Self-Assembled Black Phosphorus-Based Composite Langmuir−Blodgett Films with an Enhanced Photocurrent Generation Capability and Surface-Enhanced Raman Scattering Properties

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ABSTRACT: In this work, Langmuir−Blodgett (LB) composite thin films were successfully prepared using black phosphorus nanosheets (BPNS) and dye molecules. Black phosphorus (BP) was first exfoliated in isopropanol solution to form BPNS, and then, BPNS were modified with 4-azidobenzoic acid (Az-BPNS) to improve their stability. The characterization results showed that the synthesized Az-BPNS-dye LB films have a uniform and ordered structure. In addition, the synthesized Az-BPNS-dye LB films exhibit excellent photoelectrochemical performance, and Az-BPNS-methylene blue (MB) produces higher photocurrent compared to Az-BPNS-Neutral red (NR) films. The current work shows an effective way to prepare functionalized BP-based materials and provide evidence for their application in optoelectronic devices.

1. INTRODUCTION
Two-dimensional materials (2D) with a unique structure, size, and thickness are widely used in optical, thermal, and biomedical fields.1−3 For two-dimensional materials, the inside of each layer and the layers are respectively connected by strong chemical bonds and weak van der Waals forces, which causes the characteristic material to be easily exfoliated into a single layer or multiple layers of an ultrathin atomic material.4 Black phosphorus (BP) exhibits good properties of high electron mobility and unique structural anisotropy, making it widely applied in electronic devices, photocatalysis, and biomedicine.5−9 However, BP is easily oxidized, which leads to weakened performance of BP in some aspects.10 At present, how to improve the stability of BP has attracted more and more people’s attention. In addition, the stability of BP can be improved by modifying the surface of BP, such as coordination chemistry, surface coating, doping with other components, and surface etching. Zhao et al. designed a benzenesulfonate ligand of titanium, in which the titanium atom has an empty orbital and benzenesulfonate has a strong electron-withdrawing effect. The ligand can coordinate with the lone electron pair of black phosphorus, which makes the phosphorus atom unable to react with oxygen.11 Yuan et al. successfully prepared a heterostructure of N-doped graphene (NG) and BP with few layers, which improves the stability of BP and adjusts the electronic structure of each component, enhancing its inherent activity.12 Kaur et al. reported the preparation of a self-assembled film of phosphorene using LB technology, and the prepared film showed good electronic properties and a high current modulation.13 In addition, Mao et al. successfully prepared BP nanosheet LB thin films with great potential in optoelectronic devices.14

As an important aspect of supramolecular chemistry, supramolecular assembly technology can prepare ordered ultrathin films, which can be widely used in photovoltaic devices, gas sensors, and electrodes.15,16 In addition, the LB film technology is regarded as the most common method of molecular assembly at the gas−liquid interface, which can prepare uniform single-layer and multilayer films with controllable thickness.17 The charged molecules can form a stable monolayer at the gas/liquid interface through electrostatic interaction.18 Phenazine derivatives have the ability to be protonated easily, which may be due to the fact that phenazine derivatives contain electron-deficient π systems, nitrogen atoms with lone pairs of electrons, and three fused aromatic ring structures. These special structures of phenazine derivatives make them have good applications in the overlap of π−π electrons and are used as ionic ligands and hydrogen bond acceptors in chemical reactions, with a certain electron-accepting ability.19−21 Generally, phenazine derivatives and
other molecules realize supramolecular self-assembly through the synergistic effect of π−π stacking and hydrogen bonding. At the same time, electrostatic interaction is also a way of supramolecular self-assembly. In the process of self-assembly, the electrostatic interactions between different charged groups are called salt bonds. The rules for the action of salt bonds are divided into two aspects: one is the number of charges, and the other is the distance between group charges. The more charged groups, the smaller the distance, and the greater the energy of the salt bond. Therefore, dye molecules containing phenazine groups were selected as subphases, and it was used for LB film assembly with surface-modified BP.

In this study, black phosphorus nanosheets (BPNS) were obtained by liquid exfoliation, and then, 4-azidobenzoic acid was used to modify BPNS (Az-BPNS). TEM, SEM, and AFM characterization methods proved that dye molecules and Az-BPNS formed dense films with a uniform structure using LB technology. The results indicate that the obtained Az-BPNS-dye composite films have good performance in photoelectric conversion. This work proves that BP-based composite films can be used as an effective tool in photoelectric conversion.

