Au/g-C₃N₄ heterostructure sensitized by black phosphorus for full solar spectrum waste-to-hydrogen conversion

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ABSTRACT Photocatalytic water splitting with simultaneous degradation of organic pollutants is an effective strategy to alleviate the increasingly serious energy and environmental crisis. However, the photocatalytic activity is restricted by the high charge recombination rate and limited sunlight utilization. Herein, black phosphorus (BP) with a broad sunlight response range was utilized as a photosensitizer to enhance the photocatalytic performance of the Au/carbon nitride (CN) heterostructure. The as-prepared BP/Au/CN exhibited a significantly enhanced H₂ generation rate of 1400.8 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under UV-vis light irradiation, which is almost 70 times higher than that of bare CN and BP/CN and 2 folds higher than that of the Au/CN heterojunction. Specifically, the optimal BP/Au/CN sample presented a waste-to-hydrogen production rate of 195.8 $\mu\text{mol h}^{-1} \text{g}^{-1}$ with the degradation of bisphenol A, verifying the synergistic effect of the ternary heterojunction. The photocatalytic mechanism was systematically studied by the combination of experiments and theoretical calculations. The improved photocatalytic performance was derived from the overall sunlight absorption ability of BP, effective electron transfer media and plasmonic character of Au nanoparticles, as well as the matched work function and strong interaction of the three components. A unidirectional electron transfer from BP to Au and then to CN was established, which effectively improved the charge transfer capability, resulting from the appropriate Ohmic contact of Au and BP and the Schottky barrier constructed in Au/CN hybrid.

Keywords: Au/carbon nitride, black phosphorus, photocatalysis, H₂ production, waste treatment

INTRODUCTION

Photocatalysis is an effective method to utilize solar light for energy conversion and organic pollution removal. However, the rapid recombination of photogenerated electrons and holes in pure water restricts the photocatalytic efficiency. The charge separation efficiency and photocatalytic activity can be enhanced by adding proper hole sacrificial agents into the catalytic system.

The quantum efficiency could reach 95% by adding effective hole sacrificial agents [1]. Although the incorporation of the sacrificial agent achieved a high quantum efficiency, it increased the economic cost and wasted the highly reactive oxygen species [2–10]. Therefore, it is necessary to find a substitute for the traditional sacrificial agents to improve solar energy efficiency.

The photogenerated holes or $\cdot\text{OH}$ radicals are the main active substances in the degradation process of organic pollutants, and the organic pollutants can be a potential substitution of the traditional sacrificial agent in the hydrogen evolution reaction (HER). Simultaneous pollution degradation and hydrogen production can improve the energy efficiency and reduce the overall energy consumption [11–18]. Recently, several types of organic pollutants or antibiotics were used in photocatalytic hydrogen production reactions. Chen's group [14] found that g-C₃N₄ achieved the degradation of roxithromycin with improved photocatalytic efficiency of hydrogen production. Li and his co-workers [16] demonstrated carbon/carbon nitride porous nanotubes photocatalyst with high efficiency of water splitting and bisphenol A (BPA) degradation. Therefore, the development of hydrogen production technology from organic pollutant wastewater is a promising way to enhance the photocatalytic hydrogen production efficiency with low energy consumption. However, most photocatalysts reported so far can only utilize ultraviolet-visible light, and the near-infrared light that accounts for 50% of the sunlight has not been effectively utilized.

Moreover, the synergistic mechanism of photocatalytic oxidation (degradation) and reduction (hydrogen evolution) reaction remains to be further studied. Therefore, it is meaningful to construct a highly efficient and stable visible-near infrared response photocatalyst and explore the photocatalytic mechanism systematically. In recent years, black phosphorus (BP) presented broad application prospects as a visible near-infrared photocatalyst due to its unique tunable bandgap, abundant raw material storage, and excellent photoelectric properties [19–23]. However, the high charge recombination rate of BP reduces its photocatalytic activity. The construction of heterojunction is expected to improve the charge separation efficiency. Two-dimensional (2D) g-C₃N₄ (CN) with rich raw materials, non-

