Efficient Charge Migration in Chemically-Bonded Prussian Blue Analogue/CdS with Beaded Structure for Photocatalytic H₂ Evolution

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ABSTRACT: The design of a powerful heterojunction structure and the study of the interfacial charge migration pathway at the atomic level are essential to mitigate the photocorrosion and recombination of electron–hole pairs of CdS in photocatalytic hydrogen evolution (PHE). A temperature-induced self-assembly strategy has been proposed for the syntheses of Prussian blue analogue (PBA)/CdS nanocomposites with beaded structure. The specially designed structure had evenly exposed CdS which can efficiently harvest visible light and inhibit photocorrosion; meanwhile, PBA with a large cavity provided channels for mass transfer and photocatalytic reaction centers. Remarkably, PB-Co/CdS-LT-3 exhibits a PHE rate of 57 228 μmol h⁻¹ g⁻¹, far exceeding that of CdS or PB-Co and comparable to those of most reported crystalline porous material-based photocatalysts. The high performances are associated with efficient charge migration from CdS to PB-Co through CN-Cd electron bridges, as revealed by the DFT calculations. This work sheds light on the exploration of heterostructure materials in efficient PHE.

KEYWORDS: Prussian blue analogue, CdS nanowires, beaded structure, photocatalytic hydrogen evolution, electron bridge

INTRODUCTION

The renewable-light-powered photocatalytic hydrogen evolution (PHE), serving as a potential means to store sunlight for clean chemical fuel products, has emerged as one of the most promising solutions to mitigate the global energy and environmental crisis.¹⁻³ To promote the practical applications of this technology, enormous efforts have been made and mostly focused on semiconductor-based materials owing to their advantages like efficient harvesting of visible light, hindering the recombination of photogenerated charge, boosting the rate of photogenerated electrons to H⁺, etc.⁴⁻⁶ Among them, cadmium sulfide (CdS) with excellent visible-light response and suitable conduction band position has been intensively investigated as a promising photocatalyst in PHE.⁷⁻⁹ Nonetheless, the inherent instability of CdS imparts it with bottlenecks like serious photocorrosion, fast charge carrier recombination, limited catalytic sites, etc.¹⁰ To conquer it, numerous endeavors like morphology-control strategies or construction of hybrid materials with other materials like carbon materials (e.g., graphene oxide),¹¹ semiconductors (e.g., TiO₂),¹² or noble metals (e.g., Pt)¹³ have been made to improve the catalytic activity of CdS. However, the morphology control strategies are still limited by the inert shortcomings of CdS, and the hybrid components applied are mostly nanocomposites with unclear or nonporous structure, in which precise regulation of the surface electronic structure at the atomic level is difficult and diffusion of substrates or products is unfavorable. Further, for the commonly investigated hybrid components like noble metals, which are loaded as efficient cocatalysts to promote PHE performances, their scarcity and high price critically impede the industrial-scale applications in solar-to-H₂ conversion.¹⁴ Thus far, the presented PHE performances of CdS-based PHE photocatalysts are far from meeting the basic demands of practical applications. Therefore, it is of high significance to explore powerful and cheap CdS-based photocatalysts that can eliminate the usage of noble-metal cocatalysts and possess satisfactory efficiency with a clear mechanism.

