

Supporting Information

Controllable Preparation of Crystalline Red Phosphorus and Its Photocatalytic Properties

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Experimental Procedures

Chemicals: Amorphous red phosphorus (ARP, Shanghai Aladdin Bio-Chem Technology Co., Ltd., 99.999%), Bismuth (Bi, Shanghai Aladdin Bio-Chem Technology Co., Ltd., 99.9%), Methyl orange (MO, Tianjin Damao Chemical Reagent Factory, AR), Methanol (CH₄O, Chengdu Kelong Chemical Co., Ltd., AR, ≥99.5%), Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Shanghai Chemical Reagent Co., Ltd., Pt ≥37.0%), Sodium sulfate anhydrous (Na₂SO₄, Tianjin Damao Chemical Reagent Factory, AR, ≥99%), Ethanol (Chengdu Kelong Chemical Co., Ltd., ≥99.7%). Quartz ampoules were purchased from Donghai County Shengyi Quartz Products Co., Ltd.

Sample Preparation: Specifically, amorphous red phosphorus, bismuth were used directly without further purification. 300 mg of commercial ARP and 30 mg of Bi were vacuum sealed in a glass ampoule (inner diameter of 0.7 cm and effective length of 10 cm) and placed in a muffle furnace for reaction.

Synthetic Procedures

1). Preparation of crystalline red phosphorous microbelts: The ampoule was heated to 550°C at 5 °C per minute, held for 2 h, cooled to 300 °C at 2°C per minute, held for 10 h. Finally, the equipment naturally drops to ambient temperature.

2). Preparation of crystalline red phosphorous microrod: The ampoule was heated to 580°C at 5°C per minute, held for 2 h, cooled to ambient temperature at 1°C per minute.

Instrument characterization

The crystalline phosphorus material was dispersed in anhydrous ethanol solution, and the solute was evenly dispersed by slight shaking. Instilled 20 microliters of solution on a 200-mesh micro-grid copper net and putted it in a vacuum drying oven at 60°C for 6 hours for solvent evaporation. The grid was then transferred to the TEM holder for transmission characterization. During the entire transmission sample preparation process, the copper grid was exposed to air for about 10 minutes. Low-magnification TEM images were taken using JEM-2100Plus (JEOL Co., Ltd.) with an accelerating voltage of 200 kV. High-resolution TEM measurements were performed on a JEM-ARM 300F (Cold Field Emission Gun) at an acceleration voltage of 200 kV. SEM samples were prepared by directly attaching the prepared crystalline phosphorous to the conductive tape of the stage. SEM was carried out on

JIB-4700F (JEOL), the equipment is equipped with 15 KV. During the transfer to the SEM chamber, the stage was exposed to the air for about 2 minutes to be mounted on the holder, and the holder was evacuated for about 5 minutes before inserting into the microscope. Powder X-ray diffraction (XRD) patterns were recorded using a Smart Lab 9 kW (45 KV, 200 mA) X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were acquired on a Laser Microscopic Raman Imaging Spectrometer (DXRxi) with a 532 nm laser. The UV-Vis diffuse reflectance spectrum adopts Cary 5000 instrument, the maximum absorbance was 8 Abs. The UPS and XPS measurements of the samples were performed by ThermoFisher, Nexsa equipped with a low-power Al K α X-ray source. Photographs were taken with an optical microscope and digital camera.

Theoretical calculation

A Periodic plane wave density functional theory (DFT) calculations of the crystal structure optimization was performed using the Vienna Ab-initio Simulation Package (VASP). The projector augmented plane wave (PAW) pseudo potential basis set and generalized gradient approximation (GGA) functional by the PBE parametrization was employed in these calculations. A kinetic energy cutoff of 520 eV for the plane wave expansion is used for all systems. To achieve high accuracy, the Brillouin zone integration was sampled with 5 x 5 x 3 k-grid mesh. The unit cell of CRPMB was taken from the Inorganic Crystal Structure Database (ICSD, Coll code: 404896).¹ The lattice parameters of the optimized unit cell are: $a = 7.029 \text{ \AA}$, $b = 11.433 \text{ \AA}$, $c = 16.593 \text{ \AA}$, $\beta = 114.201^\circ$.

