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Phosphorization-derived MoP@MoO_{3-x} nanowires for selective photocatalytic oxidation of benzyl alcohol to benzaldehyde

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Abstract

The selective oxidation of small molecules to high-value-added products is regarded as a promising approach to alleviating the worldwide energy crisis. In this work, heterogenous non-noble-metal molybdenum(III) phosphide (MoP) catalysts were anchored onto MoO_{3-x} nanowires $(MoP@MoO_{3-x})$ via a facile phosphorization method using various amounts of phosphorus precursor. Because of the combined attributes of the MoP and the MoO_{3-x} nanowires, the novel MoP@MoO_{3-x} nanowire catalysts not only provide more active sites but also enhance electron-hole separation efficiency. The results show that the selective transformation of benzyl alcohol to benzaldehyde was achieved with 67% selectivity. A comprehensive study including field-emission transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, Brunauer-Emmett-Teller analysis, X-ray diffraction analysis, UV-vis diffuse reflectance spectrum, electron-spin resonance, photocurrent measurements, electrochemical impedance spectroscopy, and density functional theory (DFT) computations was conducted. The selective photocatalytic oxidation results and the DFT calculations indicate that the MoP particles anchored onto the MoO_{3-x} substrate display an important role in enhancing the selective photocatalytic oxidation of benzyl alcohol.

Keywords: MoP@*MoO*_{3-x}; *phosphorization*; *nanowires*; *selectivity*; *benzaldehyde*

1. Introduction

Within the chemical industry, finding a sustainable and green organic synthesis method to selectively oxidize alcohols into relevant aldehydes is considered a promising direction. Among the various investigated methods, photocatalysis has been regarded as a useful approach to selectively oxidizing alcohols [1-4] because it is economical and environmentally friendly. By contrast, other traditional oxidation methods have unavoidable drawbacks, such as the requirement of a strong oxidant (i.e., dichromate or permanganate ion) [5]. Extensive effort has been devoted to developing an efficient catalyst that enables O_2 to be used as the oxidant and generates H_2O_2 and H_2O as the sole byproducts [6-8]. Although many researchers have found that semiconductors and noble metals can achieve selective oxidation with solar light and O_2 [9-11], achieving highly selective oxidation remains a challenge.

Molybdenum-based oxides or sulfides are regarded as highly efficient catalysts because of their special structures and multivalent molybdenum [12-15]. Among them, MoO₃ displays numerous advantages, including a facile synthesis method, good physical stability, good electrochemical performance, low cost, and environmental friendliness [16]. Recently, researchers have focused mainly on compositing it with various carbon-based materials (e.g., graphene, carbon nanotubes, and activated carbons) [17-19], combining it with conducting polymers (e.g., polypyrrole or polyaniline) [20], and compositing it with various metal oxides (e.g., TiO₂,

WO₃, or In₂O₃) [**21-23**]. Even though these studies have achieved some breakthroughs, some essential problems remain unsolved, limiting the applicability of the catalysts. The main issue is that an entirely uniform distribution cannot be achieved between the MoO₃ and other materials.

Noble metals such as Pd or Pt display ideal selective oxidation performance [24-26]. However, their high cost precludes their widespread application, which directs our efforts toward earth-abundant compounds. Recently, transition-metal phosphides such as MoP, FeP, CoP, and Ni₂P have been widely investigated because of their cost effectiveness, and they are being considered as substitutes for Pd or Pt [27-30]. Among them, MoP is a highly efficient cocatalyst because of its good conductivity, moderate stability, and exceptional catalytic performance [31]. Zhang et al. synthesized MoP@Mo₂C@C, which exhibited high catalytic performance over a wide pH range [32], and Yin et al. prepared MoP@CdS nanorods as a heterojunction catalyst with abundant active sites to enhance photocatalytic performance [33]. However, these methods result in the agglomeration of MoP on the surface of the substrate, inhibiting catalytic performance.

