

Ultrafast Charge Separation for Full Solar Spectrum-Activated Photocatalytic H₂ Generation in a Black Phosphorus-Au-CdS Heterostructure

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S Supporting Information

ABSTRACT: Two-dimensional layered black phosphorus (BP) with a tunable band gap of 0.3-2.0 eV has received great interest in broadspectrum-active photocatalysis, but rapid charge recombination limits its potential applications. Herein, we report that BP quantum dots (QDs) work as active photosensitizer in a ternary heterostructure consisting of BP QDs, Au nanorods (NRs), and CdS nanowires (NWs), which efficiently photocatalytically generates H_2 at full solar spectrum, especially in the near-infrared (NIR) region. The superior performance of the BP-Au-CdS heterostructure arises from the overall photoabsorption contribution, the dual role (electron relay and plasmonic electron donor) of Au NRs, as well as the appropriate band alignment and strong coupling between the three components. Tracking the electron and hole transfers via femtosecond transient absorption spectroscopy shows a unidirectional electron flow from BP



to Au and then to CdS, which has been achieved by the high conduction band level of BP, the well-harnessed work function match in BP-Au, and the well-established Schottky barrier in Au-CdS heterojunction.

ydrogen (H₂) production through photocatalytic water splitting is a promising technique to provide Lean solar fuels to solve the current energy crisis.¹ Since the pioneering work on water splitting by TiO₂ under ultraviolet (UV) light in 1972,² the search for diversified semiconductor photocatalysts has attracted extensive interest.³⁻⁵ To date, considerable progresses have been made in developing UV- and visible-light-activated photocatalytic systems for efficient splitting of water, and several semiconductor photocatalysts with promising photocatalytic performances have been found, such as TiO₂ and ZnO in the UV region^{6,7} and g-C₃N₄, CdS, and ZnIn₂S₄ in the visible region.⁸⁻¹⁰ However, as is well-known, UV and visible light energy amounts to no more than 50% of solar energy, and the abundant near-infrared (NIR) light cannot be utilized to activate the vast majority of semiconductor photocatalysts.¹¹ Therefore, it is particularly urgent to develop a photocatalyst with broadband solar absorption especially covering the NIR range.

Since the first report on field-effect transistors in 2014, black phosphorus (BP), a new two-dimensional (2D) van der Waals crystal with a puckered hexagonal structure, has attracted a great deal of attention because of its unique layered structure and a layer-dependent band gap of 0.3-2.0 eV.¹²⁻¹⁵ The easily adjustable band gap makes BP a promising absorber of broad solar light, from UV to NIR.¹⁴ Recently, Yang et al. demonstrated the potential of BP nanosheets (NSs) as watersplitting photocatalysts for visible light H_2 evolution.¹⁶ However, the photocatalytic activity of the bare BP nanostructure was very low because the rapid charge recombination induced an ultrashort charge carrier lifetime of several picoseconds.¹⁷ One approach to prolong the charge lifetime of BP is to hybridize with other semiconductor photocatalysts to separate electron-hole pairs spatially. For example, Lee et al. reported that the BP@TiO2 hybrid

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Figure 1. Calculated electrostatic potentials for Au–CdS (a) and BP–Au (b) heterojunction slab models. The blue and green dashed lines denote Fermi level and the vacuum energy level, respectively. The orange, pink, yellow, and purple balls represent Au, Cd, S, and P atoms, respectively.



Figure 2. TEM (a, c, and e) and HRTEM (b, d, and f) images of CdS (a and b), Au-CdS (c and d), and BP-Au-CdS (e and f).

photocatalyst showed enhanced photocatalytic performance compared with pure few-layered BP.¹⁸ Unfortunately, the strategy of heterojunction construction also achieved limited success because of the unmatched work function between BP and many other semiconductor materials. The formation of a large Schottky barrier means low charge-transfer efficiency from BP into the neighboring semiconductor. To solve this problem, in BP-based field-effect transistor nanodevices, the deposition of Au or Ni layers as contacts between BP and semiconductor substrates is necessary to facilitate an Ohmic contact and decrease the Schottky barrier.^{19,20} As for photocatalysis, the aforementioned finding may shed light on enhancing the carrier transport of BP-based photocatalysts.