Porous coordination polymers (PCPs) as a category of functional porous materials have gained broad interest and been widely studied in many applications like gas adsorption/separation, energy storage and photocatalysis, etc.¹⁵⁻¹⁷ Compared with traditional carbon materials, noble metals,
and semiconductors, crystallized PCPs with well-defined crystal structures might be ideal model catalysts to study the structure–function relationship in PHE. Prussian blue analogues (PBA), as a subgroup of typical PCPs possessing a general chemical formula of $A\text{M}[M (CN)_6]$ ($A$ = alkaline metal ions, $M/M = \text{Fe, Co, Mn, etc.}$), have been commonly applied in commercial products like paint, ink, and crayons.\textsuperscript{18,19} However, thus far, PBA have been rarely reported applied in commercial products like paint, ink, and visible-light region, largely limiting their applications in solar energy utilization.\textsuperscript{20–25} To solve it, the introduction of photosensitizers to generate hybrid materials with synergistic effect might be a desirable strategy to boost their photocatalysis ability and also conquer the inherent instability of some photosensitizers such as CdS. PBA might serve as promising alternatives to cooperate with CdS owing to (1) the large cavity in the structure might be favorable for the efficient diffusion of substrates or products;\textsuperscript{25} (2) cyanide groups ($\equiv$CN) existing in PBA might promote the visible-light absorption ability, modify the band structure, and serve as efficient electron-consuming agents with the aim of driving the transfer kinetics of photogenerated holes and electrons;\textsuperscript{24,25} and (3) the $\equiv$CN in PBA have the possibility in formation of strong interactions like chemical bonds with CdS to largely improve the structural stability of the hybrid materials. For most reported CdS-based hybrid materials, the connections between CdS and hybrid components are generally weak (e.g., van der Waals force or hydrogen bonds) or mostly unclear, which results in poor stability, unsatisfactory PHE efficiency, or an unclear photocatalysis mechanism. In this regard, the material design principles are also hard to change from trial-and-error to rational design.\textsuperscript{26} Further, it is still a huge challenge to control the morphology for CdS-based hybrid materials to get rid of the bottlenecks of CdS and regulate the surface electronic structure at the atomic level to maximize the synergistic effect of the hybrid components in PHE. Therefore, it is meaningful and desirable to develop porous and morphology-controlled photocatalysts that can synergistically combine PBA with CdS through strong and clear interactions to largely improve the PHE efficiency.

Herein, we report a series of noble-metal-free PB-Co/CdS hybrid photocatalysts with beaded structure through a facile temperate-induced self-assembly (TISA) method (Figure 1). Comprehensive characterizations and theoretical calculations prove that strong chemical bonds (i.e., CN-Cd) were generated between PB-Co and CdS in PB-Co/CdS, possessing tightly connected and well-tuned beaded structure morphology. The chemical bonds generated between them can serve as the electron bridges, in which photoinduced electrons generated from CdS can efficiently transfer to the photocatalysis centers in PB-Co to boost the PHE performances. It is noteworthy that the best of them, PB-Co/CdS-LT-3, presents an efficient PHE activity of $7228 \text{ \mu mol h}^{-1} \text{g}^{-1}$, about $\sim 7\sim 136$, and $\sim 3$-fold higher than those of CdS nanowires (CdS NWs), PB-Co, and physical mixtures, respectively, when lactic acid aqueous solution is used as the sacrificial agent. In addition, an apparent quantum yield of 7.2% can be achieved under monochromatic light irradiation at 420 nm. The photogenerated carriers are effectively separated through electron bridges (i.e., CN-Cd) in PB-Co/CdS-LT-3, as supported by the DFT calculations. Although some materials with beaded structures have been reported, such as C/Co-MnO NWs,\textsuperscript{27} CeO$_2$/NiO heterojunction,\textsuperscript{28} and CZ-800,\textsuperscript{29} the main components of them are carbon materials, metallic oxide, and metal sulfide, respectively. Works that are based on crystalline PCPs and investigate the influence of bonding interaction or morphologies on photocatalytic hydrogen evolution have been rarely reported. This work focuses on validating the superior roles of coordination bonds inside the heterojunction and beaded structure in efficient PHE, which paves a new avenue in exploring powerful hydrogen evolution catalysts.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of the PB-Co/CdS