Inspired by this approach, in the present work, we deposited MoP uniformly onto MoO₃ nanowires using an in situ phosphorization method. The MoO₃ acts as both a substrate and the precursor of MoP. As a result, MoP was synthesized from MoO₃ and a phosphorus precursor (NaH₂PO₂) via a facile sintering phosphorization method. With this method, the MoP was loaded uniformly onto the surface of MoO₃, which exhibits highly

oxidation selective activity. Samples with various degrees of phosphorization were synthesized, and the optimum degree of phosphorization was determined. In addition, we conducted density functional theory (DFT) calculations to gain deeper insight into the highly selective oxidation performance of the MoP(a)MoO_{3-x} catalysts.

2. Experimental

2.1. Materials synthesis

2.1.1. Preparation of MoO_3 nanowires.

We synthesized the MoO₃ nanowires by the hydrothermal method, as described in our previous work [15]. Generally, 2 g of Mo particles were dispersed into 50 mL of pure water under continuously stirring to achieve a homogenous solution. And then, H_2O_2 solution (30 wt%; 80 mL) was slowly added to form a light-yellow aqueous solution; the solution was then kept stirring for another 4 h. After which, the precursor solution was then subsequently transferred into a Teflon-lined stainless-steel autoclave, and kept at 180 °C for 120 h. After that, the as obtained solid was washed with water and ethanol for several times. For the uniform phosphorization, the MoO₃ nanowire solution was removed by freeze-drying to form an aerogellike solid (**Fig. S1**).

2.1.2. Synthesis of $MoP@MoO_{3-x}$ nanowires.

The white MoO₃ nanowires (50 mg) and NaH₂PO₂ (0.2 g) were separately placed in an alumina tube with a cover. The alumina tube was heated at 5 °C/min to 750 °C under an Ar atmosphere and maintained at this temperature for 4 h. After the heat treatment, the black products were washed for several times with water and ethanol. The as-synthesized catalysts were named MoP@MoO_{3-x}-1. Meanwhile, a series of samples synthesized with various amounts of NaH₂PO₂ (0.4 g, 0.6 g, 0.8 g) were denoted as MoP@MoO_{3-x}-2, MoP@MoO_{3-x}-3, and MoP@MoO_{3-x}-4, respectively. A digital image of the MoP@MoO_{3-x}-3 nanowires are shown in **Fig. S1**.

2.1.3. Preparation of pristine MoP catalysts.

MoP was synthesized with the molybdenum and phosphorous precursor. Typically, 2.66 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 1.98 g $(NH_4)_2HPO_4$, and 6.34 g of citric acid (CA) as a chelating agent were dissolved in 100 mL of purified water to form the aqueous solution. And then, it was kept at 90 °C under continuously stirring and then further dried at 120 °C until the sample turned into solid. As obtained catalyst was grounded in the agate mortar, and then calcined at 500 °C for 10 h in the tube furnace, which was subsequently reduced with the stream of 5 % H₂/N₂ at 850 °C for 5 h (5 °C·min⁻¹) and then cooled to the room temperature [**34-35**].

2.2. Characterization

The crystal structure of the catalysts were measured by XRD (D2) PHASER, Bruker). The morphology was detected via scanning electron microscopy (SU8010, Hitachi), and field-emission transmission electron microscopy (FE-TEM) images were obtained by a Jeol JEM-2100F electron microscope. The samples were also analyzed by XPS (ESCA LAB MK-II, VG Scientific Co.). The specific surface area of the catalysts were measured by the adsorption analyzer (BEL BELSORP) on the basis of adsorption data acquired in the partial pressure (P/P_0) range from 0.02 to 0.25. UV-vis diffuse reflectance spectroscopy (U-3010, Hitachi) was conducted at room temperature using the Kubelka–Munk approach with BaSO₄ as a reference. Steady-state/time-resolved PL emission spectra (320 nm excitation) were recorded with a fluorescence spectrophotometer at room temperature. ESR signals were recorded on a Bruker ESR A300 spectrometer at room temperature (298 K). EIS was conducted by an Ivium electrochemical station with a three-electrode system in which a modified Ni foam electrode, Ag/AgCl electrode, and Pt wire were used as the working, reference, and counter electrode, respectively. The measurements condition were conducted as follows: an applied sine-wave potential of 5 mV amplitude, a frequency range from 0.1 Hz to 10 kHz, and the 3 M Na₂SO₄ as the electrolyte,