2. RESULTS AND DISCUSSION

Figure 1 shows the synthesis illustration of the Az-BPNS-dye composite film. BP nanosheets (BPNS) were successfully prepared using a typical liquid exfoliation in isopropanol. In order to avoid the oxidation of BPNS, 4-azidobenzoic acid was used to modify BPNS through chemical reaction, and the obtained sample was named Az-BPNS. Through an LB method, Az-BPNS solution was dispersed on the surface of the dye solution, and we waited for a period of time to ensure that the solvent was completely evaporated, and then, the barriers would move to form Az-BPNS-dye composite LB films. The resulting composite films were transferred to ITO glass to explore their photoelectrochemical properties.

The particle size distribution diagram of the prepared BPNS is shown in Figure 2a. The result shows that the size of BPNS is mainly between 200 and 400 nm, and the average size distribution is about 290 nm. The image inserted in Figure 1 shows that the color of the prepared BPNS colloidal solution is brown, and the higher the concentration of BPNS, the darker the color of the colloidal solution. The Tyndall effect occurred when the light beam passed through the BPNS solution, indicating that the BPNS were evenly distributed in the solution and the BPNS colloidal solution was successfully prepared. A transmission electron microscope (TEM) image of BPNS in Figure 2c indicates that the typical few-layer BPNS were successfully prepared with a size of 200−300 nm. The X-ray diffraction (XRD) patterns of BPNS and Az-BPNS are analyzed, and the results are shown in Figure 2c. The characteristic peaks at 16.8, 26.9, 34.2, 35.5, and 52.3° correspond to the (020), (021), (040), (111), and (060) planes of BPNS, respectively. As for Az-BPNS, the characteristic peak of BPNS remains unchanged, demonstrating that the addition of azide does not change the interlayer distance of BPNS.

The elemental composition and chemical structure of Az-BPNS were explored by X-ray photoelectron spectroscopy (XPS). Figure 3 exhibits the characteristic peaks of O 1s, P 2p, and P 2s. As for the high-resolution P 2p spectrum of the original BPNS (Figure 3b), two strong peaks appeared at 129.6 and 130.4 eV can be assigned to P 2p3/2 and P 2p1/2 of the P−P bond. Furthermore, the broad peak around 134.3 eV can be attributed to PO


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experiments. For further analysis of the morphologies of the prepared Az-BPNS-dye composite films, TEM images are shown in Figure 4c,d. It can be seen that the Az-BPNS-dye monolayer films have a dense and uniform structure, and some BPNS are also observed in TEM images. These data indicate that the Az-BPNS-dye composite films have been successfully

Figure 2. (a) Hydrodynamic size of BPNS (the inset image is BPNS colloidal solution). (b) TEM image of BPNS. (c) XRD and (d) Raman spectrum of Az-BPNS and BPNS. (e) SEM image of Az-BPNS with (f–i) element mappings. Photograph courtesy of “Ran Wang”. Copyright 2020.

Figure 3. XPS spectra of (a) full spectrum, (b) P 2p of the BPNS, and (c) P 2p and (d) N 1s of Az-BPNS.
The results of FT-IR spectra are also used to confirm the successful synthesis of Az-BPNS-dye composite films. From Figure 4e, the peaks around 2918 and 2848 cm$^{-1}$ correspond to the C$-\text{H}$ stretching vibration on the methyl structure. The peaks assigned to the N$-\text{H}$ bond appeared at 3357 and 3224 cm$^{-1}$. Due to the electrostatic interaction between the amino group of NR molecules and the carboxylic acid group of Az-BPNS, the position of the N$-\text{H}$ bond absorption peak is changed. The peaks at 1598, 1623, 1612, and 1601 cm$^{-1}$ can be attributed to the C$-\text{C}$ and C$-\text{N}$ plane vibration peaks of the benzene ring surface framework of MB and NR.

The atomic force microscope (AFM) images in Figure 5 are used to characterize the nanostructure of single-layer Az-BPNS-dye LB films. In addition, the used films were transferred on freshly cleaved mica using a vertical lifting method. The results demonstrated that different Az-BPNS-dye composite films showed different nanostructure morphologies. Figure 5a,b shows the AFM image of Az-BPNS-MB films at different surface pressures. The prepared Az-BPNS-MB film has a height of about 0.5 and 1.5 nm when the surface pressure is 10 and 20 mN/m, respectively. The results indicated that the increase in surface pressure could enhance the degree of assembly. As for Az-BPNS-NR films, it can be observed that the obtained films with a dense and uniform structure have a height distribution of 0.8 and 2.5 nm under 10 and 20 mN/m, respectively. Comparing the above LB films under different pressures, it was found that the structure of the LB film is denser at 20 mN/m, indicating that Az-BPNS-dye films have a higher self-assembly degree. However, the surface structure is different for different subphases, which might be related to the molecular properties of the dye.