The synthesis procedures of PB-Co/CdS with a beaded structure are presented as follows. The CdS NWs were first synthesized through a reported solvothermal method.\textsuperscript{30} PB-Co/CdS with beaded structures were prepared at 4 °C via dropping a Co(OAc)$_2$-4H$_2$O and CdS NWs mixture solution into another solution containing K$_3[\text{Co(CN)}_6]$ and sodium dodecyl sulfate (SDS) under stirring for 1 h. After aging for 3 h, PB-Co/CdS-LT (LT stands for the sample synthesized at relative low temperature) was collected after washing with water and ethanol several times (for details, see the Experimental Section). Upon tuning the amounts of precursors, PB-Co/CdS-LT-$n$ ($n = 1–4$) with different PB-Co contents (i.e., 57.6, 70.2, 82.6, and 90.9 wt %) were prepared, respectively. As comparison, samples were also synthesized at room temperature (PB-Co/CdS-HT-3) or relatively higher temperature (60 °C) (PB-Co/CdS-HT-3). A kind of PB-Co/CdS hybrid material with CdS NWs fully covered by PB-Co (denoted as PB-Co/CdS-F-3) was successfully synthesized when the PB-Co precursor concentration was decreased by fourfold, which serves as a desired comparison. The physical mixtures of CdS nanowires and PB-Co (denoted as PB-Co/CdS-M-3) were also prepared for comparison.

Powder X-ray diffraction pattern (PXRD) tests were used to characterize the samples. The peaks of PB-Co/CdS-LT-$n$ ($n = 1–4$) match well with those of simulated CdS (JCPDS No. 1-780) and PB-Co (JCPDS No. 7-1161),\textsuperscript{31} demonstrating the formation of PB-Co and the remaining structural integrity of CdS NWs in the hybrid materials (Figure 2a and Figure S1). Similar results were also observed for PB-Co/CdS-HT-3, PB-Co/CdS-HT-3, and PB-Co/CdS-F-3 (Figure S2). The

![Figure 1](https://dx.doi.org/10.1021/jacsau.0c00082)

Figure 1. Schematic illustration of the formation of PB-Co/CdS with a beaded structure and its application in photocatalytic H$_2$ evolution.
existence of CdS NWs and PB-Co was further confirmed by the Fourier-transform infrared (FT-IR) spectra of PB-Co/CdS-LT-n (n = 1–4), PB-Co/CdS-RT-3, and PB-Co/CdS-HT-3 (Figures S3 and S4). With the increase of PB-Co content, the peak intensity of PB-Co was apparently enhanced in the PXRD and FT-IR spectra. The X-ray photoelectron spectroscopy (XPS) analysis was performed to gain further insight into the chemical composition and possible interaction of the photocatalysts. The PB-Co/CdS-LT-3 and PB-Co/CdS-M-3 show the main peaks of the elements Cd, N, Co, and S (Figure S5). The binding energy of Co 2p and N 2p (originated from the signal of −CN) for PB-Co/CdS-LT-3 (781.53, 784.52, 796.73, and 798.91 eV for Co 2p, and 398.01 eV for N 2p) is also higher than that of PB-Co/CdS-M-3 (781.24, 782.34, 794.04, and 797.64 eV for Co 2p and 397.82 eV for N 2p).32 Nevertheless, the binding energy of Cd 3d and S 2p for PB-Co/CdS-LT-3 (404.76, and 411.51 eV for Cd 3d, and 161.73 and 162.77 eV for S 2p),35 The shifted binding energy of Cd 3d, Co 2p, S 2p, and N 1s in PB-Co/CdS-LT-3 suggests the possible existence of Co-CN-Cd at the interface between PB-Co and CdS NWs.7,34

To detect the thermal stability and determine the composition of the hybrid materials, thermogravimetric analysis (TGA) tests under N2 atmosphere were conducted. The results show that PB-Co and PB-Co/CdS-LT-n (n = 1–4) hybrid materials can be stable up to 380 °C, while CdS NWs have no weight loss during the whole test (Figure S6). Based on the results of TGA and inductively coupled plasma optical-emission spectroscopy (ICP-OES) (Table S1), the loadings of the PB-Co in PB-Co/CdS-LT-n (n = 1–4) and PB-Co/CdS-F-3 were calculated to be 57.6, 70.2, 82.6, 90.9, and 76.2 wt %, respectively.