2.3. Photocatalytic evaluation

The selective photocatalytic performance of the as-synthesized catalysts was conducted by a solar simulator (Sun 2000, ABET, 70 W/m^2) (**Fig.** S2). Typically, deionized water (50 mL) was poured into the quartz bottle with catalyst (20 mg) (solution A). This suspension was then sonicated for 1 h before the photocatalytic performance measurement to reach an adsorption-desorption equilibrium. And then, the benzyl alcohol (0.1 mL) was mixed with 30 mL of acetonitrile (solution B). Lastly, the Solution A was mixed with solution B to turn the biphasic system into a single phase. After the solution was stirred for 60 min, O_2 was purging for 15 min under continuous stirring. The measurement conditions and results are surmarized in **Table S1.** During the photocatalytic reaction, ~0.5 mL of the solution was sampled each 2 h and filtered with the syringe filter (0.22 μ m) to remove the solid. The concentrations of benzyl alcohol and benzaldehyde were determined by high-performance liquid chromatography on a YL9110 chromatograph (Younglin Co. Ltd., Korea) consisting of a YL9110 quaternary pump and an Optima Pak C18 column (5 μ m, 250 × 4.6 mm², RS Tech Corp., Daejeon, Korea). Methanol/water (50:50, v/v) solution with a flow rate at 1.0 mL/min was used as the mobile phase. Besides, the injection volume was 10 μ L, the detection wavelength was set as 254 nm, and the column temperature was 30 °C. The external standard method was used to analyze the benzaldehyde product (Fig. S3).

Meanwhile, in order to further detect the photocatalytic reaction on the oxidation sites, the parallel test measuring the oxygen evolution was also

conducted to confirm it (**Fig. S4**). The oxygen evolution of as-obtained MoP@MoO_{3-x}-3 catalysts was carried out using a Labsolar-IIIAG photocatalytic system (Beijing Perfectlight Technology Co. Ltd). This system is composed of a 300 W Xe lamp as the light source, a glass reactor vessel, a gas chromatograph (GC 9190, argon as carrier gas), and an evacuation system. Before the test, 20 mg of catalysts were poured into 50 mL deionized water, along with 0.5 g AgNO₃ as the sacrificial reagent for electrons. Meanwhile, in order to confirm whether the benzyl alcohol will be oxidized on the oxidation sites or not. Another 0.1 mL of benzyl alcohol was mixed with 30 mL of acetonitrile. Lastly, two kind of solutions were mixed directly to turn the biphasic system into a single phase. The reaction was measured under flowing Ar for 30 min to remove air before irradiation. During the photocatalytic experiment, the produced oxygen was analyzed by gas chromatography each hour.

2.4. Preparation of photoanodes and photocurrent measurements

Fluorine doped tin oxide coated (FTO) glass was prepared by sequentially washing with acetone, distilled water, and ethanol for three times. And then, 5.0 mg photocatalyst was dispersed in 1 ml isopropanol containing 20 μ l nafion and under ultrasonic treatment for 30 min. Subsequently, above suspension was dropped onto the surface of the FTO glass with exposed 1 \times 1 cm² area. After drying in the oven for 4 h, the electrode was calcined at 200 °C in N₂ for 2 h to improve the adhesion.

Besides, the boundary of FTO glass was protected by transparent tape. Here, FTO glass acted as working electrode, Ag/AgCl as reference electrode (3.0 M KCl) and a Pt electrode as counter electrode. The 0.5 M Na₂SO₄ aqueous solution was used as electrolyte solution. Meanwhile, before testing, the electrolyte solution was purged for 60 min with N₂. The photocurrent measurements were carried out at 0.6 V (vs. Ag/AgCl) and under a solar simulator device (Sun 2000, ABET).