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toxic, and simple preparation process was widely investigated in photocatalytic water splitting reactions. The charge separation efficiency of BP was enhanced through the construction of heterojunction between BP and CN [24–27]. However, the photocatalytic activity is still far from the ideal goal, which is due to the internal charge recombination of CN and BP. A suitable electron transfer medium between BP and CN can be used to improve their charge transfer efficiency as well as photocatalytic activity. Among various materials, gold nanoparticles (Au NPs) with a unique surface plasma resonance (SPR) effect served as an electron transfer medium during photocatalysis [28–31]. Zhu *et al.* [29] designed BP-sensitized Au/La₂Ti₂O₇ nanostructures, which presented excellent photocatalytic activities in the full solar region. Zhang and his co-workers [30] prepared a BP-Au-CdS heterostructure with Au as an electron transfer medium, which achieved highly efficient photocatalytic water splitting in the presence of ultrafast charge separation. The above studies show that semiconductor photocatalysts and Au NPs with matched work functions could significantly improve the photocatalytic efficiency by regulating the charge transfer mechanism. Therefore, the introduction of Au NPs between BP and CN is expected to change the electron transfer by constructing Au electron transfer media. The unique SPR effect of Au also helps to improve the utilization rate of sunlight and photocatalytic activity. Nevertheless, there are no reports about the design of Au to optimize the photocatalytic performance of the BP/CN heterojunction, especially in the field of hydrogen production from wastewater in the UV-vis region.

In this paper, BP/Au/CN ternary photocatalyst was designed and applied to the water splitting of BPA wastewater. The as-prepared BP/Au/CN exhibited a significantly enhanced H₂ generation rate of 1400.8 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under UV-vis light irradiation, which was almost ~ 70 times higher than that of the bare CN and BP/CN sample and even 2 folds larger than that of the Au/CN heterojunction. In addition, the photocatalytic activity for BPA wastewater reached 195.8 $\mu\text{mol h}^{-1} \text{g}^{-1}$ without extra co-catalysts or sacrificial agents. The mechanism was investigated by experimental characterizations and density functional theory (DFT) calculations. BP absorbs the whole range of sunlight under the irradiation of full-spectrum light. The Fermi energy level of the p-type BP is higher than the work function of Au, the excited electrons of BP were transferred to the surface of Au owing to the well-established Ohmic contact. Au NPs also absorbed a certain amount of visible light to generate hot electrons in the presence of SPR effect, which was finally transferred

to the conduction band of n-type CN driven by the Schottky barrier. This work offered a theoretical and experimental reference to design widespread full-solar-spectrum responsive photocatalysts for waste-to-energy conversion.

EXPERIMENTAL SECTION

Chemicals and reagents

Melamine and triethanolamine (TEOA) of analytical grade were obtained from Macklin, bulk BP was purchased from Smart elements, chloroauric acid (HAuCl₄) was obtained from Nanjing Chemical Reagent Co., Ltd, and cyanuric acid was purchased from Adamas.

Synthesis of porous CN nanosheets

The synthesis of porous CN nanosheets was shown in route 1 of Fig. 1. Melamine (1 g) and 5 g of cyanuric acid were mixed and ground for 3 min, and then the mixture was transferred to the tube furnace and heated at 550°C for 2 h. The obtained product was collected and ground for further experiments.

Synthesis of BP/CN

Generally, 60 mg of CN and 5 mg of BP were mixed and ground for 5 min, and then 30 mL of ultra-pure water was added. The suspension was further dispersed by ultrasound for 1 h and reacted under the hydrothermal condition at 150°C for 2 h in an oven. The obtained product was then centrifugated, washed, and dried in an oven at 60°C for further use.

Synthesis of Au/CN

First, 1 mL of chloroauric acid (40 mg mL⁻¹) was added to a round-bottom flask containing 130 mL of purified water, followed by 12 mL of sodium citrate aqueous solution (1 wt%). The round-bottom flask was then heated to the boiling point in an oil bath. Finally, 148 mg of CN was added to the mixture solution, the boiling solution was further stirred for 8 min for sufficient reaction. After gradually cooling to room temperature, the resulting hybrid was centrifugated and washed several times with ultra-pure water and ethanol, and dried at 60°C for further experiments.