Figure 4. Surface pressure-area isotherm of (a) Az-BPNS (100 μL) on the different subphases and (b) Az-BPNS solution with different volumes dispersed on MB subphases. TEM images of prepared (c) Az-BPNS-MB monolayer film and (d) Az-BPNS-NR composite film at 20 mN/m. (e) XRD patterns of the Az-BPNS-dye multilayer films on glass flakes at 20 mN/m.

The accumulation type of Az-BPNS-dye composite multilayer films transferred on quartz substrates was also studied, as shown in Figure 6. For MB solution, the characteristic absorption peak appeared at 292 nm corresponds to the π−π$^*$ transfer of the three fused aromatic rings in the structure of the phenazine derivative. The other two peaks around 664 and 613 nm can be assigned to the monomer absorption and the shoulder of the H-aggregate, respectively. However, the Az-BPNS-MB film showed an absorption peak at 598 nm, and the blueshift might be attributed to the formation of H-aggregation of MB dye molecules. As shown in Figure 8b, for NR dye solution, there are three fused aromatic ring π−π$^*$ transfer characteristic peaks assigned to the phenazine structure appeared at 273 nm. Furthermore, the adsorption peak at 530 nm can be attributed to formation of protonation. The characteristic peak of the Az-BPNS-NR composite film at 530 nm was blueshifted to 450 nm, indicating that the dye molecules exist on the composite film in the form of H-aggregates. The results of UV spectra indicate that the Az-BPNS and dye molecules electrostatically interact to form H-aggregates.

Surface-enhanced Raman scattering (SERS) can be widely used in chemical and biochemical species analysis because it will reflect a lot of molecular structure information. The enhancement of SERS is based on the mechanism of an electromagnetic field and chemical enhancement. Among them, the mechanism of chemical enhancement is that non-noble metal materials are used as SERS active substrates, and the electron–hole pairs can be generated by charge transfer.
between the SERS substrate and the molecules under the action of excitation light.9 Electronic resonance molecules will generate electronic resonance because of the recombination of electron–hole pairs, which will increase the polarization rate. Figure 7a,b shows the SERS spectra of different layers of Az-BPNS-dye composite films on R6G molecules. In addition, the
Az-BPNS-MB composite film exhibits a better SERS effect compared with the Az-BPNS-NR composite film. Moreover, the 30-layer Az-BPNS-MB composite film (Az-BPNS-MB-30) was selected as the best film substrate for subsequent experimental characterization.

The Raman enhancement factor (EF) of the Az-BPNS-MB-30 substrate is calculated as follows:

$$EF = \frac{I_{\text{surf}}}{I_{\text{bulk}}} \times \frac{N_{\text{bulk}}}{N_{\text{surf}}}$$  \hspace{1cm} (1)

Among them, $I_{\text{surf}}$ and $I_{\text{bulk}}$ correspond to the area of the same Raman vibration band in the substrate and the bulk sample, respectively. $N_{\text{surf}}$ and $N_{\text{bulk}}$ are the R6G molecule number on the prepared Az-BPNS-MB-30 thin film and a pure silicon substrate, respectively. In addition, the obtained SERS spectra were excited by Raman scattering light at 532 nm. Figure 7c shows the Raman spectrum of the Az-BPNS-MB-30 substrate on R6G molecules. Furthermore, the $I_{\text{surf}}$ and $I_{\text{bulk}}$ values are obtained using the same Raman vibration band (1363 cm$^{-1}$). The $I_{\text{surf}}$ value ($\sim 8.97 \times 10^4$) and $I_{\text{bulk}}$ value ($\sim 8.57 \times 10^3$) can be obtained by dropping 10 $\mu$L R6G solution (10$^{-3}$ M) on the Az-BPNS-MB-30 substrate (1 × 1 cm$^2$). Therefore, the value of $I_{\text{surf}}/I_{\text{bulk}}$ is calculated to be 10.5. For R6G molecules, the $N_{\text{bulk}}$ can be calculated by using formula 2:

$$N_{\text{bulk}} = S_{\text{laser}} \times d \times \rho \times \frac{N_A}{M}$$  \hspace{1cm} (2)