2.5. Computational method

First-principles DFT calculation analysis was conducted by a projector-augmented wave (PAW) method [**36**]. Perdew–Burke–Ernzerhof exchange-correlation functional of the generalized-gradient approximation (PBE-GGA) [**37**] was used for the exchange-correlation functional. Among all calculation procedure, the plane-wave expansion of the wave functions with an energy cutoff of 400 eV was displayed. As for the relaxation, force tolerance was set as 0.05 eV/Å. The formation energy (*E*) of the MoP@MoO₃ structure was obtained as follows:

$$E_{\text{binding}} = E_{\text{A+B}} - (E_{\text{A}} + E_{\text{B}})$$

where E_{A+B} is the total energy of MoP@MoO₃, E_A is the total energy of MoP surface, and E_B is the total energy of MoO₃ surface. According to this equation, a more negative $E_{binding}$ means better stability.

3. Results and discussion

3.1. Physical properties of MoP@MoO_{3-x} nanowires



Fig. 1 (a) Schematic of the synthesis process of MoP@MoO_{3-x} nanowires; (b) XRD spectra of the as synthesized catalysts; (c) Raman spectrum of the as synthesized catalysts.

In this paper, we rationally designed and constructed MoP@MoO_{3-x} nanowires using MoO₃ nanowires as the substrate. The two-step synthesis process of the MoP@MoO_{3-x} nanowires is displayed in **Fig. 1** (a). First, the MoO₃ nanowires were prepared via a hydrothermal method. The as-obtained MoO₃ nanowires were then partially phosphatized using various amounts of

NaH₂PO₂ heated at 750 °C in a H₂ (5%)/Ar atmosphere to obtain the MoP@MoO_{3-x} nanowires. As displayed in **Fig. 1** (b), the XRD patterns of the MoP@MoO_{3-x}-1, MoP@MoO_{3-x}-2, MoP@MoO_{3-x}-3, and MoP@MoO_{3-x}-4 exhibited the same peaks ($2\theta \approx 25.7^{\circ}$, 36.7° , and 53.2°) [**38**] as the pattern of the prepared MoO₃ nanowires (PDF #78-1072). In addition, peaks of MoP ($2\theta \approx 28.0^{\circ}$, 32.1° , 43.0° , and 57.3°) [**39**] are observed among the peaks of MoP@MoO_{3-x} nanowires (PDF#24-0771). On the basis of these results, we concluded that the MoP@MoO_{3-x} nanowires were synthesized successfully.

The size statistics of the MoP@MoO_{3-x}-3 nanowires show that almost all of them exhibit a diameter of 200–500 nm (**Fig. S5**). To further demonstrate the contraction between MoO₃ and MoP, we performed Raman measurements. As exhibited in **Fig. 1** (c), the Raman band at 821 cm⁻¹ can be attributed to the vibration of the Mo=O bond. Meanwhile, after deposition of MoP onto the surface of MoO₃ nanowires, the Mo=O bond position shifts to 810 cm⁻¹, meaning a bond formation according to the phosphorization reaction, providing further evidence of the formation of MoP@MoO_{3-x} nanowires.



3.2. Intrinsic properties of $MoP@MoO_{3-x}$ -3 nanowires

Fig. 2 (a) SEM of the MoO₃ nanowires; (b) TEM of the MoO₃ nanowires; (c) SEM of the MoP@MoO_{3-x}-3 nanowires; (d) TEM of the MoP@MoO_{3-x}-3; (e), (f) and (g) HRTEM images of MoP@MoO_{3-x}-3; (h) EDX spectrum of MoP@MoO_{3-x}-3; (i) elemental

mapping patterns of MoP@MoO_{3-x}-3.