Synthesis of BP/Au/CN

The synthesis of BP/Au/CN is shown in stage 2 of Fig. 1. Au/CN (94 mg) and a certain amount of BP (3, 6, and 11 mg) were mixed and ground for 5 min, and then 30 mL of ultra-pure

Figure 1 The schematic route of the preparation process of BP/Au/CN.

water was added to the mixture and ultrasound for 1 h. The mixture was transferred to a Teflon-lined autoclave and reacted at 150°C for 2 h. The hybrid was then centrifugated, washed, and dried at 60°C in an oven for further experiments. The ternary heterojunction with 6 mg of BP was chosen as the optimized sample for further characterization.

RESULTS AND DISCUSSION

Morphology and structure

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the micromorphologies of CN, Au/CN, and BP/Au/CN. As shown in Fig. 2a, the CN sample was self-assembled into a porous nanosheet structure with lots of small pieces, which showed a large surface area of $81.30 \text{ m}^2 \text{ g}^{-1}$ (Fig. S1). Au NPs grew on the surface of CN with good dispersibility in Fig. 2b, which endowed Au/CN with a higher surface area of $85.08 \text{ m}^2 \text{ g}^{-1}$. Moreover, BP was face-to-face embedded on the Au/CN nanosheets to form a 2D/0D/2D heterojunction, as shown in Fig. S2 and Fig. 2c. In the high resolution TEM (HRTEM) image of BP/Au/CN (Fig. 2d), there was no obvious lattice of CN owing to the poor crystallinity of CN, in which the clear spacing of 0.35 and 0.23 nm corresponded to the classical (021) crystal plane of BP and the typical (111) crystal plane of Au NPs [23], respectively. The close lattice contact of the three-phase demonstrated the successful synthesis of the ternary heterojunction [32]. In addition, the energy dispersive spectroscopy (EDS) mapping illustrated the co-existence of C, N, Au, and P elements, as shown in Fig. 2e. The BP nanosheet mainly grew on the surface of the Au NPs to form the

2D/0D/2D ternary heterojunction with high-quality lattice contact, which was conducive to the charge transfer and separation process [33].

The crystal planes of CN, BP/CN, Au/CN, and BP/Au/CN were characterized by powder X-ray diffraction (XRD), as shown in Fig. 3a. CN presented two characteristic peaks at 13.5° and 27.5° , which were attributed to the triazine ring in (100) plane and conjugated aromatic ring in (002) crystal planes (JCPDS 87-1526, marked as &) [6]. There were three obvious additional peaks at 38.6° , 44.9° , and 64.6° in the Au/CN sample, which were indexed to the (111), (200), and (220) crystal planes of the Au species (JCPDS 80-0019, marked as @) [29]. The BP/CN sample showed three new peaks at 16.8° , 34.9° , and 56.8° , corresponding to the (020), (040), and (060) planes of BP (JCPDS 73-1358, marked as #) [3], respectively. All diffraction peaks of CN, Au, and BP existed in the XRD pattern of the BP/Au/CN sample, confirming the ternary materials were successfully prepared. To further investigate the surface functional component of CN, BP/CN, Au/CN, and BP/Au/CN, Fourier transform infrared (FT-IR) spectra are conducted in Fig. 3b. The obvious peak of the CN sample at 811 cm^{-1} corresponded to the vibration bending of the triazine ring. The wide absorption band ranging from 1211 to 1647 cm^{-1} was attributed to the stretching vibration of C=N or C-N. Besides, the typical peaks at $3047\text{--}3500 \text{ cm}^{-1}$ were assigned to the vibration modes of N-H or O-H, which were mainly derived from the amino group and the adsorbed water molecules on the surface of the photocatalyst. No obvious peak changes was found for CN after the introduction of Au NPs and BP nanosheets, indicating the main structure of CN was well preserved.

Figure 2 SEM images of (a) CN and (b) Au/CN. (c) TEM, (d) HRTEM, and (e) EDS mapping images of BP/Au/CN.