In this work, we develop new ternary heterostructures by putting together BP quantum dots (QDs), Au nanorods (NRs), and CdS nanowires (NWs) for the first time. The outstanding photoconversion efficiency of BP–Au–CdS is demonstrated by their unprecedented photocatalytic H_2 evolution activity under UV–NIR light irradiation, which is significantly better than those of CdS, BP–CdS, and Au–CdS, as well as most of the broad-spectrum-activated photocatalysts reported to date. The hybird nanostructure presents several superiorities other than simply extending the light harvesting: (1) BP QDs exhibit unique optical properties due to quantum confinement and edge effects, and the broadened band gap and up-shifted conduction band (CB) edge endow the photogenerated electrons in BP QDs with improved reduction activity. (2) Au NRs serve as electron relays to facilitate a charge-transfer channel between BP and CdS, while the high lattice match between Au NRs and CdS enables the effective electron delivery from Au to CdS. (3) Au NRs with visible and NIR plasmonic absorption offer hot electrons to CdS, further contributing to the photocatalytic performance. The present work not only proposes an effective strategy for prolonging the photogenerated charge lifetime of BP but also deepens the understanding of the charge-transfer dynamics in ternary heterostructure photocatalysts.

As a critical parameter commonly used as an intrinsic reference for electron-transfer potential in a semiconductormetal hybrid structure, work functions of the materials were first evaluated. In our design, Au NRs enclosed by (100) facets are chosen as plasmonic nanostructures not only to harvest vis–NIR light but also to serve as electron relays.²¹ The firstprinciples calculations show that the Au(100) surface and the



Figure 3. Photocatalytic H_2 production over different samples under UV-vis-NIR irradiation (a). Comparison of H_2 production rate over different samples under UV-vis-NIR, vis-NIR, and NIR light irradiation (b). DRS (left axis, red line) and AQE (right axis, blue column) of BP-Au-CdS (c). Cycle stability test on BP-Au-CdS photocatalytic H_2 production under UV-vis-NIR irradiation (d).

(100) surface of CdS NW have work functions of 5.09 and 4.31 eV, respectively (Figure S1). Generally, the Schottky barrier can be formed between metal and an n-type semiconductor when the work function of the metal (W_m) is greater than that of the semiconductor (W_s) $(W_m > W_s)$.²² Hence, as illustrated in Figure 1a, the formation of the Schottky barrier in the Au–CdS heterojunction is favorable for facilitating the injection of hot electrons from Au to CdS while suppressing the backflow of injected electrons from CdS to Au. In the case of Au(100) surface (5.06 eV) and monolayer BP (4.86 eV) (Figure S2), the Schottky barrier cannot be formed because of the match of their work functions, so that the bidirectional migration of electrons between BP and Au may be well-harnessed because of the well-established Ohmic contact (Figure 1b).²³

Our experiments began with the synthesis of CdS NWs, Au NRs, and BP QDs by a hydrothermal process, seed-mediated strategy, and liquid exfoliation method, respectively. Their initial morphologies were observed by transmission electron microscopy (TEM). CdS NWs show a uniform one-dimensional (1D) morphology with a diameter of about 50 nm and length in the range of $3-10 \ \mu m$ (Figure 2a). From highresolution TEM (HRTEM) images, clear lattice fringes with a d-spacing of 0.33 nm are observed (Figure 2b), which correspond to the (002) plane of CdS. Au NRs possess an average aspect ratio of 4 (24.3 nm in diameter and 99.3 nm in length) (Figure S3a), leading to a longitudinal surface plasmon resonance (LSPR) absorption peak located at 860 nm (Figure S3b). Ultrasmall BP QDs with a lateral size of 4.1 ± 0.7 nm and corresponding crystal lattice fringes of 0.26 nm are observed in Figure S4a-c. The obtained BP QDs exhibit a broad absorption from the UV to the NIR range, giving a band gap of 1.31 eV (Figure S 4d). Figure S5 presents scanning electron microscopy (SEM) images of Au-CdS heterostructures with different Au contents. After the Au NRs are decorated on the