SEM and TEM observations revealed that the MoP@MoO_{3-x}-3 nanowires consisted of MoP nanoparticles and MoO₃ nanowires with a porous structure (Fig. 2 (a)-(g)). As shown in Fig. 2 (a) and (b), the MoO_3 nanowires exhibited a smooth surface. However, after the phosphorization process, the surface became rough and porous (Fig. 2 (c), (d) and (e)). Meanwhile, some black particles were deposited on the surface of the $MoP@MoO_{3-x}$ -3 nanowires uniformly, possibly because of the MoP (Fig. 2 (c)-(e)). In addition, HRTEM was used to obtain crystal information, showing that the MoP grew on the surface of the MoP@MoO_{3-x}-3 nanowires (Fig. 2 (g)), which is in agreement with the XRD results. As displayed in Fig. 2 (g), the MoP crystallites had seven layers of 1.89 nm thickness; the lattice-fringe spacing was calculated to be 0.27 nm, which can be assigned to the (100) plane of MoP [40]. HRTEM images of MoP@MoO_{3-x}-1, MoP@MoO_{3-x}-2, and MoP@MoO_{3-x}-4, which show similar results, are presented in Fig. S6. Beyond that, the EDX spectra of MoP@ MoO_{3-x} -3 (Fig. 2 (h)) proves the existence of Mo, O, and P elements. The element mapping images (Fig. 2 (i)) of the MoP@MoO_{3-x}-3 nanowires indicate that the Mo, O, and P were dispersed homogeneously on the surface, consistent with the TEM observations. The corresponding TEM, EDX, and element mapping analyses of MoP@MoO_{3-x}-1, MoP@MoO_{3-x}-2, MoP@MoO_{3-x}-3, and MoP@MoO_{3-x}-4 are also shown (Fig. S7, S8, S9, and S10, respectively).

To further confirm the stability of the catalysts, we imaged MoP@MoO_{3-x}-3 by TEM before and after the photocatalysis experiments (**Fig. S11**), revealing that the morphology remained unchanged; thus, the material was stable. In addition, the specific surface area of the as-prepared catalysts are displayed in **Fig. S12** and **Table S2**; the MoP@MoO_{3-x}-3 exhibited a specific surface area of $32.237 \text{ m}^2 \text{ g}^{-1}$.



Fig. 3 (a) Survey spectrum of MoO₃ nanowires and MoP@MoO_{3-x}-3; (b) Mo 3d spectrum of MoO₃ nanowires and MoP@MoO_{3-x}-3; (c) O 1s spectrum of MoO₃ nanowires and MoP@MoO_{3-x}-3; (d) P 2p spectrum of MoP@MoO_{3-x}-3.

To reveal the chemical states environment of the catalysts, the X-ray photoelectron spectroscopy (XPS) was conducted to analysize them. As illustrated in **Fig. 3** (a), three elements were present: Mo, O, and P. Meanwhile, the peaks located at 39.2 and 66.0 eV can assign to the Mo 4p and Mo 3s, respectively [**41-42**]. The high-resolution Mo peaks of MoO₃ and MoP@MoO_{3-x}-3 were deconvoluted into two and five peaks, respectively (**Fig. 3** (b)). The peaks at 232.7 and 235.8 eV in the spectrum of MoO₃ can be owning to the Mo⁶⁺ 3d_{5/2} and 3d_{3/2} states [**43**], respectively. Among the five peaks in the spectrum of MoP@MoO_{3-x}-3, the peaks of Mo⁶⁺ 3d_{5/2} and 3d_{3/2} are found at the same energies. Meanwhile, the peaks at 229.1, 231.5, and 234.5 eV indicate the Mo⁴⁺ 3d_{5/2}, Mo⁵⁺ 3d_{5/2}, and Mo⁵⁺ 3d_{3/2} states, respectively [**44-46**]. On the basis of these results, we concluded that the MoO₃ nanowires were partially reduced by the phosphorization procedure.

Fig. 3 (c) shows the O 1s XPS spectrum. The peak at 531.0 eV corresponds to Mo–O [47]. The P $2p_{3/2}$ region shows peaks at 129.5 and 133.8 eV (**Fig. 3** (d)) [48]. The P $2p_{3/2}$ peak at the lower binding energy (129.5 eV) indicates the existence of phosphide, possibly because of Mo–P [32]. The P $2p_{3/2}$ peak at the higher binding energy (133.8 eV) is a typical position of phosphorus oxide and is therefore assigned to P–O [49-50]. In combination with the XRD and TEM results, the XPS analysis confirms that the MoP particles were deposited onto the surface of the MoO₃ nanowires.



Fig. 4 (a) Valence-band XPS spectra of MoO₃ nanowires and MoP@MoO_{3-x}-3; (b) Mott-Schottky spectra of the MoO₃ nanowires and MoP@MoO_{3-x}-3; (c) band position of the MoO₃ nanowires and MoP@MoO_{3-x}-3 (as calculated from the valence band XPS spectra and Mott-Schottky spectra); (d) electrostatic potential of MoP (0 0 1)@MoO₃ (0 1 0) (the red line is the Fermi level, and black line and purple line are the vacuum levels of the MoO₃ and MoP, respectively.)