X-ray photoelectron spectroscopy (XPS) spectra of CN, BP, Au/CN, and BP/Au/CN were conducted to study the valence states and electron transfer direction. The characteristic peaks of C 1s, N 1s, P 2p, and Au 4f are shown in Fig. S3. In the high-resolution XPS spectrum of C 1s (Fig. 4a), all C 1s curves of CN, Au/CN, and BP/Au/CN were fitted into two separate peaks, originating from C–C and N–C=N, respectively [4]. Moreover, the N 1s spectra contained three individual peaks (Fig. 4b), located at 398.81, 400.81, and 404.25 eV, respectively, corresponding to C–N=C, N–(C)₃ and π -excitations [9]. Compared with pure CN, the peaks of Au/CN slightly shifted to lower binding energy, suggesting that the electron was probably

transferred from Au to CN [34].

Compared with Au/CN, the introduction of BP into Au/CN brought a downward shift in the binding energy, suggesting that the electron of BP was probably transferred to Au NPs. As revealed in Fig. 4c, the P 2p XPS spectra of BP and BP/Au/CN were divided into three peaks, assigning to P 2p_{3/2}, P 2p_{1/2}, and oxidized phosphorus (PO_x) [20], respectively. BP was slightly oxidized by oxygen in the air, and the component of PO_x in BP was 16.8%. The BP surface was further oxidized during the hydrothermal reaction, and the specific percentage of PO_x in BP/Au/CN was relatively higher than that in BP (22.3%). Compared with BP, the peaks of BP/Au/CN shifted to higher binding

Figure 3 (a) XRD patterns and (b) FT-IR spectra of CN, BP/CN, Au/CN, and BP/Au/CN.

Figure 4 High-resolution (a) C 1s and (b) N 1s XPS curves of CN, Au/CN, and BP/Au/CN; (c) high-resolution P 2p XPS curves of BP and BP/Au/CN; (d) high-resolution Au 4f XPS curves of Au/CN and BP/Au/CN.

energies by 0.39 eV ($P\ 2p_{3/2}$) and 0.36 eV ($P\ 2p_{1/2}$), which further indicated that certain electrons were transferred from BP to Au NPs. Moreover, there were two divided characteristic peaks at 83.89 and 87.55 eV in the Au 4f XPS spectra of Au/CN and BP/Au/CN, indicating the presence of Au^0 in the composite (Fig. 4d) [28]. The above XPS results further confirm the successful preparation of high-quality BP/Au/CN heterojunction. The electron transfer direction is probably from BP to Au and finally the CN surface.

Photocatalytic performance

The activities of the photocatalyst for hydrogen production and degradation of BPA were systematically investigated. As shown in Fig. 5a, CN presented a quite low photocatalytic activity of about $20.1\ \mu\text{mol h}^{-1}\text{g}^{-1}$, which was due to the high charge recombination rate and low visible light utilization rate. The introduction of BP into CN still resulted in a restricted activity

because of the insufficient charge transfer capability [35]. Au was deposited on the surface of the CN, and the Schottky heterojunction between CN and Au greatly improved the charge injection ability. Besides, the unique SPR effect improved the sunlight absorption ability. Thus, the HER activity was greatly increased to $650.2\ \mu\text{mol h}^{-1}\text{g}^{-1}$. When the optimum amount of BP (6 wt%) was hybridized with Au/CN, the enhanced HER was recognized both under UV-vis ($1400.8\ \mu\text{mol h}^{-1}\text{g}^{-1}$ Fig. 5b) and visible light ($1020.5\ \mu\text{mol h}^{-1}\text{g}^{-1}$, Fig. S4) irradiation, which was ascribed to the enhanced electron injection capability and whole light absorption capability of BP. In addition, CN showed trace photocatalytic activity for water splitting without any sacrificial agent, while BP/Au/CN sample illustrated a low HER activity of $124.4\ \mu\text{mol g}^{-1}\text{h}^{-1}$, as given in Fig. 5c. However, after 2.4 mg of BPA was added to the photocatalytic system, an obvious higher HER activity of $195.8\ \mu\text{mol g}^{-1}\text{h}^{-1}$ was achieved *via* a synergistic effect of BPA degradation, which was almost two times higher