Among them, $S_{\text{laser}}$ represents the area of the laser spot (1 $\mu$m in diameter), $\rho$ corresponds to the density of the R6G solid with the value of 0.79 g/cm$^3$, $d$ corresponds to the depth of the Raman with the value of about 10 $\mu$m, and $M$ (479.01 g/mol) and $N_A$ (6.022 $\times$ 10$^{23}$) represent the molar mass and Avogadro’s number of R6G, respectively. The value of $N_{\text{bulk}}$ is further calculated to be 0.77 $\times$ 10$^{10}$. In addition, the projected area of R6G molecules is about 2 nm$^2$, and the laser irradiation area is about 0.8 $\mu$m$^2$. Assuming that there are R6G molecules on the surface of the Az-BPNS-MB-30 film substrate, so, the $N_{\text{surf}}$ value is calculated to be 4 $\times$ 10$^7$. According to formula 2, the EF of the Az-BPNS-MB-30 substrate can be calculated to be $\sim 1.995 \times 10^3$, indicating the good SERS performance of the prepared uniform Az-BPNS-MB composite film.

In order to evaluate the reproducibility between the substrates, the SERS spectra of R6G (10$^{-3}$ M) were collected at 36 random positions on six Az-BPNS-MB substrates (30 layers), as shown in Figure 7d. The results showed that the spectral positions and intensities of all 36 pots were almost the same, indicating the high reproducibility of the Az-BPNS-MB film. In addition, the uniformity of the same composite film in the entire region was analyzed. The SERS mapping image of the R6G molecule (10$^{-3}$ M) at 1361 cm$^{-1}$ and the relative intensity bar graph through point-by-point are shown in Figure 7ef. The relatively uniform color distribution represents the good uniformity of the prepared Az-BPNS-MB film. As shown in Figure 7f, the calculated relative standard deviation (RSD) of the Raman intensity (4.17%) proves that the Az-BPNS-MB film has a large area.

When the Az-BPNS-dye composite LB film is used as the working electrode (We), the ground-state electrons of the accumulated dye molecules will be excited under the xenon lamp (simulating sunlight). Molecules in the excited state quickly collect electrons on ITO glass and transfer them to the external circuit; after that, it will return to the auxiliary electrode (Ce). Since the potential of the electrolyte electron pair is lower than the redox potential of the dye, the dye molecules in the oxidized state are easily reduced by the electrolyte in the reduced state. Then, the oxidized electrolyte diffuses into a Ce to regenerate electrons, thereby generating current.$^{31}$ The transient photocurrent response of the thin film anode over time was recorded by time amperometry (the light on/off period is 30 s) and is shown in Figure 8a. Anode photocurrent increases when lighting starts and decreases when lighting stops. Compared to Az-BPNS, MB, and NR film anodes, the Az-BPNS-MB composite film anode can produce a higher photocurrent. It should be noted that the Az-BPNS-NR composite film shows good stability in the cycle of continuous on/off. Figure 8b shows the transient photocurrent response spectra of the prepared films under visible light irradiation. It can be seen from the $J-V$ characteristic curve of the LB film electrode that the current density of the Az-BPNS-MB composite film is higher than that of other film electrodes, indicating that there are more photoexcited electrons in the Az-BPNS-MB composite film electrode flowing to the cathode. The diameter of the semicircle can be used to obtain charge transfer resistance. Figure 8c shows the electrochemical impedance spectroscopy (EIS) response of the composite film anode under illumination, and it can be clearly found that the semicircle is associated with the charge transfer resistance.
of the electrode film. In the EIS Nyquist results, it can be seen that the Az-BPNS-MB film electrode shows a smaller diameter of the semicircle. The reduction of the charge transfer resistance clearly confirmed that the interface charge transfer in the Az-BPNS-MB composite film electrode was easier. The above results demonstrate that the Az-BPNS-dye composite LB film electrode is more conducive to charge transfer compared to the pure Az-BPNS film and pure dye film electrodes. These results may be due to the fact that the internal voids of pure dye molecules will lead to the spatial separation of photogenerated carriers. However, through the LB technology, the dye molecules can interact closely with the Az-BPNS, resulting in the formation of H and/or J arrangements in the composite film, which effectively accelerates the transport of photoelectrons. In a word, the prepared Az-BPNS-dye composite LB films exhibit a good photocurrent generation capability compared with previous work. In addition, the current research study also provides a new direction for the potential applications of self-assembled composite materials.

3. CONCLUSIONS

In conclusion, self-assembled Az-BPNS-dye composite LB films with an ordered structure were successfully synthesized. Az-BPNS and dye molecules containing electron-deficient systems can self-assemble to form a customizable composite film through π−π stacking or electrostatic forces. The obtained Az-BPNS-dye composite films showed excellent reproducibility...
and uniformity through SERS performance tests. In addition, the Az-BPNS-MB composite film exhibited better photoelectric conversion properties compared to the Az-BPNS-NR composite film. This work provides support for the application of BP-based multifunctional composite films as an electronic device in photoelectric conversion.