surface of CdS through the ligand exchange process, an effective 1D–1D interfacial interaction is constructed (Figure 2c). The crystal lattice fringes of 0.20 nm detected on the NR are attributed to the Au(002) facet (Figure 2d). Interestingly, it is found that the lattice spacing of CdS and that of Au are periodically overlapped, implying a high interface lattice match between the CdS and Au phases and consequently an enhanced separation and transfer of photoinduced electron-hole pairs at the interface (Figure 2d; Figure S6 and the corresponding discussion).²⁴ Figure 2e displays BP QDs deposited Au-CdS (BP-Au-CdS) ternary composites obtained through a facile self-assembly approach. The HRTEM image clearly shows the different lattice fringes of 0.32, 0.20, and 0.26 nm, corresponding to CdS, Au, and BP, respectively (Figure 2f). The SEM images, corresponding energy-dispersive X-ray (EDX) elemental mapping, and EDX analysis (Figures S7-S9) further demonstrate the hybridization of BP and Au–CdS. In particular, EDX mapping on the high-angle annular darkfield scanning transmission electron microscopy image of BP-Au-CdS in Figure S10 shows the aggregation of BP QDs on the surface of Au NRs and a very little amount of BP deposited directly on the surface of CdS. As for BP-CdS with equivalent BP addition, it is observed that only a small fraction of BP QDs attached on the CdS NW, while a large proportion of them were scattered around (Figure S11). These results originate from the fact that the electrostatic attractive interaction between negatively charged BP QDs and positively charged Au NRs is able to endow the two ingredients with an efficient interfacial interaction (Figure S12),²⁵ while the low interface adhesion formation energy between BP QDs and CdS NWs is insufficient to establish interfacial connection (Figure S13, Table S1, and the corresponding discussion).²⁴

The phase identification of the as-synthesized CdS, Au–CdS, and BP–Au–CdS were performed by X-ray diffraction (XRD)



Figure 4. Normalized transient absorption traces observed at 480 nm (a) and 737 nm (b) for different samples. Bold lines indicate multiexponential curves fitted to kinetic traces. Schematic illustration of electron-transfer pathway in the BP-Au-CdS system (c).

(Figure S14). No signal assigned to BP is detectable in the BP– Au–CdS composites, as a result of its low weight ratio (~1 wt %). To verify the existence of BP in the composites, Raman spectroscopy was measured. As shown in Figure S15, both BP QDs and BP-Au-CdS exhibit characteristic peaks at 360.0, 435.5, and 463.2 cm⁻¹, which can be assigned to A_g^{-1} , B_{2g} , and A_g^2 phonon modes of vibration originating from in-plane (B_{2g} and A_g^2 and out-of-plane (A_g^1) vibrational modes of BP, respectively,²⁷ indicating the successful deposition of BP on Au-CdS. X-ray photoelectron spectroscopy (XPS) spectra of Cd 3d, S 2p, Au 4f, and P 2p were measured (Figure S16 and corresponding discussion). The peak shifts after the formation of the composite exhibit the interaction between Au NRs and CdS, as well as BP and Au-CdS. The optical absorption properties of the solid samples were analyzed by UV-vis-NIR diffuse reflectance spectra (DRS) (Figure S17). Bare CdS shows an absorption edge at 520 nm, corresponding to a band gap of 2.38 eV. After loading Au NRs, two additional absorption bands centered at the visible and NIR regions appear in Au-CdS composites, as a consequence of the transverse surface plasmon resonance (TSPR) and LSPR photoabsorption of Au NRs, respectively. Compared to the bare Au NRs colloid (Figure S3b), both TSPR and LSPR absorption of the Au-CdS sample are red-shifted because of the electron transfer from Au to CdS. In contrast, neither TSPR nor LSPR absorption of BP-Au shifts after the decoration of BP QDs onto Au NRs as a result of the bidirectional migration of electrons between BP and Au (Figure S18). When BP is hybridized with CdS, a tail absorption edge following the main absorption of CdS is observed and assigned to the absorption of BP QDs (Figure S4d). For BP-Au-CdS, integrated absorptions of CdS, Au, and BP are observed from the UV to the NIR range, showing its capability for the utilization of a long-wavelength solar spectrum.

