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Searching for inexpensive and earth-abundant photocatalysts with high activities has attracted considerable research in recent years. In this work, semimetallic tungsten diphosphide (WP₂) micro-particles are explored as a novel photocatalyst at the first time. The WP₂ particles were synthesized through solid-state reaction route via vacuum encapsulation technique following by water washing. The first principle calculations and electric transport measurements show a semimetallic characteristics of WP₂, however a strong absorption in the UV range is observed. The prepared WP₂ particles exhibit an admirable photocatalytic activity towards oxidation of methyl orange and reduction of water for H₂ evolution with the assist of co-catalyst element Pt under UV light irradiation. Hydroxyl radical detected by fluorescence spectroscopy in the solution in the presence of WP₂ under UV light irradiation confirms the photocatalytic. Furthermore, the photocatalyst shows a good photostability and reusability even after three successive experiment runs. Based on the experimental measurements and theoretical calculations, a possible photocatalytic mechanism is proposed for semimetallic WP₂. The present study provides a chance for practical applications of semimetallic material WP₂ in the field of photocatalysis.

Introduction

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Global energy and environment crisis is a big challenge that every country has to face to, intensive research interest has been devoted to searching for active photocatalysts to solve this crisis. Among which photocatalytic conversion of solar energy has been attracting worldwide attention.1-3 In the past decades, semiconductor photocatalysis, as a "green" technology, has been widely used for the degradation of organic dye, hydrogen evolution from water and removal of toxic gases.⁴⁻⁵ Along this lines, hundreds of materials have been investigated as the potential photocatalysts, including oxides, sulfide, nitrides and phosphates. For example, for the high photocatalytic efficiency and photostability, TiO₂ is the most widely used and studied photocatalyst so far.6-10 The other photocatalysts were also prepared, such as Ni decorated CdS nanorods enhanced the photocatalytic hydrogen evolution under a redox shuttle mechanism.¹¹ Cu₂O microcrystals are found to perform efficiently in hydrogen generation and formaldehyde degradation at room temperature.¹² Ag₃PO₄ with high photocatalytic activity and Cu₂(OH)PO₄ exhibiting promising photocatalytic properties in the near infrared

However, as a new and unconventional class of photocatalysts with the application potential, metallic materials have been discovered. For example, Sr_{1-x}NbO₃ was discovered as an active metallic photocatalyst by Irvine et al,¹⁷ and they demonstrated that metallic perovskite oxides facilitate kinetic charge separation which is effective in degrade methylene blue, as well as in hydrogen and oxygen evolution from water. Black bismuth was also reported as semimetal photocatalyst for NO oxidation in air.¹⁸ And most recently, transition metal phosphide MoP₂ was discovered as a semimetallic photocatalyst with high photoactivity to efficiently decompose methyl orange and produce hydrogen from water.¹⁹ The above semimetallic materials have the unusual electronic properties which result from its small electron effective mass, large mean free path and so on. And



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high carrier mobility in these materials may allow effective separation of carriers, especially if the carrier can be rapidly transferred.¹⁸These discoveries provide a new perspective for photocatalyst screening and a direction to search for novel photocatalysts with metallic behaviors.

Transition-metal phosphides are an important class of compounds with metalloid characteristics and good electrical conductivity,²⁰which are studied as highly efficient electrocatalyst, such as MoP, WP, FeP, CoP, Cu₃P, ²⁰⁻²⁴ but the photocatalytic properties of these materials have not been intensively studied. We recently reported that MoP₂ as a semimetallic photocatalyst towards decomposing methyl orange and producing hydrogen from water.¹⁹ Analogy to transition metal phosphide MoP₂, WP₂ has the same orthorhombic crystal structure and a similar band structures with MoP₂ in which the VB and CB overlap at the Fermi level, indicating a semimetallic property, which is consistent with the early article, ²⁵ and the property was experimentally confirmed by the electrical resistivity measurements in this work. WP2 was first synthesized by S. Rundqvist et al $^{\rm 26}$ in 1963 through the reaction of element tungsten and red phosphorus. This traditional method needs to cost much energies for reaction at a very high temperature of 1100 °C and a very long reaction time of several days. Very recently, Li et al 27 synthesized WP2 nanorods with excellent performance as an efficient hydrogen evolution reaction electrocatalys. The WP₂ nanorods were synthesized through phosphidation of (NH4)_{0.25}WO₃ nanorods precursor which were prepared by complicated chemical methods.