4. MATERIALS AND METHODS

4.1. Materials. In this work, the used isopropyl alcohol solvent and N,N-dimethylamide (DMF) were purchased from Kermel Chemical Reagent Company (Tianjin, China). Neutral red (NR), methylene blue (MB), and 4-azidobenzoic acid were obtained from Aladdin Reagent Plant (Shanghai, China). Aqueous ammonia (NH₃·H₂O, 25 wt %) and hydrochloric acid (HCl, 37 wt %) were purchased from Kaitong Chemical Reagent Company (Tianjin, China). Black phosphorus (BP) was prepared under high pressure and high temperature.45

4.2. Preparation of 4-Azidobenzoic Acid-Modified BP Nanosheets (Az-BPNS). Black phosphorus powder (10 mg) was put into DMF solution (10 mL), and then, the resulting mixture solution was bubbled with N₂ and sonicated for 24 h under an ice bath. Next, the obtained BP solution was centrifuged at 2000 rpm for 15 min to collect the supernatant and then bubbled by N₂ for later experiments. Next, 4-azidobenzoic acid (40 mg) was fully dissolved in 20 mL of a N,N-dimethylamide (DMF) solvent, and then, it was mixed with the prepared BPNS solution. The resulting solution was bubbled with N₂, and then, the mixture solution was stirred vigorously for 48 h at 140 °C to obtain Az-BPNS solution. The Az-BPNS solution was subsequently centrifuged for 20 min at 12000 rpm to collect the precipitate, and then, it was washed with isopropyl alcohol solution several times. Finally, the collected sample was dried in a vacuum drying oven at 50 °C to obtain Az-BPNS solid powder.

4.3. Preparation of Az-BPNS/Dye LB Films. A KSV-NIMA instrument was used to prepare and transfer LB films in this experiment. First, an LB trough was filled with dye solution with the concentration of 1 × 10⁻³ mol/L, and then, the 0.8 mg/mL Az-BPNS isopropanol solution was spread uniformly on the surface of the dye subphase. After the solvent was completely evaporated, the film was obtained at a compression speed of 10 cm²/min. According to the curves of the different volumes of Az-BPNS solution spread on the MB subphase, 100 μL was selected in the later experiments. In addition, the morphology and spectral characterization of the prepared single-layer or multilayer films were performed by transferring films on the glass flakes, quartz, CaF₂ substrates, and fresh cleaved mica. It should be noted that the used glass and quartz substrates were carefully washed with mixture solution of NH₄OH/H₂O₂/H₂O (volume ratio = 1:1:5) and ultrapure water. Moreover, when the subphase was MB or NR solution, the obtained film was named as the Az-BPNS-MB film or the Az-BPNS-NR film, respectively.

4.4. Photoelectric Performance of Composite Films. As a new analytical technique, photoelectrochemistry combines the characteristics of photochemistry and electrochemistry. Light is used as the excitation signal, the photoelectrochemical substance is excited to undergo electron–hole pair separation, and the resulting photocurrent or photovoltage is used as the detection signal. Under the standard three-electrode configuration, photoelectrochemical measurement was analyzed using a CHI660 electrochemical workstation. In addition, LB composite films were used as the anode, Pt foil and a Ag/AgCl electrode were used as a counter electrode and a reference electrode in a 1 M KOH electrolyte, respectively. Moreover, a 300 W xenon lamp was coupled with a 1.5g AM filter to be used as a simulated solar light source with I₀ = 100 mW/cm². For EIS measurement, the AC voltage

Figure 8. (a) I–T curves, (b) linear scanning voltammogram (LSV) curves, and (c) electrochemical impedance spectroscopy (EIS) curves of the prepared multilayer composite films.
amplitude was 10 mV, and the DC bias was 0.23 V relative to Ag/AgCl with the frequency range of $10^{-1}$ to $10^{-3}$ Hz.

4.5. Characterization. The structures of the samples were characterized by transmission electron microscopy (TEM, HT7700, High-Technologies Corp., Ibaraki, Japan). Scanning electron microscopy (SEM) images were obtained using a FEI QUANTA 250 (FEI Corporate, Hillsboro, OR, U.S.A.). X-ray photoelectronspectroscopy (XPS) spectra of BPNS and Az-BPNS were monitored using a Thermo Scientific ESCALab 250Xi XPS (Thermo Fisher Scientific, San Jose, CA, USA). A Nanoscope model MultiMode 8 scanning probe microscope (Veeco Instrument, USA) was used to obtain atomic force microscopy (AFM) images of Az-BPNS-dye films. An X-ray diffraction (XRD) study was performed using an X-ray diffractometer (SMART LAB, Rigaku) with Cu Kα X-ray radiation ($\lambda \approx 1.54 \AA$). Fourier infrared spectroscopy (FT-IR, Thermo Nicolet Corporation) was performed to obtain FT-IR spectra of samples. Confocal Raman microscopy (Horiba Jobin Yvon Xplora PLUS) was performed to characterize the Raman spectra. UV−vis spectra of the composite films were monitored using a Shimadzu UV-2550 system (Shimadzu Corporation, Japan).