The photocatalytic activities of BP-Au-CdS in reductive generation of H₂ were examined in aqueous solutions containing Na₂S/Na₂SO₃ as sacrificial electron donors during simulated solar (UV-vis-NIR) light and wavelengths longer than 420 nm (vis–NIR) and 700 nm (NIR) light irradiation. From Figure 3a, the amount of H₂ generated from the BP-Au-CdS system increased with time and reached 30.3 mmol g⁻¹ under solar light for 3 h. As reference experiments, only 1.88, 2.17, and 11.1 mmol g^{-1} was detected under similar conditions using CdS, BP-CdS, and Au-CdS photocatalysts, respectively. Negligible H₂ production was observed with bare Au NRs and BP QDs, as well as BP-Au composite, because the energetic electrons cannot be effectively extracted and migrated to participate in photocatalytic processes.²⁵ These results indicate that the interaction between BP, Au, and CdS plays a crucial role in the photocatalytic H₂ production. The optimal amount of Au NRs and BP QDs in the present BP-Au-CdS system was demonstrated to be 3 and 1 wt %, respectively (Figure S19), which led to a H_2 production rate of 10.1 mmol $g^{-1} h^{-1}$ in the full solar spectrum region (Figure 3b, black column). As the irradiated wavelength was longer than 420 nm, similar phenomena were observed, in which the H₂ generation rate of BP-Au-CdS (8.6 mmol $g^{-1}h^{-1}$) was 17, 14, and 2.4 times those of CdS (0.52 mmol $g^{-1}h^{-1}$), BP-CdS (0.60 mmol $g^{-1} h^{-1}$), and Au–CdS (3.6 mmol $g^{-1} h^{-1}$), respectively (Figure 3b, red column). When it comes to NIR light ($\lambda > 700$ nm) illumination, the photocatalytic H₂ evolution rates of BP-Au-CdS and Au-CdS were measured to be 4.3 and 1.2 mmol g⁻¹ h⁻¹, respectively (Figure 3b, blue column). CdS and BP-CdS exhibited no obvious photocatalytic activity at wavelengths longer than 700 nm. On the one hand, the lowenergy photons coming from the filtered Xe lamp could not cause the band gap photoexcitation of CdS. On the other hand, the interface adhesion formation energy between BP and CdS

Table 1. Lifetime (τ_i) and Amplitudes (A_i) of the Transient Absorption Decays at the Au and BP Signal Regions for Different Samples

Au signal					BP signal						
sample	A_1	τ_1 (ps)	A_2	$ au_2$ (ps)	sample	A_1	τ_1 (ps)	A_2	$\tau_2 \text{ (ps)}$	A_3	τ_3 (ps)
Au	1	3.0 ± 0.2			BP	0.43	1.7 ± 0.3	0.57	10 ± 2		
BP-Au	1	4.0 ± 1			BP-Au	0.14	8.0 ± 4	0.86	130 ± 70		
Au-CdS	0.3	13 ± 5	0.7	2200 ± 800	BP-CdS	0.72	6.0 ± 3	0.28	500 ± 200		
					BP-Au-CdS	0.12	11 ± 3	0.32	400 ± 100	0.56	3000 ± 900

was too low to establish strong connection, resulting in a poor interfacial charge transfer from BP to ${\rm CdS.}^{26}$

The wavelength-dependent apparent quantum efficiency (AQE) of H₂ production over BP-Au-CdS was measured to determine that the activity was driven by the light-excited electrons in each component under the optimal conditions. As shown in Figure 3c, the action spectrum of the AQE is basically in agreement with the absorption spectrum. Compared with analogous plasmon-mediated and BP-based photocatalysts, the ultrahigh AQE of $2.3 \pm 0.2\%$ at 900 \pm 5 nm irradiation makes the BP-Au-CdS an efficient photocatalyst under the NIR light (Table S2), which represents exciting progress in full solar spectrum photocatalytic H₂ production. The photocatalytic stability of BP-Au-CdS was investigated by cyclic photocatalytic H₂ evolution experiments (Figure 3d). After 2 recycles, the catalysts were stored for 3 weeks and still revealed similar activity. Furthermore, no obvious change was observed in Raman spectra of the ternary composite after the photocatalytic reaction (Figure S20), showing that BP-Au-CdS can be used as a stable photocatalyst.

The effect of Au and BP decoration on charge carrier dynamics over the BP-Au-CdS system was studied using broadband ultrafast transient absorption (TA) spectroscopy. In Figure S21 we show the typical differential absorption (ΔA) spectra for the bare Au and BP, as well as Au-CdS and BP-Au-CdS composites at early delay time.²⁸ Following 620 nm pump light excitation, the ΔA spectra reveal a pronounced signal around 620 nm in all samples attributed to the scattering effect.^{29,30} After the scattering signals are eliminated, for Au and Au-CdS samples, the same broad absorptions are seen at around 490 nm (Figure S21a,b), which corresponds to the TSPR feature of Au NRs.³¹ In Figure S21c, the broad bleach feature ranging from 700 to 750 nm is related to the holes photoexcited in BP.³² Thus, the signals of Au and BP features are separated (Figure S21d) and the investigation of carrier transport behaviors over each component of the composites can be achieved.