In this work, we develop a cheap and conventional method to synthesize WP_2 particles. Namely, simple solid-state reaction of WO_3 and red phosphorus can synthesize high crystalline WP_2 particles. The obtained WP_2 particles were explored the photocatalytic properties which, to our best knowledge, has not been reported before. The results show that WP_2 particles can efficiently photodegrade the methyl orange (MO) and evolve hydrogen from water and has a good photostability and reusability, indicating the potentials as a new photocatalyst. The photoactivities of the sample are confirmed by the detection of the existence of the hydroxyl radical by fluorescence spectroscopy in solution in the presence of WP_2 under UV light irradiation. Based on the experimental measurements and theoretical calculations, a possible photocatalytic mechanism is proposed.

Experimental Section

Synthesis of WP₂ photocatalyst

All the purchased and used chemical reagents were analytical grade without further purification. The WP_2 particles were prepared by solid-phase reaction in evacuated and sealed silica tubes at a certain reaction temperature. Tungsten trioxide (WO₃) and element red phosphorus (P) were used as the tungsten and phosphorus sources, respectively. The reaction details are as follows: 0.5 g tungsten trioxide and 0.3 g

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element red phosphorus were uniformly mixed and Accumme sealed (~ 7×10^{-4} Pa) in a silica tube. The RJ: the CODE Was2 path into a muffle furnace which was heated to 950 °C in 95 minutes and kept at this temperature for 5 h. Then the furnace was cooled down to room temperature naturally. Powders sample was collected from the silica tube. The powders sample are black particles mixed with a few white particles. Considering the fact that the white particles are reliable to deliquesce in air, we believe that they are side product of P₂O₅. After washed the powders by water for several times the impurities P₂O₅ were successfully removed. After the washing treatment, the sample was dried under 60 °C in a vacuum oven for 12 hours.

Photocatalytic degradation experiment

The photocatalytic degradation activities of the synthesized WP₂ sample were examined by monitoring the photocatalytic degradation of methyl orange (MO) in aqueous solution under UV light irradiation. The light source for photocatalysis was a high pressure mercury lamp, which provided the UV light. The experiments were carried out at room temperature in order to eliminate temperature effects. In each experiment, a certain amount of WP₂ photocatalyst were added into 50 mL MO solution with a concentration of 5 mg/L. Prior to irradiation, the suspensions were magnetically stirred in dark for 30 minutes to achieve adsorption equilibrium between the MO molecules and the photocatalyst. During the light irradiation process, the suspensions were periodically withdraw, centrifuged to separate the photocatalyst and used for absorbance measurements by a UV-Vis spectrophotometer. A blank test was also carried out on an aqueous MO solution without photocatalyst under the same light irradiation condition to evaluate the efficiency of the photocatalyst.

Photocatalytic H₂ production

The hydrogen generation reactions of the WP₂ photocatalyst were carried out in an outer irradiation-type photoreactor connected to a closed gas-circulation system. Typically, 70 mg of WP₂ photocatalyst were added into 50 mL solution containing 20 vol% triethanolamine (TEA) as a sacrificial reagent to capture the photo-generated holes. 2 wt% Pt were loaded on the surface of the WP₂ photocatalyst by the in situ photo-deposition method using H₂PtCl₆. The top of the reactor was tightly closed by a silica rubber. A 350 W high pressure mercury lamp was applied as the UV light source, which was positioned above the side of the photo-reactor. The WP2 photocatalyst were continuously dispersed in the aqueous TEA solution by a magnetic stirrer during the light irradiation. The photocatalytic reaction was performed at room temperature. The photocatalytic H₂ evolution rate was analysed by gas chromatograph (GC9790II, FULI) with thermal conductivity detector.