Photocatalytic experiments

1. Hydrogen evolution test: The photocatalytic hydrogen production experiment was carried out in a closed gas circulation reaction system (Labsolar-6a, Beijing Perfectlight Co., Ltd., China). The solution was irradiated with a solar simulator-300W xenon lamp. Disperse 30 mg of the sample into 100 mL of water (10 vol% methanol as a sacrificial agent and 1 wt% Pt as a co-catalyst). The equipment is equipped with a 5 \AA molecular sieve column and a thermal conductivity detector (TCD) to determine the amount of hydrogen produced by the photocatalytic reaction by gas chromatography (GC-2014, Shimadzu, Japan).

2. Degradation of methyl orange test: PCX50C Discover Multi-channel Photocatalytic Reaction System (Beijing Perfect Light Technology Co., Ltd.) as a visible light source. 10 mg of sample was dispersed into 50 mL of 100 ppm methyl orange solution. Before irradiation,

the mixed solution was oscillated in dark at 300 rpm for 1 h to achieve the adsorption-desorption balance. Photocatalytic degradation tests were then performed under light. Within a certain period of time, 3 mL of suspension was extracted with a syringe, and the catalyst particles were removed by 0.22 μm of the needle filter (polyether sulfone PES). The absorbance of the solution was determined by ultraviolet-visible-near infrared spectrophotometer (Cary 5000, Agilent).

3. Electrochemical test: In a typical photoelectrochemical measurements experiment, 5 mg of the sample was dispersed in 1 mL of ethanol solution. Then, the suspension is drop-cast on the FTO conductive glass. The photoelectrochemical evaluation was carried out in a three-electrode system, where the sample of interest was used as the working electrode, and the aluminum foil and saturated Ag/AgCl were the counter electrode and the reference electrode, respectively. The electrolyte is 0.1M Na_2SO_4 . A 300 W xenon solitary light is used as the radiation source. Use electrochemical workstation CHI 660D to test linear sweep and transient current.

Results and Discussion

Under the catalysis of bismuth element, an effective temperature control program can realize the directional conversion of amorphous red phosphorus. The Hittorf phosphorous microrods are obtained by increasing the growth temperature above 580°C on the basis of the synthesis of orange-red phosphorous microbelts. In the cooling procedure, the heat preservation procedure at about 485°C resulted in the coexistence of orange-red phosphorous microrods and purple phosphorous microbelts (Figure S1), indicating that the synthesis temperature of the orange-red phosphorous microrods was lower than that of the Hittorf phosphorous microbelts. In addition, the SEM-EDS spectrum shows that both products are composed of a single phosphorus element, and σ is about zero, reflecting the accuracy of the data. This result indicates that the process of catalyzing the amorphous red phosphorus by bismuth may only participate in the transition of the intermediate state, leading to the orientation change of the material structure and energy, which is also in line with the typical chemical gas transportation process.

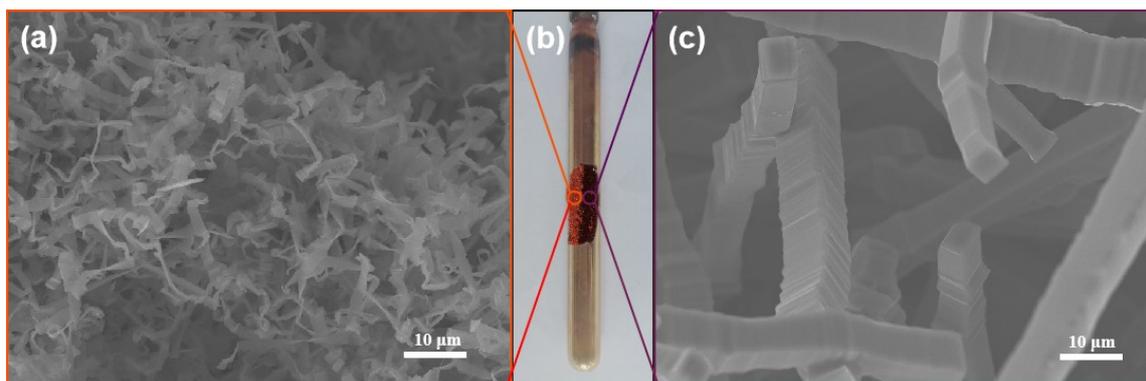


Figure S1. (b) The optical photograph of the ampoule after the reaction, the inset is the product obtained after the ampoule is destroyed; (a) the SEM image of the orange-red part in the figure (b); (c) the SEM image of the purple part in the figure (b).