Figure 5 (a) Time-dependent H₂ generation amount under UV-vis light irradiation over CN, BP/CN, Au/CN, and BP/Au/CN samples, (b) photocatalytic H₂ production rate of CN, BP/CN, Au/CN, and BP/Au/CN samples under UV-vis light irradiation, (c) photocatalytic activity of CN, BP/Au/CN, and BP/Au/CN+BPA samples without any sacrificial agents, (d) photocatalytic stability of BP/Au/CN+BPA samples for 10 h, (e) the XRD spectra of BP/Au/CN before and after photocatalysis, and (f) degradation efficiency of BPA by BP/Au/CN.

than the efficiency without the addition of BPA, achieving the improvement of HER and degradation of organic pollutants at the same time. In addition, the BP/Au/CN sample still possessed long-term photocatalytic stability, as presented in Fig. 5d. The photocatalytic activity almost remained unchanged after 10 h of photocatalytic reaction. As revealed in the XRD (Fig. 5e), infrared spectra (Fig. S5), XPS (C 1s, N 1s, Au 4f, P 2p, Fig. S6), and HRTEM image (Fig. S7) of the BP/Au/CN sample after photocatalysis, apart from the slight increase of the PO_x percent in P 2p spectrum (from 22.3% to 29.0%), the characteristic diffraction peaks and lattice fringe had no obvious change, indicating that the BP/Au/CN heterojunction presented well photocatalytic stability [36]. According to the literature reported, the PO_x on the surface of BP prevented further oxidation of the inner layer [37,38]. Therefore, the oxidation degree of BP in the BP/Au/CN photocatalyst was acceptable after photocatalysis for 10 h. To elucidate the reasons for its increased activity, the degradation pathways of BPA were investigated by combining liquid chromatography-mass spectrometry (LC-MS) and electron paramagnetic resonance (EPR).

As shown in Table S1, there was still a certain amount of undegraded BPA after 10 h of vacuum photocatalytic, indicating that BPA was enough during the photocatalytic water splitting. However, once the degradation experiment of BPA was conducted, BPA was rapidly degraded within 20 min in the air condition (Fig. 5f). The control experiments were conducted to analyze the reasons for the difference in degradation rate, in which the main degradation active substance including electron (e^-), holes (h^+), $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ upon photocatalytic reaction were investigated. AgNO_3 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, $t\text{-BuOH}$, and benzoquinone (BQ) (2 mmol) were added into 60 mL of BPA solution (2.4 mg) as the electron, hole, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ sacrificial agent, respectively. The results of the trapping experiments are exhibited in Fig. S8. The degradation efficiency of BPA decreased from 99.1% to

88.6% and 82.2 with the addition of AgNO_3 and $t\text{-BuOH}$, while that was reduced to 40.5% and 13.6% after adding $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and BQ quenchers, indicating that $\cdot\text{OH}$, h^+ and $\text{O}_2^{\cdot-}$ all played important roles in the degradation process. The water-splitting experiment was conducted in the vacuum, and $\text{O}_2^{\cdot-}$ cannot be generated without O_2 , which resulted in the lower degradation efficiency of BPA upon water splitting and gave BPA a certain advantage in the long-term photocatalytic hydrogen production. Based on the result of the trapping experiment, $\cdot\text{OH}$ and h^+ were the main active substance in water splitting, and the EPR measurement was conducted to detect $\cdot\text{OH}$ and h^+ signals. There were obvious $\cdot\text{OH}$ and h^+ signals of the BP/Au/CN samples upon light on in Fig. 6a, b. In addition, the chemical names and structures of the detected eleven intermediates were listed in Fig. 6c. According to the detected products and literature [39], there were three possible degradation pathways of BPA by BP/Au/CN. First, active substance h^+ and $\cdot\text{OH}$ were generated upon photocatalysis, and the phenyl ring of BPA with high electron density was destructed to form product B, product C, or product D/E (hydroquinone/phenol). In path two, the rings of product C were opened to generate product F by the oxidation reaction. The hydroquinone and phenol were dehydrogenated to form Product G (dehydrogenation) and Product H (oxidizing reaction) in another pathway. The aldehyde group of product H was further oxidized to the carboxyl group of product I, and Product D, E, and I were oxidized to product J. The aromatic ring of Product B, F, H, and J was then attacked to form ring-opened product K and product L, which were finally transformed into H_2O and CO_2 .