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## Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional atomic crystals. PNAS 2005, 102, 10451−10453.

(2) Kurapati, R.; Kostarelos, K.; Prato, M.; Bianco, A. Biomedical uses for 2D materials beyond graphene: current advances and challenges ahead. Adv. Mater. 2016, 28, 6052−6074.

(3) Sun, Z.; Martinez, A.; Wang, F. Optical modulators with 2D layered materials. Nat. Photonics 2016, 10, 227.

(4) Butler, S. J.; O’Hare, E. G.; Iqbal, S.; Bates, D.; Gutiérrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Iamschilin, P.; Johnston-Halperin, E.; Kuno, M.; Flashman, E. C.; Robinson, R. D.; Ruoff, R. S.; Salahuddin, S.; Shan, J.; Shi, L.; Spencer, M. G.; Terrones, M.; Windl, W.; Goldberger, J. E. Progress, challenges, and opportunities in two-dimensional materials beyond graphene. ACS Nano 2013, 7, 2989−2926.

(5) Yin, F.; Hu, K.; Chen, S.; Wang, D.; Zhang, J.; Xie, M.; Yang, D.; Qiu, M.; Zhang, H.; Li, Z-G. Black phosphorus quantum dot based novel siRNA delivery systems in human pluripotent teratoma PA-1 cells. J. Mater. Chem. B 2017, 5, 5433−5440.

(6) Li, L.; Yu, Y.; Ye, G. J.; Ge, Q.; Ou, X.; Wu, H.; Feng, D.; Chen, X. H.; Zhang, Y. Black phosphorus field-effect transistors. Nat. Nanotechnol. 2014, 9, 372−377.

(7) Zhu, M.; Fujitsuka, M.; Zeng, L.; Liu, M.; Majima, T. Dual function of graphene oxide for assisted exfoliation of black phosphorus and electron shuttle in promoting visible and near-infrared photocatalytic H2 evolution. Appl. Catal., B 2019, 256, 117864.

(8) Zhu, M.; Sun, Z.; Fujitsuka, M.; Majima, T. Z-Scheme Photocatalytic Water Splitting on a 2D Heterostructure of Black Phosphorus/Bismuth Vanadate Using Visible Light. Angew. Chem., Int. Ed. 2018, 57, 2160−2164.

(9) Wang, R.; Yan, X.; Ge, B.; Zhou, J.; Wang, M.; Zhang, L.; Jiao, T.; Facile Preparation of Self-Assembled Black Phosphorus-Dye Composite Films for Chemical Gas Sensors and Surface-Enhanced Raman Scattering Performances. ACS Sustainable Chem. Eng. 2020, 8, 4521−4536.

(10) Hu, Z.; Li, Q.; Lei, B.; Zhou, Q.; Xiang, D.; Lu, Z.; Hu, F.; Wang, J.; Ren, Y.; Guo, R.; Goki, E.; Wang, L.; Han, C.; Wang, J.; Chen, W. Water-catalyzed oxidation of few-layer black phosphorous in a dark environment. Angew. Chem., Int. Ed. 2017, 56, 9131−9135.

(11) Zhao, Y.; Wang, H.; Huang, H.; Xiao, Q.; Xu, Y.; Guo, Z.; Xie, H.; Shao, J.; Sun, Z.; Han, W.; Yu, X-F.; Li, P.; Chu, P. K. Surface Coordination of Black Phosphorus for Robust Air and Water Stability. Angew. Chem., Int. Ed. 2016, 55, 5003−5007.

(12) Yuan, Z.; Li, J.; Yang, M.; Fang, Z.; Jian, J.; Yu, D.; Chen, X.; Dai, L. Ultrathin Black Phosphorus-on-Nitrogen Doped Graphene for Efficient Overall Water Splitting: Dual Modulation Roles of Directional Interfacial Charge Transfer. J. Am. Chem. Soc. 2019, 141, 4972−4979.