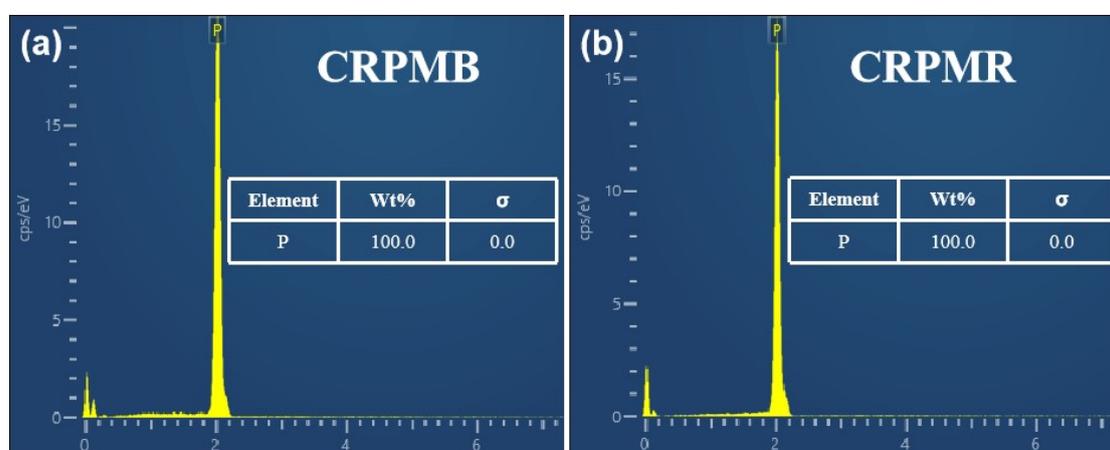


Figure S2. SEM-EDS spectras of (a) CRPMB and (b) CRPMR.

The Rietveld software refined the XRD spectrum of the synthesized CRPMB samples. According to the previously reported lattice constants of $[P12(4)]P2[$ optimized by GGA, LDA and -D2 methods, the XRD spectra of CRPMB samples were refined (Figure S3, S4).² It is found that the confidence factor (<10) of -D2 is within the acceptable range (Table S1), which means that the lattice constants $a=7.01$, $b=11.43$, $c=16.64$ and $\beta=114.44$ match the crystal structure of CRPMB. The cross symbols represent the observed profile; the red line is the calculated profile; the blue vertical marks indicate the Bragg position of $[P12(4)]P2[$ (P21/C); the green line shows the difference between the observed profile and the calculated profile.

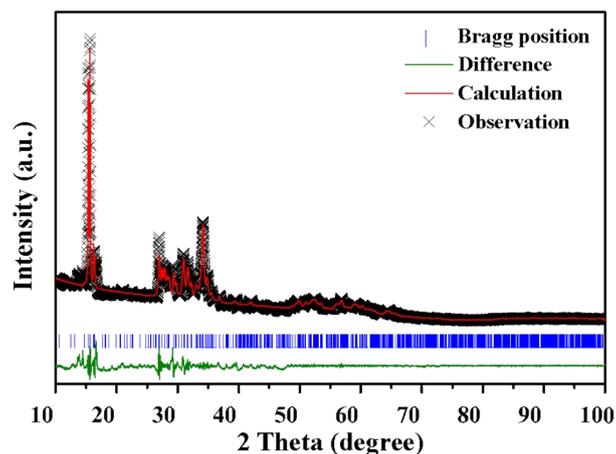


Figure S3. Rietveld refined the XRD spectrum of the synthesized CRPMB sample, in which the lattice constant was taken from the optimized value of -D2.