To characterize the morphology of the obtained samples, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed. CdS NWs show regular nanowire morphology with average diameter of ∼60 nm and length of ∼1.0 μm (Figure S7). PB-Co displays a kind of spherical nanoparticle morphology with size of about 200–600 nm (Figure S8). Interestingly, a kind of unique beaded morphology is detected for PB-Co/CdS-LT-n (n = 1–4) (Figures S9–S13). Taking PB-Co/CdS-LT-3 as an example, SEM and TEM images at both high and low magnifications show that spherical PB-Co nanoparticles (size, ∼200–600 nm) (Figure S12) are uniformly penetrated by CdS NWs (length, ∼1.0 μm), which demonstrates the generated heterojunction between CdS NWs and PB-Co (Figures 2b, c, and Figure S11). It implies the possible existence of coordination bonds at the interface between PB-Co and CdS NWs. The high-resolution transmission electronic microscopy (HRTEM) image demonstrates that the CdS backbone with 0.336 nm in plane lattice spacing can be assigned to the (002) plane of hexagonal CdS (Figure 2d).35 Moreover, PB-Co/CdS-LT-3 with beaded structure morphology was then observed by the high-angle annular dark-field (HAADF) microscopy (Figure 2e). The corresponding element mappings show the existence of Co, N, Cd, and S, confirming the formation of a unique structure with PB-Co nanoparticles attached to the outer surface of the CdS NWs (Figure 2e). As further proved by the energy dispersive X-ray (EDX) spectra, PB-Co/CdS-LT-3 shows the existence of Co, N, Cd, and S elements (Figure S18). Obtained through such a facile TISA method, diverse loadings of PB-Co in the systems can be easily tuned to find out the best ratio of PB-Co/CdS-LT. As revealed in the SEM and TEM tests, the morphology of PB-Co/CdS-LT-4 with higher PB-Co loading presents excessive amount of PB-Co unpenetrated with CdS NWs compared with that of PB-Co/CdS-LT-3 (Figure S13). While for PB-Co/CdS-LT-1 and PB-Co/CdS-LT-2 with higher CdS loadings, large amounts of CdS NWs are unloaded with PB-Co (Figures S9 and S10). This indicates PB-Co/CdS-LT-3 with best ratio of PB-Co and CdS can result in well-controlled morphology where PB-Co nanoparticles are uniformly and tightly attached onto CdS NWs.

Moreover, the powerful TISA method that can generate PB-Co/CdS hybrid materials with beaded structure can be readily tuned with the change of temperature. Taking PB-Co/CdS-3 with the best beaded morphology (obtained at 4 °C) for example, PB-Co/CdS-RT-3 shows a completely different morphology if the synthesis temperature of PB-Co/CdS-3 is room temperature, in which PB-Co nanoparticles exhibit clear cubic shape with much larger size (∼1 μm) while the uniformity is relatively poorer than that of PB-Co/CdS-LT-3 (Figure S14). Further, when the temperature is increased to 60 °C, PB-Co/CdS-HT-3 displays morphology similar to that of PB-Co/CdS-RT-3 except that the size of PB-Co particles

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Figure 2. Characterization of the PB-Co/CdS-LT-3 hybrid material. (a) The PXRD pattern of PB-Co/CdS-LT-3. (b) SEM image of PB-Co/CdS-LT-3. (c) TEM image and (d) HRTEM image of PB-Co/CdS-LT-3. (e) EDX elemental mapping of Co, N, Cd, and S in PB-Co/CdS-LT-3.
(~1.5 μm) is larger (Figure S15). This demonstrates that the slow nucleation rate of PB-Co in low temperature might be essential to achieve the hybrid material with well-tuned beaded structure. Except for the morphology tuned through the change of temperature, PB-Co/CdS-LT-3 is successfully synthesized, serving as a desired comparison to investigate the significance of visible-light response and effect of morphology in PHE (Figures S16 and S17).