Trapping experiment of hydroxyl radicals (•OH)



Fig. 1 (a) XRD patterns and (b) crystal structure of the synthesized $\mathsf{WP}_2.$

During the photocatalytic degradation reaction, the •OH formed on the surface of the irradiated photocatalyst was detected by the fluorescence technique using terephthalic acid (TA) as a probe molecule. In a brief experimental procedure, 70 mg of WP₂ photocatalyst were dispersed in 50 mL of a mixture of a 5×10⁻⁴ mol/L aqueous TA solution and a 2×10⁻³ mol/L NaOH solution. The resulting solution was magnetically stirred and the suspension was exposed to the light. At a certain time intervals, the suspensions was collected and centrifuged to measure the maximum fluorescence intensity using the fluorescence spectrophotometer with an excitation wavelength of 315 nm.

Theoretical calculations

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All the calculations were performed at the generalized gradient approximation function of the Perdew-Burke-Ernzerhof form²⁸ with the projector-augment wave potential implemented in the simulation package VASP. ²⁹ The cut-off energy for the plane wave was chosen to be 500 eV, with 10×10^{-5} eV per atom for SCF tolerance. Monkhorst-Pack k-points were set to be $5\times5\times5$. The electronic structures were calculated based on the fully relaxed lattice parameters and ionic positions. For the calculation of the density of the states (DOS), a large $7\times7\times7$ k-points set was used.

Characterization

The crystal structures of the samples were obtained by X-ray diffractometer (Rigaku D/MAX2500PC) with Cu K α radiation (1.54 Å). Diffraction angle (2-theta) ranges from 5° to 90° and the scanning rate is 4° / min. The field emission scanning electron microscopy (FE-SEM, TESCAN MIRA 3) with an energy dispersive X-ray spectrometer (EDX) and a transmission electron microscopy (TEM, ZEISS Libra 200FE) were employed for the morphological observation, the size, and structure of the samples. The absorption at about 465nm were conducted to identify the concentration of MO by using a UV-Vir spectrophotometer (Shimadzu UV-3600). The fluorescence measurements were recorded on a Hitachi F4500 fluorescence spectrophotometer at an excitation wavelength of 315 nm.

Results and Discussion



Fig. 2 (a) Typical FE-SEM image, (b) the magnified SEM image of the WP_2 particles, (c) EDX and (d) HRTEM image of the WP_2 photocatalyst.

The crystal structure and phase purity of the sample were characterized by XRD. Fig. 1a shows the XRD patterns of the WP₂ sample, which was synthesized via a solid-phase reaction method at the reaction temperature of 950 °C for 5 hours followed with water washing to remove the impurities P2O5. The diffraction peaks can be indexed to the typical peaks of WP₂ (space group: Cmc2₁, JCPDS card no. 76-2364), and the sharp and strong diffraction peaks indicate that the obtained product is high crystalline. The crystal structure of the WP₂ is shown in Fig. 1b, which corresponds to the orthorhombic structure and the lattice constants are a=3.1649, b=11.1599 and c=4.9732 Å, respectively. It should be noted that no other peaks related to any impurities phase are observed, which indicates that the obtained WP₂ sample is with a high purity. Comparing with the reaction of element tungsten with red phosphorus ²⁶ and phosphidation of (NH4)_{0.25}WO₃ nanorods precursor, ²⁷ our method of simple solid-state reaction of WO₃ and red phosphorus is convenient and much efficient.