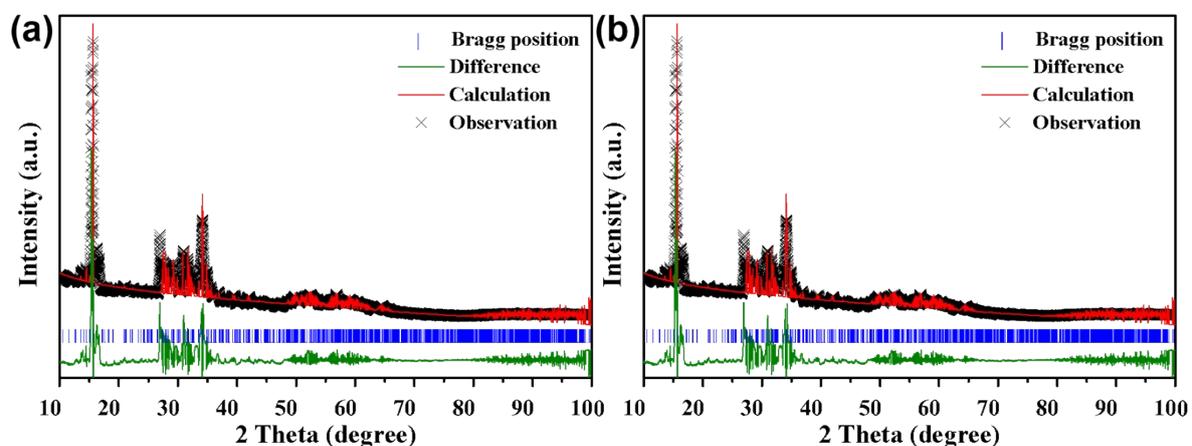


Figure S4. Rietveld refined the XRD spectrum of the synthesized CRPMB sample, in which the lattice constant was taken from the optimized value of (a) GGA and (b) LDA.

Table S1. Confidence factor obtained by refined XRD spectra of synthesized CRPMB samples with lattice constants of -D2, GGA, and LDA.

Confidence factor	-D2	GGA	LDA
Rp	4.055	13.140	8.368
Rwp	6.157	21.465	13.935

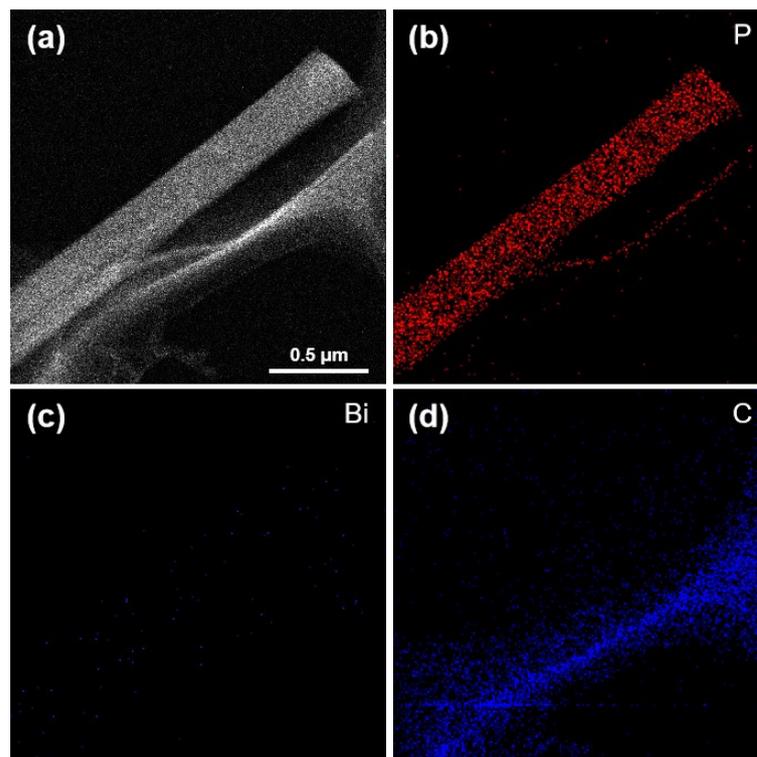


Figure S5. HAADF-STEM and corresponding EDS element map of an orange-red phosphorous nanobelt.