Optoelectronic Properties and Photocatalytic H₂ of PB-Co/CdS

Evolution of UV–vis diffuse reflectance spectra (DRS) is utilized to detect the optical properties of the obtained samples (Figure 3a). Bare CdS NWs display an absorption edge around 550 nm, and PB-Co exhibits a characteristic absorption band centered at 500 nm, which coincides with the results in the reported literature.36,37 The absorbance spectrum of PB-Co/CdS-LT-3 shows the integrated features of CdS NWs and PB-Co, in which a sharp absorption edge rises at about 550 nm and a broad absorption range is detected in the visible-light region. The corresponding band gaps for CdS NWs and PB-Co are estimated to be 2.33 and 2.05 eV, respectively (inset of Figure 3a). The effective optical band gap of CdS nanowires changes with PB-Co, which is attributed to the high loadings of Pb-Co on the surface of the CdS NWs uniformly. The enhanced charge-separation efficiency is further confirmed by the photoluminescence (PL) emission spectra (Figure 3d). Compared with CdS NWs, the emission intensity of PB-Co/CdS-LT-3 is significantly quenched, indicating that PB-Co as electron-consuming agents can efficiently trap electrons photoinduced from CdS NWs through the possible interaction between them, which simultaneously suppress the charge recombination process and enhance the photocatalytic activity.39

Combining the unique chemically bonded beaded structure, enhanced charge-separation efficiency, and low interfacial charge-transfer resistance in the system, the thus-obtained hybrid materials might possess superior performances in PHE. To evaluate their PHE properties, the tests are conducted under visible-light irradiation (>420 nm) using lactic acid as sacrificial agents. As shown in Figure 4a, the PHE rate is negligible when PB-Co is used as the photocatalyst, implying PB-Co to be an inactive photocatalyst by itself. Under the same conditions, pristine CdS NWs shows a low H₂ evolution rate of 8590 μmol h⁻¹ g⁻¹, which matches well with previously reported results owing to its fast charge carrier recombination, serious photocorrosion, and the lack of catalytic sites.40 Surprisingly, the H₂ production performance of PB-Co/CdS-LT-3 is significantly quenched, indicating that PB-Co as electron-consuming agents can efficiently trap electrons photoinduced from CdS NWs through the possible interaction between them, which simultaneously suppress the charge recombination process and enhance the photocatalytic activity.39

Figure 3. Optical properties of CdS NWs, PB-Co, and PB-Co/CdS-LT-3. (a) UV/vis diffuse reflectance spectra for CdS NWs, PB-Co, and PB-Co/CdS-LT-3. (b) Mott–Schottky plots for CdS NWs and PB-Co. (c) EIS Nyquist plots and (d) photoluminescence spectra for CdS NWs, PB-Co, and PB-Co/CdS-LT-3 (excitation wavelength λₑₓ = 350 nm).

Figure 4. Comparison of the PHE performances of different photocatalysts. (a) The PHE rates of different samples. (b) The photocatalytic stability of PB-Co/CdS-LT-3. (c) Comparison of the PHE rate among PB-Co/CdS-LT-3 and representative crystalline porous material-based photocatalysts (for details, see Tables S3 and S4).
LT-3 (57 228 μmol h⁻¹ g⁻¹) is largely enhanced after the synergistic integration of PB-Co and CdS NWs in the unique beaded structure, which is comparable to those of most reported crystalline porous material-based photocatalysts and also superior to some CdS-based materials (Figure 4c and Tables S3 and S4). Moreover, the photoactivity of PB-Co/CdS-LT-3 is also higher than those of PB-Co/CdS-LT-1 (46 945 μmol h⁻¹ g⁻¹), PB-Co/CdS-LT-2 (53 338 μmol h⁻¹ g⁻¹), and PB-Co/CdS-LT-4 (26 747 μmol h⁻¹ g⁻¹), which further supports the superiority of PB-Co/CdS-LT-3 with the best morphology. To demonstrate that the produced H₂ comes from water rather than lactic acid, photocatalytic experiments using different sacrificial agents have been conducted (Figure S22). The rates of H₂ production were 22 112, 25 635, and 43 059 μmol h⁻¹ g⁻¹ in the presence of L-(+)-ascorbic acid, l-ascorbic acid sodium, and sodium lactate aqueous solutions, respectively. The above results reveal that H₂ comes from water rather than lactic acid.