The morphology of the prepared WP_2 -based photocatalyst was characterized by the field emission scanning electron



Fig. 3 UV-vis absorption spectra of the WP₂-based photocatalyst. Inset: the corresponding Kubelka – Munk transformed spectrum.

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Fig. 4 Calculated electronic band structure (left) and DOS (right) of WP₂.

microscopy (FE-SEM). Fig. 2a shows that the obtained WP₂ samples are composed of particles with the size of about 2-3 micrometers. Fig. 2b shows the magnified SEM image of the sample, it can be observed that the WP₂ particles have a lotus root-like structure with smooth surface. Energy dispersive Xray spectrometer (EDX) measurement as shown in Fig. 2c shows that the atomic ratio of W: P is about 1: 2.11, which is consistent with the stoichiometric composition of the pure WP₂. The transmission electron microscopy (TEM) image was provided for further insight into the microstructure of the obtained product as shown in Fig. 2d. The observed lattice fringes with a d-spacing of 0.342 nm and 0.305 nm in the highresolution TEM image match well with the (021) and (110) crystal plane distances of WP2, which also shows that high crystalline WP₂ particles are synthesized.

The optical property of the as-prepared WP₂ photocatalyst was studied by UV-vis absorption spectra, the result is shown in Fig. 3. The band gap energy of WP_2 can be estimated from the following equation: ³⁰⁻³¹

$\alpha hv = A (hv - E_g)^{n/2}$

Where $\alpha,~h,~\nu$ and E_g are the absorption coefficient, Plank's constant, light frequency, and the band gap energy, respectively, and A is a constant. The factor n depends on the characteristics of the optical transition of a semiconductor (n=1 for direct transition and n=4 for indirect transition). The inset shows the corresponding Kubelka-Munk transformed spectrum, from which we can obtain that the band gap energy is about 3.42 eV.

In order to study the electronic structure of the as-prepared WP₂ photocatalyst, we conducted first-principle calculations of the band structures and density of states (DOS) for the crystal WP₂, which are shown in Fig. 4. The Fermi level was set as $E_f=0$. The calculated results show that the Fermi level is located in the overlap region between the bottom of the CB and the top of the VB, which indicates a semimetallic behavior. The electrical resistivity measurements show a linear dependence of the temperature and a slow increase in the resistivity with the temperature increases, which also confirms the metallic characteristics of WP₂ (Fig. S1⁺). Unlike the band structure of well-described typical semiconductors, the VB and CB of WP₂



Fig. 5 Schematic band structure and transition mechanism of WP₂.

overlap at the Fermi level, so the strong absorption observed in the UV range in Fig. 3 cannot be explained by the traditional transition mechanism that the electrons transition from the occupied VB to the unoccupied CB. This phenomenon was also observed from semimetal Bi and MoP2, 18-19 and the observed band gap was assigned the transition from the occupied level to the valence band. Along this line, we describe the band structure and transition mechanism of WP₂ in Fig. 5. From the calculation results, we can see that an indirect transition from the subbands blow the VB to VB (Fig. 4) can be possible under UV light excitation. B₁ and B₋₁ depict the bands above the CB and blow the VB, respectively, as shown in Fig. 5. According to the model, the observed band gap energy can be assigned to a B₋₁ to VB transition from an occupied level to the valence band. Here, we should know that the calculated value is smaller than the experimental value as the result of the well know band gap underestimation within the framework of standard DFT.18

The photocatalytic activities of the synthesized WP₂ sample were evaluated for the degradation of MO under UV light irradiation. Fig. 6a shows the degradation efficiency for MO varies with different dosage of WP₂ photocatalysts. The degradation efficiency of MO is 78%, 92%, 100%, 100% for the WP₂ dosage of 30, 50, 70, 90 mg, respectively, from which we can see that the MO is completely degraded with the dosage is 70 mg, when increased the dosage of the ptotocatalyst furthermore, the change of the degradation efficiency of MO is not obvious. In the view of the degradation efficiency and the saving of the ptotocatalyst, we selected 70 mg as the best dosage of WP₂ for the degradation reaction. Fig. 6b shows the



Fig. 6 (a) the degradation efficiency of MO with different dosage of photocatalyst, (b) photocatalytic degradation of MO in aqueous solution under UV light irradiation.