Photocatalytic mechanism

The wide sunlight absorption region

The sunlight absorption ability of CN, Au/CN, BP/CN, and BP/

Figure 6 (a) TEMPO h^+ , (b) DMPO $\cdot\text{OH}$ EPR spectra of BP/Au/CN with the irradiation light on/off, and (c) the proposed photocatalytic degradation intermediates and pathways of BPA by BP/Au/CN. TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl; DMPO: 5,5-dimethyl-1-pyrroline-*N*-oxide. A: BPA; B: 2-phenylbutanedioic acid; C: 4-(propan-2-yl)benzene-1,2-diol; D: hydroquinone; E: phenol; F: (2Z,4Z)-3-(propan-2-yl)hexa-2,4-dienedioic acid; G: 4-(prop-1-en-2-yl)phenol; H: 1-(4-hydroxyphenyl)ethan-1-one; I: 4-hydroxybenzoic acid; J: cyclohexa-2,5-diene-1,4-dione; K: valeric acid; L: succinic acid.

Au/CN were evaluated by the UV-vis spectra. As presented in Fig. 7a, CN showed an absorption edge at 430 nm with a bandgap of 2.7 eV (Fig. 7b). The sunlight absorption range was extended to the visible light region after Au NPs deposited on the surface of CN, and a typical SPR absorption centered at around 540 nm was recognized [28–31]. The solar absorption intensity of BP/Au/CN is even stronger than that of the BP/CN sample.

The BP/Au/CN hybrid material successfully combined the strong UV light absorption of CN, the special SPR effect of Au, and the typical full-spectrum absorption of BP, and a wide and intensive sunlight absorption from UV to the full-spectrum region was observed. The result showed that the BP/Au/CN hybrid can be used as an efficient photocatalyst for full-spectrum solar response. In addition, the UV-vis spectrum of BP/Au/CN + BPA was carried out to investigate the influence of BPA on the incident length of the UV-vis light, as revealed in Fig. S9. There was no obvious difference in the UV-vis spectrum after the addition of BPA, indicating that BPA almost did not affect the incident length of the UV-vis light. The conduction band (CB) and valence band (VB) values of CN and BP were further studied by the XPS VB spectra. As given in Fig. 7c, the XPS VB values of CN and BP were 1.5 and 0.57 eV, respectively, and the VB values were further converted to the standard electrode (normal hydrogen electrode (NHE)) potential concerning hydrogen (E_{NHE}) according to Equation (1):

$$E_{\text{NHE}}/\text{V} = \Phi + E_{\text{VL}}/\text{eV} - 4.44, \quad (1)$$

where Φ is the analyzer electron work function of the XPS instrument (4.30 eV), and E_{VL} is the value of vacuum level [35].

Therefore, the VB values of CN and BP were 1.36 and 0.43 V vs. NHE, respectively. In addition, the bandgap of the BP with few layers was about 1.5 eV in our previous study. Consequently, the CB values of CN and BP were -1.34 and -1.07 V, respectively. The CB value and bandgap of CN from experiments were consistent with the DFT calculation results. As shown in Fig. 7d and Table S2, the calculated bandgaps of CN and BP were 1.79 and 2.83 eV, respectively. Besides, the total density of states (DOS) of CN and BP presented energy level interleaving, which was beneficial to the separation of charges and the improvement of photocatalytic activity [40].

The enhanced charge transfer capability and dynamics

The charge transfer capability and dynamics were evaluated by transient photocurrent, steady-state photoluminescence (PL) and fluorescence decay, and linear sweep voltammetry (LSV) spectra. As shown in Fig. 8a, all samples expressed an obvious photocurrent response under sunlight irradiation. Pure CN had a very weak photocurrent density owing to the fast recombination of charges. The BP/CN sample presented an enhanced photocurrent response than CN due to the wide sunlight absorption of BP, which helped to generate more photo-generated charges. Au/CN also showed higher photocurrent density than CN in the presence of the SPR effect brought by Au. Besides, a certain electron injection existed between Au and CN, which also contributed to the enhancement of photocurrent density. The photocurrent value of Au/CN was higher than that of BP/CN at the very beginning. However, the photocurrent value of Au/CN gradually declined after 100 s of irradiation,

Figure 7 (a) UV spectra of CN, Au/CN, BP/CN, and BP/Au/CN; (b) bandgap of CN; (c) XPS VB spectra of CN and BP; (d) density of states of BP and CN. HOMO: the highest occupied molecular orbital.