As reported previously, the conduction band (CB) and valence band (VB) positions determine the performance of a photocatalyst: higher CB and VB positions result in greater photocatalytic activity [51-53]. As shown in Fig. 4 (a), the positions of the VB of the MoO₃ nanowires and

MoP@MoO_{3-x}-3 were confirmed from the VB XPS spectra to be 3.21 and 2.01 eV, respectively. Meanwhile, the CB positions of MoO₃ nanowires and MoP@MoO_{3-x}-3 were confirmed from the Mott–Schottky spectra (**Fig. 4** (b)) to be 0.12 and -0.42 eV, respectively. As previously mentioned, the band positions of the MoO₃ nanowires and MoP@MoO_{3-x}-3 (calculated from the VB XPS spectra and Mott–Schottky spectra) were determined (**Fig. 4** (c)). The CB position of the MoP@MoO_{3-x}-3 (-0.42 eV) was more negative than that of the MoO₃ nanowires (0.12 eV), indicating that the MoP@MoO_{3-x}-3 composite catalysts should exhibit high catalytic activity, as later confirmed in photocatalysis experiments (**Fig. 7**).

To confirm the aforementioned results, we conducted density function theory (DFT) calculations. Work function (W_F) of the composite catalysts were calculated to reveal details of the charge transfer on its surface. As shown in **Fig. 4** (d), the W_F of the MoP (0 0 1) in the MoP (0 0 1)@MoO₃ (0 1 0), as obtained from aligning the Fermi level relative to the vacuum level, was 6.16 eV; the W_F of the MoO₃ (0 1 0) was found to be 5.52 eV. As reported previously, electrons can flow from a surface with a lower W_F to a surface with a higher W_F [**54**]. Under the irradiation, the electrons will move to the CB of the MoO3-x to form the superoxide radicals and take part in the reaction. Meanwhile, the MoP will act as the "oxygen evolution cocatalyst" on the VB and will produce the oxygen directly. as displayed in **Fig. S14**. The photocatalytic performance analysis and DFT calculation collectively



reveal that the MoP functions as a "oxygen evolution cocatalyst" in the photocatalytic oxidation of benzyl alcohol.

Fig. 5 (a) Top view of a 9×6 unit of the MoO₃ (010) surface; (b) top view of a 6×4 unit of the MoP (001) surface; (c) heterostructure of the MoP@MoO₃ calculated by the DFT method; (d) charge density difference of the MoP@MoO_{3-x} heterostructure; calculated band structures of the as prepared catalysts (e) MoO₃, (f) MoP, (g) MoP@MoO_{3-x}, where the Fermi level was set to zero.

To better characterize the electronic structures of the composite catalysts, top views of the (010) and (001) surfaces of MoO_3 and MoP are illustrated in **Fig. 5** (a) and (b), respectively. In order to build a DFT calculation model of a $MoP@MoO_3$ heterojunction, we selected a large

vacuum space of 19.607 Å in the x direction and 11.265 Å in the y direction of MoO₃ to evaluate the influence of the interaction between the two materials. After the geometry optimization, the vacuum space of 19.468 Å in the x direction and 11.240 Å in the y direction of MoP was calculated to optimize the electronic structure (Fig. 5 (c)). As displayed in Fig. 5 (d), the charge density difference of the MoP@ MoO_{3-x} heterostructure demonstrates the existence of an internal electric field between the MoO₃ and the MoP. Meanwhile, the electronic structure and total density of states (DOS) of MoO_3 and MoP are displayed in Fig. 5 (e) and (f), respectively. In the case of MoO_3 , the bandgap was calculated to be 2.93 eV (Fig. 5 (e)), in agreement with the findings obtained by the VB XPS spectra and Mott-Schottky spectra (Fig. 4 (c)). In addition, the electronic structure and total DOS reveal that the MoP exhibits metallic properties. As displayed in Fig. 5 (f), the metallic character arises because of the nonzero DOS across the Fermi level. The d orbital of the Mo, in particular, is partially occupied by the Fermi level, which will result in it accepting more electrons. The DOS of the $MoP@MoO_{3-x}$ (Fig. 5 (g)) shows that the DOS also passes through the Fermi level, indicating that the composite catalyst exhibits metallic character. On the basis of these results, we conclude that, the MoP will act as the "oxygen evolution cocatalyst". So, the photogenerated electrons will move to the CB of MoO_{3-x} , resulting in the formation of superoxide radicals. Meanwhile, the holes left on the VB will transfer to the MoP particles and take part in the oxygen evolution. Meanwhile, the superoxide radicals will take part in the