To further investigate the superiority of the PB-Co/CdS hybrid materials with beaded structure, contrast samples like the PB-Co/CdS-M-3 and PB-Co/CdS-F-3 are prepared to test their performances. Specifically, a simple physical mixture of PB-Co and CdS NWs shows a low H₂ evolution rate of 20 120 μmol h⁻¹ g⁻¹ (Figure S21), which is much smaller than that of the PB-Co/CdS-LT-3 (57 228 μmol h⁻¹ g⁻¹), indicating the tightly connected heterojunction for PB-Co/CdS-LT-3 is indeed favorable to enhance the PHE activity. Furthermore, PB-Co/CdS-F-3 shows a PHE performance of 34 563 μmol h⁻¹ g⁻¹, indicating poorer photoacceptor efficiency would result in lower performance (Figure S21). Moreover, the properties of materials synthesized at various temperatures are also investigated. PB-Co/CdS-RT-3 and PB-Co/CdS-HT-3 display 38 590 and 27 503 μmol h⁻¹ g⁻¹ PHE rates, respectively, which are also lower than that of PB-Co/CdS-LT-3 (Figure S21). This might be attributed to the fact that the larger particle sizes and poorer contact between PB-Co and CdS would limit their mass transfer and charge-hole separation efficiency. In addition, the quantum efficiency (QE) of PB-Co/CdS-LT-3 achieves 7.20% at 420 nm, which is the highest among other samples (Table S2) and above average among previously reported coordination compound-based materials even for the hybridization of CdS (Figure S30).

The recyclability is an importance parameter as it determines the durability of catalysts. Taking PB-Co/CdS-LT-3 for instance, a negligible decrease in H₂ evolution rate was detected after four cycling tests (Figure 4b). The structure and morphology of PB-Co/CdS-LT-3 after four consecutive cycles were also characterized by PXRD, SEM, and TEM tests. The crystalline structure and morphology of PB-Co/CdS-LT-3 remain almost unchanged after PHE tests (Figures S23–S24), which suggests high durability of this powerful material in PHE. Finally, we also tested the SEM, TEM, and PXRD of pure PB-Co before and after the photocatalysis test (Figures S25–S26), which can further prove the stability of PB-Co.

The DFT Calculation and Reaction Mechanism

Above all, the PB-Co/CdS hybrid material with well-tuned beaded morphology endows these materials with excellent photocatalysis performances. The superiority of the PB-Co/CdS-LT-3 with beaded structure is further revealed as follows. Here, we propose four types of structures (i.e., pure CdS, the physical mixture sample, PB-Co/CdS-F-3, and PB-Co/CdS-LT-3) and discuss their possible mechanisms in PHE (Figure 5a), the evenly exposed CdS NWs possess excellent visible-light absorbance ability and can act as light-harvest agent under visible light to generate electrons. Then, the photogenerated electrons by CdS NWs could immediately be delivered to the CB of PB-Co through the strong coordination bond that acts as the electron bridge for the efficient transport of the photogenerated electrons to produce hydrogen. Then, the holes of CdS NWs left can react with lactic acid to complete the catalytic cycle (Figure S27). As a result, the photo-generated electron–hole pairs can be separated efficiently in the photocatalytic system of PB-Co/CdS-LT-3 to significantly enhance the PHE activity compared with CdS NWs and the physical mixtures, which might be ascribed to the strong coordination bond that acts as the electron bridge for the efficient transport of the photogenerated electrons (Figure 5b). When the CdS NWs was fully covered with PB-Co, the PB-Co/CdS-F-3 has poorer visible-light response, thus leading to a relatively low performance (Figure 5a). DFT calculations are further carried out to investigate the interface interaction between PB-Co and CdS. All of the calculations are performed within the framework of DFT implemented in the Vienna ab initio simulation package (VASP). The generalized gradient approximation with the functional is described by the Perdew–Burke–Ernzerhof (PBE) type. The projector-augmented wave (PAW) method was applied to describe the wave functions in the core regions, while the valence wave

Figure 5. Photocatalytic mechanism of the charge transfer for PHE over the PB-Co/CdS-LT-3. (a) Four types of structures. (b) Electron localization function (ELF) for hybrid structure of PB-Co/CdS-LT-3 with an isosurface value of 0.51. (c) Calculated electrostatic potential of CdS and PB-Co and (d) schematic energy-level diagrams of PB-Co/CdS-LT-3.