Figure 8 Transient photocurrent measurement with a bias voltage of 0 V (a), PL spectra (b), LSV curves (c), and fluorescence lifetimes of (d) CN, Au/CN, BP/CN, and BP/Au/CN.

which was due to the low stability of the Au/CN sample. Thus, the carrier transfer ability of the Au/CN sample was higher than that of BP/CN. The stability of BP/CN was better than that of Au/CN. Both intensity and stability of photocurrent were improved after introducing BP to BP/Au/CN ternary heterojunction, which was ascribed to the broad sunlight absorption region and efficient charge separation at the interfaces. The photocurrent of BP/Au/CN showed an increasing trend with time, which was attributed to the faster charge generation rate than the recombination rate [41–45].

Fig. 8b reveals the PL spectra of CN, Au/CN, BP/CN, and BP/Au/CN. The emission peak of CN was centered at 465 nm with the excitation wavelength of 330 nm, and BP/CN exhibited much lower emission peaks than pure CN, implying that the charge recombination was effectively suppressed. Compared with BP/CN, the PL intensity of BP/CN was restrained after the addition of Au NPs, which was due to the change of the charge transfer pathway and the inhibition of the charge recombination rate. In addition, the LSV curves in Fig. 8c indicated that the current of the BP/Au/CN composite was higher than that of pure CN and BP/CN in the dark condition, indicating that BP/Au/CN had the highest charge separation rate. The time-resolved PL decay curves were measured to further investigate the charge transfer dynamics, and the corresponding average lifetimes were calculated according to Equation (2) [46–48]:

$$\tau = \frac{\tau_1^2 \times B_1 + \tau_2^2 \times B_2 + \tau_3^2 \times B_3}{\tau_1 \times B_1 + \tau_2 \times B_2 + \tau_3 \times B_3}, \quad (2)$$

where τ_1 , τ_2 , τ_3 are the three radiative lifetimes of charge changes, and A , B_1 , B_2 , B_3 are constant. As illustrated in Fig. 8d and Table S3, the average fluorescence lifetimes of the relevant catalysts

followed the order: BP/Au/CN > Au/CN > BP/CN > CN. The average PL lifetime of BP/Au/CN was much longer than that of CN by altering the contribution of each lifetime. All values were significantly different from those of CN or BP/CN, suggesting that the BP/Au/CN sample had distinguished emission pathways from the pure CN and BP/CN. A certain interface interaction occurred between CN and BP by the introduction of Au NPs, which greatly enhanced the charge transfer capability and suppressed the charge recombination strength by shortening overlap between electrons and holes [49–53]. The high charge transfer ability of BP/Au/CN was in good agreement with the transient photocurrent, PL, and LSV results.

The Fermi levels of BP, Au, and CN were calculated to further understand the charge transfer mechanism, which served as an intrinsic reference to evaluate the charge transfer directions in the BP/Au/CN semiconductor-metal composite system. As the first-principles calculations illustrated in Fig. 9a–c, the work functions of BP, Au (100) and CN were 4.66, 5.19, and 4.37 eV, respectively. The Schottky barrier was constructed between Au and an n-type CN because of the higher work function of Au than CN. Therefore, the hot electron in Au was injected from Au to CN. However, owing to the matched work functions of Au (5.19 eV) and p-type BP (4.66 eV), the well-established Ohmic contact was formed between them [30]. The relative positions of work functions of BP, Au, and CN were also verified by the ultraviolet photoelectron spectroscopy (UPS) experimental results. As shown in Fig. 9d–f, the E_{cutoff} of CN, BP, and Au was 17.9, 17.6, and 17.1 eV, respectively. Thus, the calculated work function values of CN, BP, and Au were 3.3, 3.5, and 4.0 eV vs. vacuum, and the relative positions of the work functions were consistent with the theoretical results.

Figure 9 The calculated work functions of (a) BP, (b) Au, and (c) CN, UPS spectra of (d) BP, (e) Au, and (f) CN.