photocatalytic oxidation of benzyl alcohol, resulting in the enhancement of electron–hole transfer efficiency. However, the DFT calculation results also indicate that oxygen atoms near the "phosphorus pot" of MoP will offer additional active sites on the surface of MoO₃, resulting in the formation of P–O bonds within the MoP@MoO_{3–x} electronic structure (**Fig. 3** (d)).



Fig. 6 (a) Transient photocurrent response of the as-synthesized catalysts; (b) PL spectra of the as-synthesized catalysts; (c) DMPO spin-trapping ESR spectra of the as-synthesized catalysts for $\cdot O-2$ (under simulated solar light irradiation); (d) EIS spectrum of the as-synthesized catalysts.

The highly rate of the transfer and separation of electron–hole pairs during a photocatalytic reaction will strongly influence the performance of the photocatalyst. Hence, we conducted photocurrent and photoluminescence (PL) analyses to characterize the separation rate of the generated charge carriers (electron-hole pairs) [55]. As displayed in Fig. 6 (a), twenty light on-off cycles were applied and a fast photocurrent response was observed, revealing good charge transfer characteristics. The MoP@MoO_{3-x}-3 composite catalyst displayed the highest photocurrent intensity, indicating that it exhibits the best charge transfer efficiency among the as-prepared samples [56]. The PL spectra of the as-synthesized catalysts are shown in Fig. 6 (b). The MoP@MoO_{3-x}-3 shows much weaker PL emission intensity than the other photocatalysts, indicating that it exhibits the best separation rate of electron-hole pairs, consistent with its photocatalytic performance (Fig. 7 (a)-(c)).

To detect the signal of $\cdot O$ - 2 during the photocatalytic reaction, ESR spin-trap spectra were acquired using DMPO as a trapping agent (**Fig. 6** (c)). Characteristic peaks of the DMPO- $\cdot O$ - 2 species are clearly obtained under simulated solar-light irradiation, revealing the formation of $\cdot O$ - 2. Moreover, the spectrum of MoP@MoO_{3-x}-3 displays stronger $\cdot O$ - 2 signals than the spectrum of the pristine MoO₃ nanowires, revealing that many more $\cdot O$ - 2 radicals formed over the MoP@MoO_{3-x}-3 surface than over the MoO₃ surface.

EIS analysis (**Fig. 6** (d)) was also conducted to confirm the aforementioned results. The MoP@ MoO_{3-x} -3 nanowires display the smallest semicircle radius among the as synthesized catalysts. A smaller semicircle radius indicates a lower resistance and faster electron transfer ability during the catalytic reaction [**57**].

As displayed in Supplementary **Fig. S13**, the contact angles of the MoO₃ nanowires and the MoP@MoO_{3-x}-3 nanowires are 87.2° and 74.5° , respectively. The smaller contact angle of the MoP@MoO_{3-x}-3 nanowires indicates better wettability, which should enable easier contact between the substrate molecules and the catalysts, resulting in enhancement of the selective photocatalytic oxidation of benzyl alcohol. A possible mechanism based on these results and those previously discussed (**Fig. 3-6**) is displayed in **Fig. S14**.

3.3. Selective photocatalytic activity performance



Fig. 7 (a) Catalytic performance of the as-synthesized catalysts; (b) benzaldehyde conversion and selectivity of the MoP@MoO_{3-x}-3 as a function of time; (c) cycle performance of the MoP@MoO_{3-x}-3.