(13) Kaur, H.; Yadav, S.; Srivastava, A. K.; Singh, N.; Schneider, J. J.; Sinha, O. P.; Agrawal, V. V.; Srivastava, R. Large area fabrication of semiconducting phosphorene by Langmuir-Blodgett assembly. Sci. Rep. 2016, 6, 34095.

(14) Mao, J.; Ortiz, O.; Wang, J.; Malinge, A.; Badia, A.; Kénès, S.; Langmuir–Blodgett fabrication of large-area black phosphorus–C60 thin films and heterojunction photodetectors. Nanoscale 2020, 12, 19814−19823.

(15) He, Y.; Wang, R.; Jiao, T.; Yan, X.; Wang, M.; Zhang, L.; Bai, Z.; Zhang, Q.; Peng, Q. Facile preparation of self-assembled layered...
double hydroxide-based composite dye films as new chemical gas sensors. *ACS Sustainable Chem. Eng.* 2019, 7, 10888–10899.

(16) Chen, K.; Li, J.; Zhang, L.; Xing, R.; Jiao, T.; Gao, F.; Peng, Q. Facile synthesis of self-assembled carbon nanotubes/dye composite films for sensitive electrochemical determination of Cd(II) ions. *Nanotechnology* 2018, 29, 445603.

(17) Ma, K.; Wang, R.; Jiao, T.; Zhou, J.; Zhang, L.; Li, J.; Bai, Z.; Peng, Q. Preparation and aggregate state regulation of co-assembled graphene oxide-porphyrin composite Langmuir films via surface-modified graphene oxide sheets. *Colloids Surf., A* 2020, 584, 124023.

(18) Saito, K. H-Aggregate formation in squarilium Langmuir-blodgett films. *J. Phys. Chem. B* 2001, 105, 4235–4238.

(19) Xue, H.; Tang, X.-J.; Wu, L.-Z.; Zhang, L.-P.; Tung, C.-H. Highly selective colorimetric and electrochemical Pb2+ detection based on TTF-π-pyridine derivatives. *J. Org. Chem.* 2005, 70, 9727–9734.

(20) Bromborsz, S. M.; Zachcero, A. J.; Phillips, R. L.; Vazquez, D.; Wilson, A.; Bunz, U. H. F. Terpyridine-Based Cruciform–Zn2+ Complexes as Anion-Responsive Fluorophores. *Org. Lett.* 2007, 9, 4519–4522.

(21) Peng, X. J.; Tian, P. Z.; Xu, Z.; Chen, S. F.; Wong, M. S. Fluorescence-enhanced chemosensor for metal cation detection based on pyridine and carbazole. *J. Org. Chem.* 2013, 78, 13138–13135.

(22) Shao, J.; Ruan, C.; Xie, H.; Li, Z.; Wang, H.; Chu, P. K.; Yu, X.-F. Black-phosphorus-incorporated hydrgol as a sprayable and biodegradable photothermal platform for postsurgical treatment of cancer. *Adv. Sci.* 2018, 5, 1700848.

(23) Reddy, D. A.; Kim, E. H.; Gopannagari, M.; Kim, Y.; Kumar, D. P.; Kim, T. K. Few layered black phosphorus/MoS2 nanohybrid: A promising co-catalyst for solar driven hydrogen evolution. *Appl. Catal., B* 2019, 241, 491–498.

(24) Liu, M.; Zhang, L.; Wang, T. Supramolecular Chirality in Self-Assembled Systems. *Chem. Rev.* 2015, 115, 7304–7397.

(25) Liu, Y.; Hou, C.; Jiao, T.; Song, J.; Zhang, X.; Xing, R.; Zhou, J.; Zhang, L.; Peng, Q. Self-Assembled AgNP-Containing Nano-composites Constructed by Electrospinning as Efficient Dye Photocatalyst Materials for Wastewater Treatment. *Nanomaterials* 2018, 8, 35.

(26) Mitsai, E.; Kuchmizhak, A.; Pustovalov, E.; Sergeev, A.; Mironenko, A.; Bratskaya, S.; Linklater, D. P.; Balc̆ytis, A.; Ivanova, E.; Juodkazis, S. Chemically non-perturbing SERS detection of a catalytic Technology 2018, 29, 445603.

(17) Ma, K.; Wang, R.; Jiao, T.; Zhou, J.; Zhang, L.; Li, J.; Bai, Z.; Peng, Q. Preparation and aggregate state regulation of co-assembled graphene oxide-porphyrin composite Langmuir films via surface-modified graphene oxide sheets. *Colloids Surf., A* 2020, 584, 124023.

(18) Saito, K. H-Aggregate formation in squarilium Langmuir-blodgett films. *J. Phys. Chem. B* 2001, 105, 4235–4238.

