holes on the VB of CdS can migrate to the VB of Cu$_3$P, which will greatly reduce the recombination process of electron-hole pairs and further lead to enhanced stability of the CdS and an improved H$_2$ evolution rate. Therefore, efficient charge separation was successfully achieved by the nanoscale p-n junctions in Cu$_3$P/CdS. The close contact between CdS and Cu$_3$P could facilitate the charge transfer, which would improve the photocatalytic H$_2$ evolution activity and stability.

![Scheme 1. A possible reaction mechanism for photocatalytic H$_2$ evolution using the Cu$_3$P/CdS heterojunction.](image)

**Conclusions**

In conclusion, Cu$_3$P/CdS NRs core-shell heterostructures were successfully constructed by in situ deposition of Cu$_3$P onto CdS through a facile solvothermal method. Cu$_3$P nanomaterials were tightly attached to the surface of CdS, leading to the formation of p-n junctions between p-type Cu$_3$P and n-type CdS. The p-n junctions in Cu$_3$P/CdS can promote fast charge transfer and reduce charge recombination. Under optimal conditions, the Cu$_3$P/CdS exhibited a H$_2$ evolution rate of ~200 μmol·h$^{-1}$·mg$^{-1}$ with a maximum apparent quantum yield of ~25% when excited at 450 nm. The photocatalytic results indicate that Cu$_3$P is a highly active promoter when loaded on CdS to form p-n junctions for H$_2$ production. This work not only supports the possibility of using cost-effective p-type Cu$_3$P for photocatalytic H$_2$ production but also shows that a proper p-n junction structure is crucial for high photocatalytic activity in a hybrid photocatalyst.

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**Notes and references**

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† Electronic Supplementary Information (ESI) available: Experimental details, AIPS-AES data of copper in Cu$_3$P/CdS NRs, SEM images of CdS and Cu$_3$P, and SEM image of Cu$_3$P/CdS after 5 hours of visible light irradiation. See DOI: 10.1039/c000000xs

The present study shows that p-type copper phosphide (Cu₃P) can be an efficient promoter to improve photocatalytic H₂ production from water when loaded on n-type cadmium sulphide nanorods.