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Fig. 7 (a) Reusability of the WP_2 -based photocatalyst for photocatalytic degradation of MO in aqueous solution (b) XRD patterns of the photocatalysts before and after the photocatalytic reaction.

photo-degradation progress of MO under UV light irradiation with the optimized dosage. About 10% decrease of concentration of MO when the dark adsorption equilibrium achieved, the weak adsorptive capacity can be ascribed to a relatively large size with smooth surface of WP₂ particles. But nearly 100% of the dye is degraded in 100 minutes after turning on the light. A blank experiment (without photoctalyst) was also conducted, the MO was stable under UV light irradiation, which indicates that the degradation of MO was the result of WP₂ photocatalyst. As we know, MO, a typical dye which is hard to degrade, various photocatalysts were studied to remove MO.³²⁻³⁵ Comparing with the most of reported photocatalysts, our WP₂ particle photocatalyst offers a good photoactivity.

The photostability and reusability of the photocatalyst are also very important for practical application. To evaluate the stability and reusability of the WP₂ photocatalyst, three successive photocatalytic experiment runs were carried out by adding recycled WP₂ photocatalyst to fresh MO solutions with no change in the overall concentration of the catalyst under UV light irradiation. As shown in Fig. 7a, the photocatalytic activity of WP₂ for the degradation of MO does not obviously change after the recycle runs under the same experiment conditions. Furthermore, the XRD pattern of the WP₂ photocatalyst after the reaction has no obvious change comparing with the sample before the reaction as shown in Fig. 7b. The above results indicate that the as-synthesized WP₂ photocatalyst has excellent photostability and reusability for the practical applications.

During the photocatalytic process, the photo-generated electrons will join in the multistep reduction of dissolved O₂ to generate hydroxyl radicals (\bullet OH), and the photo-generated holes will oxidize the H₂O molecules to generate \bullet OH. The \bullet OH, known as a primary oxidant with strong oxidability in the photocatalytic system, can degrade the organic dye into H₂O and CO₂, so the generation of \bullet OH is important for the photocatalytic reaction, and the existence of \bullet OH can confirm the photocatalytic activity of the photocatalyst. The \bullet OH generated during the photocatalytic reaction can be easily detected by a fluorescence technique using terephthalic acid (TA) as a probe molecule, the TA can reacts with \bullet OH to produce the highly fluorescent product, 2-hydroxyterephthalic acid (TAOH).³⁶ Fig. 8 shows the \bullet OH trapping PL spectra of WP₂-based photocatalyst in TA solution under UV light



Fig. 8 Hydroxyl radicals (\bullet OH) trapping fluorescence spectra of WP₂-based photocatalyst in terephthalic acid (TA) solution under UV light irradiation.

irradiation. The maximum intensity peaks in the PL spectra are observed at approximately 428 nm with an excitation wavelength of 315 nm, demonstrating that •OH is formed on the UV light irradiated surface of the WP₂-based photocatalyst in the photocatalytic oxidation process, which is in agreement with the early articles.^{19,36} It also can be observed that the PL intensity increase gradually with increasing the light irradiation time, which indicates that TAOH accumulates in the solution and the accumulation increases continuously. The existence of •OH in the solution in the presence of WP₂ under UV light irradiation confirms the photocatalytic activity of WP₂.