Time-resolved spectra in Figure S22 reveal the decay of the plasmon component features in the Au-mediated materials. Note that TSPR features of BP-Au (496 nm) and Au-CdS (480 nm) samples were separately red and blue-shifted, as compared with those of Au NR colloids (490 nm), which were ascribed to the electron transfer from BP to Au (increasing the electron density in Au) and from Au to CdS (decreasing the electron density in Au), respectively.³³ To evaluate the decay kinetics of the photogenerated electron-hole pairs in Au components, the time profiles of absorption probed at 480 nm were fitted using a multiexponential function as displayed in Figure 4a, and their lifetimes (τ_i) and amplitudes (A_i) are summarized in Table 1. Bare Au NRs exhibited fast decay with time scale of 3.0 ps (100%), which was related to the relaxation of hot electrons consistent with previous reports on colloidal Au NRs.³⁴ The recovery kinetics of BP-Au composite was

quite similar to that of bare Au NRs and resulted in a time constant for electron-hole recombination of 4.0 ps (100%), suggesting a rapid hot electron relaxation process within Au prior to injection into BP. The transient absorption trace on the Au-CdS system was fitted to a biexponential function with time constants of 13 ps (30%) and 2200 ps (70%). The interaction between Au and CdS delayed the exciton recovery process in Au, giving rise to a prolonged lifetime of the first component (τ_1 , 13 ps). The long decay component with lifetime of τ_2 , 2200 ps, was due to the electrons injected from Au into CdS (τ_{inj}) and recovered from CdS to Au (τ_{re}).³⁵ This newly opened charge recombination channel accounted for 70% of the overall electron-hole recombinations in Au, and we obtained the electron injection time scale $\tau_{inj} = 5.3$ ps, which was far below the recombination time scale $\tau_{\rm re} \approx 2200$ ps (Figure S23 and corresponding discussion).³⁶ Benefiting from the formation of Schottky barriers, the recombination between the trapped hot electrons in CdS and the holes in Au was significantly retarded.

The recovery of the bleach features of BP component in different samples are shown in Figure S24, wherein the pronounced signal shifting observed for BP-Au and BP-Au-CdS was due to the electron-transfer interaction between BP and Au. Simultaneously, the more intense negative feature at <715 nm was observed when BP-CdS and BP-Au-CdS were assembled (Figure S24b,d). This could probably be explained by the more intense electron-hole feature from the dangling bond of BP as a result of the aggregation of BP on the CdS surface.³⁷ Comparison between the normalized transient absorption dynamics for the bleach recovery at 737 nm is presented in Figure 4b for the different BP-mediated materials. In bare BP QDs, as summarized in Table 1, two fast decay components were observed, which could be ascribed to the exciton recovery to the ground state (1.7 ps) and residual cooling of the trapped electrons in superficial defect states of BP (10 ps), respectively.^{17,32} For BP–Au, BP–CdS, and BP– Au-CdS composites, the bleach recovery kinetics were fitted to bi- or triexponential functions with two or three time constants, and each time scale represented a different electron decay process in the hybrid systems. The shortest component (τ_1) corresponded to the intrinsic recovery of BP, namely, the recombination of electron-hole pairs within BP. The second component with lifetime of several hundred picoseconds (τ_2) was due to the electrons injected from BP into the neighboring Au or CdS within a short distance.³⁸ Lacking effective diffusion, the trapped electrons in Au or CdS of binary heterostructures rapidly recombined with the holes in BP within 100-500 ps. The proportions of the transferred electrons (injection efficiency, $1 - A_1$ in BP-Au (86%) and BP-Au-CdS (88%) systems were much larger than those in the BP-CdS (28%) system, owing to the matched work function as well as the efficient interfacial interaction between BP and Au. A rapid electron injection process ($\tau_{inj} = 1.6 \text{ ps}$) from BP to Au was

observed in the BP–Au system, while the subsequent backflow of electrons from Au to BP also happened in a short period of time ($\tau_{\rm re} \approx 130 \text{ ps}$) (Figure S25 and corresponding discussion). As for the BP–Au–CdS system, the second component was followed by a long-lived component, τ_3 , corresponding to the recombination between the long-distance diffused electrons in CdS delivered through Au and the holes in BP. Such a long lifetime of 3000 ps clearly demonstrated the efficient charge carrier separation process in the BP–Au–CdS system.