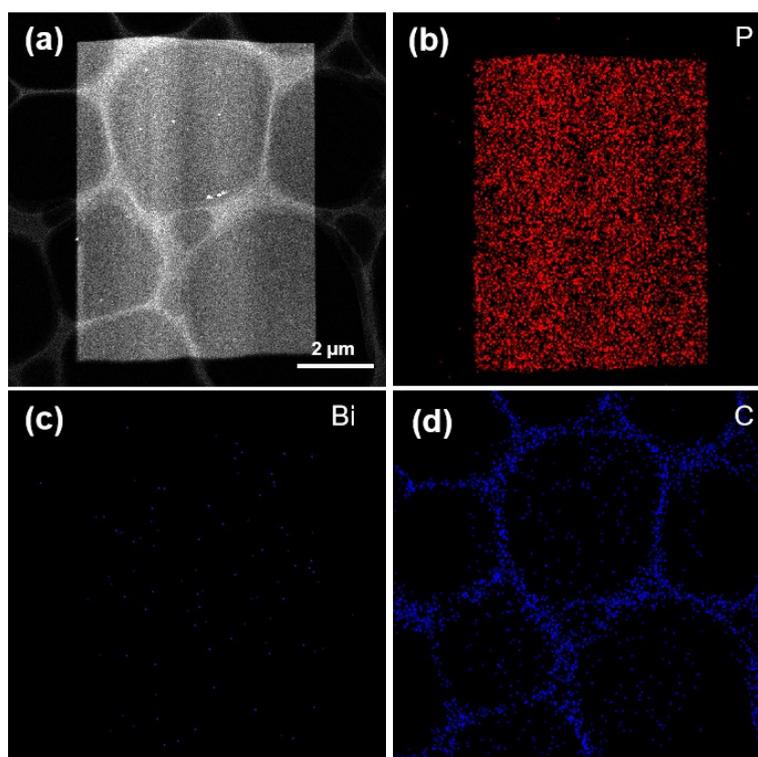


Figure S6. HAADF-STEM and corresponding EDS element map of a flake Hittorf phosphorous.

According to the UPS spectrum, the work functions of CRPMB and CRPMR are 4.38 and 5.26 eV, respectively, which obtained by subtracting the secondary electron cut-off energy from the light energy of the He I light source (21.22 eV). Furthermore, the valence bands of CRPMB and CRPMR to Fermi levels are about 0.8 and 0.2 eV. Therefore, the valence bands of CRPMB and CRPMR are respectively located at about 5.18 and 5.46 eV (relative to vacuum).³ At the same time, the band gap of CRPMB and CRPMR measured by UV-visible DRS is about 1.90 and 1.68 eV, respectively. According to the formula $EBG = EVB + ECB$, the conduction bands of CRPMB and CRPMR are calculated to be about 3.28 and 3.78 eV, respectively (relative to vacuum).⁴

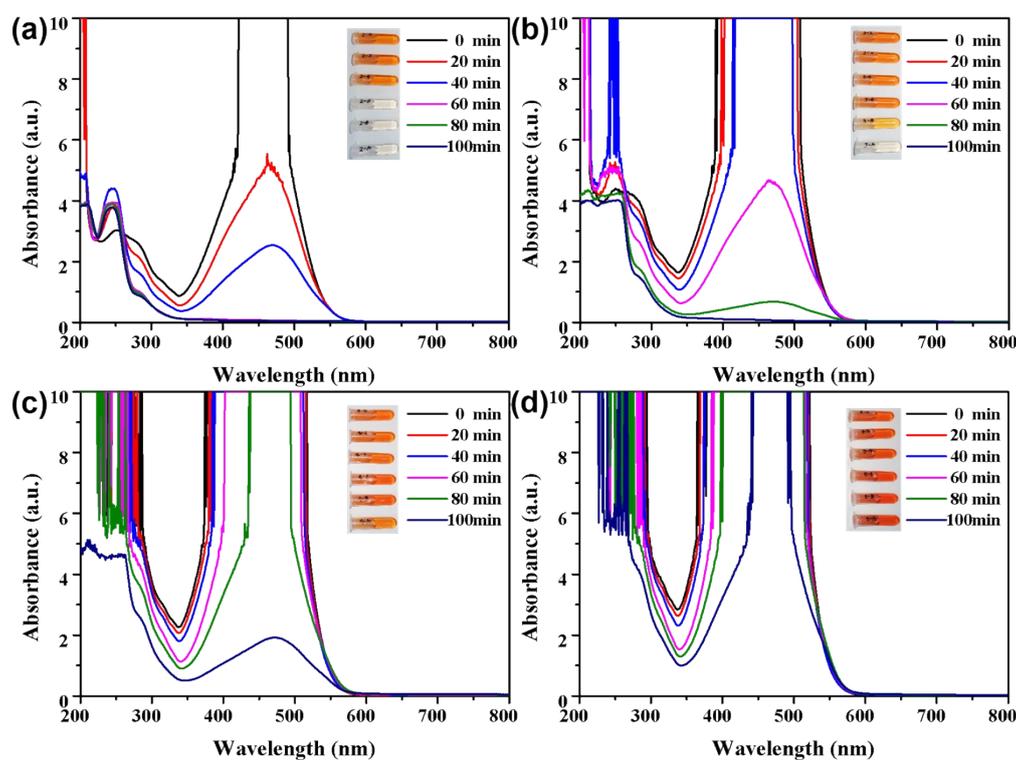


Figure S7. Absorbance images of the degradation of methyl orange at 200, 300, 400, 500 ppm in different time periods under visible light by catalyst CRPMB.

References

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