(19) Xue, H.; Tang, X.-J.; Wu, L.-Z.; Zhang, L.-P.; Tung, C.-H. Highly selective colorimetric and electrochemical Pb2+ detection based on TTF-π-pyridine derivatives. *J. Org. Chem.* 2005, 70, 9727–9734.

(20) Bromborsz, S. M.; Zachcero, A. J.; Phillips, R. L.; Vazquez, D.; Wilson, A.; Bunz, U. H. F. Terpyridine-Based Cruciform–Zn2+ Complexes as Anion-Responsive Fluorophores. *Org. Lett.* 2007, 9, 4519–4522.

(21) Peng, X. J.; Tian, P. Z.; Xu, Z.; Chen, S. F.; Wong, M. S. Fluorescence-enhanced chemosensor for metal cation detection based on pyridine and carbazole. *J. Org. Chem.* 2013, 78, 13138–13135.

(22) Shao, J.; Ruan, C.; Xie, H.; Li, Z.; Wang, H.; Chu, P. K.; Yu, X.-F. Black-phosphorus-incorporated hydrgol as a sprayable and biodegradable photothermal platform for postsurgical treatment of cancer. *Adv. Sci.* 2018, 5, 1700848.

(23) Reddy, D. A.; Kim, E. H.; Gopannagari, M.; Kim, Y.; Kumar, D. P.; Kim, T. K. Few layered black phosphorus/MoS2 nanohybrid: A promising co-catalyst for solar driven hydrogen evolution. *Appl. Catal., B* 2019, 241, 491–498.

(24) Liu, M.; Zhang, L.; Wang, T. Supramolecular Chirality in Self-Assembled Systems. *Chem. Rev.* 2015, 115, 7304–7397.

(25) Liu, Y.; Hou, C.; Jiao, T.; Song, J.; Zhang, X.; Xing, R.; Zhou, J.; Zhang, L.; Peng, Q. Self-Assembled AgNP-Containing Nano-composites Constructed by Electrospinning as Efficient Dye Photocatalyst Materials for Wastewater Treatment. *Nanomaterials* 2018, 8, 35.

(26) Mitsai, E.; Kuchmizhak, A.; Pustovalov, E.; Sergeev, A.; Mironenko, A.; Bratskaya, S.; Linklater, D. P.; Balc̆ytis, A.; Ivanova, E.; Juodkazis, S. Chemically non-perturbing SERS detection of a catalytic reaction with black silicon. *Nanoscale* 2018, 10, 9780–9787.

(27) Zou, J. Y.; Song, W. J.; Xie, W. G.; Huang, B.; Yang, H. D.; Luo, Z. A simple way to synthesize large-scale Cu2O/Ag nanoflowers for ultrasensitive surface-enhanced Raman scattering detection. *Nanotechnology* 2018, 29, 115703.

(28) Yang, L.; Wang, W.; Jiang, H.; Zhang, Q.; Shan, H.; Zhang, M.; Zhu, X.; Lv, J.; He, G.; Sun, Z. Improved SERS performance of single-crystalline TiO2 nanosheet arrays with coexposed {001} and {101} facets decorated with Ag nanoparticles. *Sens. Actuators, B* 2017, 242, 932–939.

(29) Shi, G.; Wang, M.; Zhu, Y.; Wang, Y.; Ma, W. Synthesis of flexible and stable SERS substrate based on Au nanofilms/cicada wing array for rapid detection of pesticide residues. *Opt. Commun.* 2018, 425, 49–57.

(30) Wang, Y.; Wang, M.; Sun, X.; Shi, G.; Zhang, J.; Ma, W.; Ren, L. Grating-like SERS substrate with tunable gaps based on nanorough Ag nanoslands/moth wing scale arrays for quantitative detection of cypermethrin. *Opt. Express* 2018, 26, 22168.

(31) Liu, X.; He, Y.; Zhang, G.; Wang, R.; Zhou, J.; Zhang, L.; Gu, J.; Jiao, T. Preparation and High Photocurrent Generation Enhancement of Self-Assembled Layered Double Hydroxide-Based Composite Dye Films. *Langmuir* 2020, 36, 7483–7493.

(32) Wang, M.; Shang, Z.; Yan, X.; Shi, G.; Cao, H.; Ma, W.; Jiao, T. Enhance fluorescence study of grating structure based on three kinds of optical disks. *Opt. Commun.* 2021, 481, 126522.

(33) Qian, C.; Yin, J.; Zhao, J.; Li, X.; Wang, S.; Bai, Z.; Jiao, T. Facile preparation and highly efficient photodegradation perform-