The possible mechanism for the photocatalytic degradation of MO: Based on the above experimental and theoretical results, a possible photocatalytic mechanism of WP₂ is proposed which bases on the conventional mechanism of semiconductor photocatalysts. Combined the band gap energy, we can obtain the absolute energies of the CB and VB of WP₂ according to the following two equations: ³⁰

$$E_{VB} = \chi - E_e + 1/2 E_g$$
 (a)
 $E_{CB} = E_{VB} - E_g$ (b)

Where χ is the absolute electronegativity of WP₂ (~5.18 eV), E_e is the normal hydrogen electrode scale to the absolute vacuum scale (~4.5 eV) and E_g is the band gap energy of WP₂ (~3.42 eV). Based on the above parameters, the absolute energies of CB and VB are -1.03 eV and 2.39 eV, respectively.



Fig. 9 The possible schematic illustration of the photocatalytic reaction of WP_2 for the degradation of MO in aqueous solution under UV light irradiation.

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Fig. 10 Hydrogen evolution rate of WP_2 and 2% Pt- $\mathsf{WP}_2.$

The possible photocatalytic mechanism of WP_2 is shown in Fig. 9, and the photocatalytic reactions are described as follows:

$WP_2+hv \rightarrow e^{-}(WP_2) + h^{+}(WP_2)$	(1)
$e^{-} + O_2 \rightarrow \bullet O_2^{-}$	(2)
•O ₂ ⁻ + 2e ⁻ +2H ⁺ →•OH + OH ⁻	(3)
$2H_2O+2h^+\rightarrow H_2O_2+2H^+$	(4)
H ₂ O ₂ +e ⁻ →●OH + OH ⁻	(5)
$MO+\bullet OH \rightarrow H_2O+ CO_2$	(6)

The electrons migrate from B₋₁ to VB under the UV light irradiation, leaving holes behind (equ. 1). The photo-generated electrons reduce the O₂ absorbed on the surface of the WP₂ catalyst into \bullet OH (equ. 2 and 3). Meanwhile, the left holes oxidize the H₂O into \bullet OH (equ. 4 and 5).³⁷⁻³⁸ The \bullet OH will finally degrade the MO into H₂O and CO₂ (equ. 6).

The photocatalysis technology consists of photocatalytic degradation and water splitting for hydrogen evolution, so the photocatalytic hydrogen evolution activity of the assynthesized WP₂ product is therefore investigated. The result shows that the WP₂-based photocatalyst could achieve H₂ production from water containing TEA as the sacrificial electron donor under the UV light irradiation, and a control experiment shows no H₂ production in the dark environment or without the catalyst, which indicates that the WP₂ sample plays a role as the photocatalyst under the light irradiation. The schematic illustration of hydrogen evolution of WP₂ are shown in Fig. S2⁺. Usually, loading of a small amount of noble metal (Pt) on the photocatalyst is used to improve the H₂ production in photocatalytic reaction.³⁹⁻⁴¹ As shown in Fig. 10, the hydrogen evolution rate of the bare-WP₂ is 3 µmolh⁻¹g⁻¹, and that is 8 μ molh⁻¹g⁻¹ for 2wt% Pt decorated WP₂ photocatlyst, which is about 2.7 times of the bare-WP₂. Although the hydrogen evolution rate is not high comparing with the other semiconductor catalysts, WP₂ shows promising and potential in application of the photocatalysis. Further work about the photocatalysis of WP₂ are under studied.

Conclusions

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In summary, high crystalline tungsten diphosphide (WP₂) particles were facile synthesized by solid-phase reaction of WO₃ and red phosphorus in evacuated and sealed silica tube. WP₂ is explored as a new photocatalyst which can efficiently photodegrade the methyl orange and evolve hydrogen from water under UV light irradiation and with a good photostability and reusability. The detection of the existence of the hydroxyl radical by fluorescence spectroscopy in solution in the presence of WP₂ under UV light irradiation confirms its photoactivity. Based on the experimental measurements and theoretical calculations, a possible photocatalytic mechanism is proposed. Therefore, this work provides a chance for practical applications of semimetallic material WP₂ in the field of photocatalysis.

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