Figure 10 Schematic picture of photocatalytic water splitting with BP/Au/CN by full-spectrum light irradiation.

As shown in Fig. 10, once BP/Au/CN was illuminated under the full-spectrum light, the electrons in VB of BP were excited to CB and flew to Au NPs driven by the Ohmic contact. Meanwhile, the hot electrons excited by the SPR effect were also

generated by Au NPs [54]. The above-concentrated electrons in Au NPs were then transferred to the CB of CN driven by the interfacial Schottky barrier between Au and CN. Finally, the gathered electrons on CN reduced water to H₂, and holes were

rapidly trapped by TEOA or BPA. As shown in Fig. S10, Au, BP/CN, and BP/Au/CN all presented obvious $\cdot\text{OH}$ and h^+ signals, and the introduction of Au NPs greatly improved the generation of h^+ and $\cdot\text{OH}$. As a result, the introduction of Au NPs not only absorbed full-spectrum light but also acted as an electron relay to improve the overall water splitting of the photocatalyst.

CONCLUSIONS

In conclusion, a novel ternary BP-sensitized Au/CN heterojunction was successfully designed by integrating BP nanosheets, Au NPs, and CN nanosheets for full-solar-spectrum photocatalytic waste-to-hydrogen production. Due to the extremely high utilization rate of sunlight and efficient charge transmission performance, the photocatalytic hydrogen production efficiency was significantly improved to $1400.5 \mu\text{mol h}^{-1} \text{g}^{-1}$ in the presence of TEOA. Especially, the activity reached $195.8 \mu\text{mol h}^{-1} \text{g}^{-1}$ accompanied by simultaneous degradation of BPA without any sacrificial agent. The synergistic mechanism of photocatalytic oxidation and reduction reaction was investigated. The oxidizing holes were consumed during the degradation process of BPA and the energy consumption of the system was reduced on the basis of improving the hydrogen production activity. These outstanding characteristics showed that BP and Au had great advantages to design visible-near-infrared active photocatalysts, especially in waste-to-energy conversion.

Received 3 September 2021; accepted 15 October 2021;
published online 7 December 2021

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Acknowledgements This work was supported by the National Natural Science Foundation of China (21801092, 21872001, and U1704140), the Program for the Development of Science and Technology of Jilin Province (20200801040GH), the Science and Technology Research Project of Henan Province (202102210055), the General project of Chinese postdoctoral program (2020M672263), the Key Research Programs in Universities of Henan Province (20A150031), and the Science and Technology Innovation Talent Support Program of Henan Province (19HASTIT034). Eceshi (www.eceshi.com) was acknowledged for the EPR analysis.

Author contributions Wang L designed and engineered the samples; Sun Z conceived the post-fabrication tuning of random modes; Zhao Z and Qi Y performed the experiments; Zhou G wrote the paper with the support from Zhang F. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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黑磷敏化的金/氮化碳异质结全光谱废水产氢性能研究

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摘要 光催化废水产氢技术是缓解日益严峻的能源和环境危机的有效方法。然而, 由于载流子复合率较高、太阳光利用率较低, 目前光催化活性仍然难以满足工业发展的需要。基于以上问题, 本文设计了具有全谱太阳光响应的黑磷敏化的金/氮化碳(BP/Au/CN)异质结光催化剂, 该三元异质结可以在实现降解双酚A的同时, 将水分解为氢气, 其光催化产氢活性可达到195.8 μmol h⁻¹ g⁻¹。此外, 在紫外-可见光照射下, BP/Au/CN的光催化产氢活性可以达到1400.8 μmol h⁻¹ g⁻¹, 是CN或BP/CN样品的近70倍, Au/CN异质结的2倍。光催化活性的提高表明异质结中三种元素具有良好的协同作用。本文将一系列实验表征与理论计算相结合, 对BP/Au/CN的光催化机理进行了系统研究。结果表明, 黑磷的全谱太阳光吸收能力、金的电子传输介质作用以及三种材料匹配的功函数是其光催化活性提高的关键因素。此外, 通过金和黑磷的欧姆接触以及Au/CN杂化体系中肖特基异质结的构筑, 实现了电子从黑磷到金, 再到氮化碳的单向转移, 从而提高了载流子的传输性能。