In the same manner, control TA experiments in which CdS was excited to confirm the calculated electrostatic potential results were performed upon 460 nm pump light excitation of CdS and BP–Au–CdS. The spectra of all samples revealed a pronounced feature in the wavelength range from 475 to 625 nm (Figure S26a and b), which could be assigned to the stimulated radiation of CdS. It is worth noting that the strong radiation peaks of CdS covered up the relatively weak peak profiles in Au and BP signal regions. The invariable position and intensity of the peak profile, as well as approximate time constants of radiation recovery fitted at 504 nm (Table S3), were evidenced by comparing the CdS signals of bare CdS and BP–Au–CdS composite, showing the inhibited electron transfer from CdS to Au or BP.

Based on these results, the possible mechanism for H₂ evolution over the BP-Au-CdS system is illustrated in Figure 4c. According to UV-vis-NIR absorption spectra (Figures S4d and S17) and Mott-Schottky plots (Figure S27), CB and valence band (VB) edges of BP QDs and CdS NWs are determined to be about -0.91 and 0.40 V, -0.57 and 1.81 V versus reversible hydrogen electrode (vs RHE), respectively. It is noteworthy that, as compared to bulk (ca. 0.30 eV) or flakelike BP (ca. 0.60 eV),^{16,39} BP QDs possess a larger band gap (1.31 eV) due to quantum confinement.⁴⁰ BP nanosheets have been incorporated with Au nanoparticles (NPs) and La₂Ti₂O₇ to harvest visible to NIR light for water splitting, but the obtained composite still bears low photocatalytic efficiency in the NIR region perhaps because of the narrow absorption of Au NPs and the inefficient electron extraction from BP NSs due to the low-positioned CB edge.³⁹ In our present work, an upshift of the edge positions of the CB was observed in BP QDs, which is higher than the LSPR energy level of Au NRs with LSPR absorption peak at 860 nm (-0.84 eV). When BP-Au-CdS is irradiated by UV, visible, or NIR light, BP QD is excited to generate electrons and holes in the CB and VB, respectively. Thermodynamically, electrons in BP can transfer to Au NRs. Meanwhile, hot electrons of Au NRs are also generated owing to SPR excitation. According to TA results, these electrons from excited Au NRs unidirectionally transfer to the CB of CdS, in which H^+ (water) is reduced to H_2 . Finally, holes are rapidly trapped by S^{2-}/SO_3^{2-} as a sacrificial electron donor.

In summary, a promising ternary heterostructured photocatalyst has been developed by integrating BP QDs, Au NRs, and CdS NWs (BP–Au–CdS) for full solar spectrum photocatalytic H₂ production. Taking advantage of the match of work function of BP with that of Au and the formation of the Schottky junction between Au and CdS, efficient charge separation in BP QDs was achieved by the charge delivery from BP to CdS through Au as an electron relay. Simultaneously, Au NRs were excited in the UV–NIR regions to serve as a plasmonic photosensitizer, injecting hot electrons into CdS. The established unidirectional carrier transport channel in the BP–Au–CdS system was demonstrated by transient absorption measurements, wherein the lifetime of the electron-hole pairs photogenerated in both BP and Au components increased because of effective charge separation due to injection of electrons from BP to Au and then to CdS, upon simultaneous excitation of BP and Au. The combination of the charge-transfer enhancement and the multiple light-harvesting extension of the ternary heterostructure was responsible for the superior H₂ evolution rate of 10.1 mmol g⁻¹ h⁻¹ under UV-vis-NIR illumination and the unprecedented AQE of 2.3% at 900 nm irradiation. This is the first deep investigation about the charge lifetime-related photocatalytic activity of BP QDs and will provide a stepping stone for exploiting full solar spectrum responsive heterostructure photocatalysts with high performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.8b00126.

Experimental section; calculated electrostatic potentials (Figures S1 and S2); TEM image and vis-NIR absorption spectrum (Figure S3); TEM images, statistical analysis, and UV-vis-NIR absorption spectrum (Figure S4); SEM images (Figures S5 and S7); interface models (Figures S6 and S13); SEM-EDX images (Figure S8); EDX spectra (Figure S9); STEM-EDX images (Figures S10 and S11); zeta potentials (Figure S12); interface adhesion formation energy (Table S1); XRD patterns (Figure S14); Raman spectra (Figures S15 and S20); XPS results (Figure S16); UV-vis-NIR DRS (Figure S17); vis-NIR absorption spectrum (Figure S18); photocatalytic H₂ production (Figure S19); comparison of photocatalytic activity (Table S2); TA spectra (Figures S21, S22, S24, and S26); lifetime and amplitudes (Table S3); electron-transfer pathways (Figures S23 and S25); M–S plots (Figure S27) (PDF)

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Notes

The authors declare no competing financial interest.

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