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functions are expanded as a linear combination of plane-waves with a cutoff energy of 400 eV. The total energy was converged to $10^{-5}$ eV in the geometry optimizations, and the Hellmann–Feynman force on each relaxed atom was less than 0.02 eV/Å. The effect of van der Waals interactions was also considered by using DFT-D2 scheme. The equilibrium lattice constants of CdS were optimized with $a = b = 4.16 \, \text{Å}$, $c = 6.75 \, \text{Å}$, which agree well with experimental data of 4.13 and 6.71 Å. The PB-Co contains hybrid charges of Co atoms of Co$^{2+}$ and Co$^{3+}$; the Co$^{3+}$ positions were first replaced by Fe atoms to get an initial wave function. With a converged wave function, the structure of PB-Co was further optimized with a lattice of 10.25 Å. To build the interface structure, surfaces of PB-Co (110), (011), (101), and CdS (001) were first cleaved from bulk structures. The slabs of PB-Co and CdS were extended to $2 \times 1$ and $6 \times 2$ to minimize the lattice mismatch effect (Figure S28). The vacuum space between two adjacent sheets was set to 10 Å to eliminate their interactive effect. The electron localization function (ELF) for the hybrid structure of PB-Co/CdS-LT-3 was calculated based on the optimized structure and visualized with the help of VESTA. The interface structure was constructed based on the surface planes of (110), (101), and (011) of PB-Co, on which −CN groups are terminated. Further, S- and Cd-termination are included on the CdS (001) surface (Figure 5b). The results indicate that the exposed Cd atoms on the CdS surface can form strong chemical bonds with −CN on the PB-Co surface with a bond length of ~2.3 Å. The ELF of the interface structure (Figure 5b) was calculated for bonding analysis, and it is obvious that the electrons are transferred from Cd to −CN groups through directional bonding, which exhibits chemical bond characteristics existing at the interface. To further evaluate the charge transfer, the charge density difference (CDD) and Bader charge analysis were performed; the total charge transfer from a Cd atom to PB-Co is 1.62 e− (Figure S29). Figure 5c plots the electrostatic potential of the heterostructure, which shows discontinuous potential, on one hand, accounts for the charge transfer process at the interface, and on the other hand, the potential difference may facilitate the separation of the photogenerated carriers (i.e., the electrons and holes).

## CONCLUSIONS

In conclusion, a series of PB-Co/CdS hybrid materials has been successfully synthesized through a facile TISA method. Specifically, the obtained PB-Co/CdS-LT-3 possesses excellent visible-light response, high charge-separation efficiency, and good durability, showing high promise in PHE. The best of them, PB-Co/CdS-LT-3, shows a PHE rate of 57 228 μmol h$^{-1}$ g$^{-1}$, ~7, ~136, and ~3 times faster than that of pristine CdS, PB-Co, and physical mixtures, respectively. It also exhibits a QE of 7.20% at 420 nm under visible-light irradiation. Notably, the PHE performance of PB-Co/CdS-LT-3 is comparable to the reported crystalline porous material-based photocatalysts. Further, strong chemical bonds (i.e., CN-Cd) between PB-Co and CdS have been proved by comprehensive characterizations and theoretical calculations, which can serve as a powerful electron bridge to ensure the efficient charge separation across the coordinated heterojunction interface in the hybrid materials to contribute to the high PHE performance. This work validates the superior roles of coordination bonds inside heterojunctions and beaded structures in efficient PHE and demonstrates the potential of PB-Co/CdS hybrid materials for effective photocatalytic application. We believe that the presented strategy might open up a new avenue to the development of more efficient heterogeneous catalysts for photocatalytic water splitting.

### EXPERIMENTAL SECTION

#### Synthesis of CdS NWs

Cd(NO$_3$)$_2$$\cdot$4H$_2$O (6.22 mmol) and thiourea (18.65 mmol) were dissolved in ethanediamine (50 mL), and then the mixture was transferred into a 100 mL polyethylene terephthalate (PET)-lined autoclave and heated at 180 °C for 24 h. After cooling to room temperature, the yellow powder was collected by filtration, washed with deionized water and absolute ethanol, and dried at 80 °C in air.

#### Syntheses of PB-Co/CdS-L-n (n = 1−4) and Their Comparisons

Taking the synthesis of PB-Co/CdS-LT-3 for example, K$_3$[Co(CN)$_6$]·4H$_2$O (0.25 mmol) and sodium dodecyl sulfate (SDS, 6.07 mmol) were dissolved in 50 mL of H$_2$O. Then, Co(OAc)$_2$$\cdot$4H$_2$O (0.31 mmol) and CdS (0.26 mmol) were mixed, dispersed in another 50 mL of H$_2$O, and added into the above solution drop by drop slowly under stirring for 1 h at 4 °C. After aging at 4 °C for 3 h, the as-synthesized sample was collected by centrifugation and washed with deionized water and absolute ethanol several times. To adjust the loadings of the PB-Co in PB-Co/CdS-LT, diverse amounts of CdS were tuned (PB-Co/CdS-LT-1, 0.78 mmol, PB-Co/CdS-LT-2, 0.52 mmol, and PB-Co/CdS-LT-4, 0.13 mmol). After similar treatment, the mass ratio of PB-Co in PB-Co/CdS-LT-n (n = 1−4) was tuned from 57.6 to 90.9 wt%. The preparation of PB-Co/CdS-LT-3 and PB-Co/CdS-HT-3 was similar to that of PB-Co/CdS-LT-3 except the temperatures are room temperature and 60 °C, respectively. For the synthesis of PB-Co/CdS-LT-3 (fully covered), the procedures are similar to that of PB-Co/CdS-LT-3 except that the PB-Co precursor concentration was decreased by 4-fold and the reaction time was increased to 5 h.

#### Synthesis of PB-Co

The preparation of PB-Co was similar to the reported method in ref 52.

#### Photocatalytic Experiments

The photocatalytic H$_2$ production experiments were performed via a photocatalytic H$_2$ production activity evaluation system (CEAULight, China) in a 300 mL Pyrex flask, and the opening of the flask was sealed with a silicone rubber septum. A 300 W xenon arc lamp through a UV-cut-off filter with a wavelength range from 420 to 800 nm (positioned 13 cm away from the reaction solution) was used as the visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was ~200 mW·cm$^{-2}$, which was measured by a CEL-NP2000 radiometer (CEAULight, China). In a typical experiment, the photocatalyst (10 mg) was uniformly dispersed in 50 mL 16 vol % lactic acid aqueous solution by ultrasonic dispersion. Before irradiation, the system was vacuumed for 10 min with the vacuum pump to completely remove the dissolved oxygen. The H$_2$ production amount was analyzed by gas chromatography (GC-7920, CEAULight, China) with a TCD detector. All glassware was carefully rinsed with ultrapure water prior to usage. The photocatalytic stability tests were performed using the same processing parameters. Ten milligrams of catalyst was uniformly dispersed in 50 mL 16 vol % lactic acid aqueous solution by ultrasonic dispersion for 7 h to evolve to measure the apparent quantum efficiency (QE) with a 420 ± 8 nm band-pass filter. Ten milligrams of catalyst was uniformly dispersed in 50 mL of PBS buffer solution (50 mL of 0.1 M solution at pH = 7) containing 8 vol % sodium lactate aqueous solution, 50 mL of H$_2$O containing 100 mg of sodium ascorbate (SA), and 50 mL of H$_2$O containing 200 mg l- (+)-ascorbic acid by ultrasonic dispersion for 3 h. H$_2$ evolution has also been conducted for comparison.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.0c00082.

Detailed information regarding the experimental methods, characterization analysis, and DFT calculations (PDF)

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Author Contributions

Y.-Q.L., Y.C., and M.Z. conceived and designed the project. J.-N.C., M.Z., S.-L.L., and Y.C. conducted the characterizations and designed the experiments. W.-X.J. carried out the theoretical/DFT calculations. C.J., W.-X.J., L.-Y.L., L.-Z.D., and M.L. collected and analyzed the data. M.Z. and Y.-P.C. discussed the results and prepared the manuscript. All authors reviewed and contributed to this paper.

Notes

The authors declare no competing financial interest.

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