Fig. 7 (a) depicts the catalytic benzaldehyde conversion and selectivity performance over various samples under simulated solar-light irradiation. The MoO_3 nanowires function as a catalyst for the benzaldehyde conversion, giving conversion and selectivity rates of 2% and 8%, respectively, within 12 h. Meanwhile, the pristine MoP particles displayed only a conversion and

selectivity rates of 0.7% and 4.9%, respectively. However, when MoP particles were assembled on the surface of the MoO₃ nanowires, the photocatalytic performance of the resulting MoP@MoO_{3-x} composite catalysts was clearly enhanced, with MoP@MoO_{3-x}-3 exhibiting conversion and selectivity rates of 55% and 67%, respectively, within 12 h (**Fig. 7** (b)). Meanwhile, a transformation of benzyl alcohol into benzaldehyde estimated quantum yield was calculated as 1.33% at 450 nm (Supporting Information), indicating a good performance transformation of benzyl alcohol into benzyl alcohol with various catalysts had been listed. According to the previously research, the powerful oxidation capability will result in the formation of benzoic acid (**Table S3**).

To confirm the mechanism of selective photocatalytic activity, we conducted radical (\cdot OH, \cdot O- 2, and h⁺) trapping experiments. Prior to the trapping tests, trapping agents (t-BuOH (1 mM) for \cdot OH, benzoquinone (1 mM) for $\cdot O-2$, and KI (1 mM) for h⁺) were added. The radical trapping data are displayed in Fig. S15. The $\cdot O$ - 2 clearly plays a critical role in the reaction. Although MoP@MoO_{3-x}-4 has a greater mass loading of MoP particles than MoP@MoO_{3-x}-3, it exhibits a lower a conversion rate of 42% and a lower selectivity rate of 30%; thus, the mass ratio of the MoP in the influences composites strongly their photocatalytic performance. Importantly, the selectivity of MoP@MoO_{3-x}-3 toward benzaldehyde was 67%—much higher than that of other samples—indicating that the MoP also strongly influences the reaction selectivity. After three cycles involving recovery by centrifugation, MoP@MoO_{3-x}-3 retained its photocatalytic activity and selectivity (**Fig. 7** (c)). In addition, the lack of changes in the XRD patterns and the chemical states of the cycled catalysts indicates good structural and photocatalytic stability (**Fig. S16** and **Fig. S17**). We also conducted selective photocatalytic measurements with purging of O₂ and N₂ (**Fig. S18**). The selective photocatalytic activity performance of MoP@MoO_{3-x}-3 decreased substantially with the purging of N₂, indicating the importance of O₂ (formation of \cdot O- 2) during the reaction.

On the basis of the aforementioned results, we deduced a mechanism for the selective transformation of benzyl alcohol to benzaldehyde over the MoP@MoO_{3-x}-3 composite catalyst. As obtained from **Fig. S4**, the oxygen will be produced on the VB. Considering the DFT calculation together (**Fig. 5** (d)), MoO₃ is positive and MoP is negative. As a result, the MoP will act as the "oxygen evolution cocatalyst". So, the photogenerated electrons will move to the CB of MoO_{3-x}, resulting in the formation of superoxide radicals. Meanwhile, the holes left on the VB will transfer to the MoP particles and take part in the photocatalytic oxidation of benzyl alcohol, resulting in the selective transformation of benzyl alcohol to benzaldehyde.

4. Conclusions

MoP@MoO_{3-x} composite catalysts with a heterojunction structure were prepared by assembling MoP particles onto the surface of MoO₃ nanowires as a novel catalyst for the selective transformation of benzyl alcohol to benzaldehyde. The synthesis method enabled the MoP loading percentage to be tuned via variation of the mass ratio of NaH₂PO₂ used during the phosphorization process. This heterojunction architecture with close contact between the two components provides an abundance of reactive sites and enhances the transfer and separation efficiency of electron-hole pairs. Consequently, the MoP@MoO_{3-x} heterostructure displays substantial photocatalytic activity and stability for the selective transformation of benzyl alcohol to benzaldehyde.

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Journal Pre-proofs



Research Highlights

- MoP particles were uniformly dispersed on the MoO₃ nanowires by the phosphorization method.
- Various percentage of MoP particles loading was regulated by different phosphorous precursor.
- Enhanced selective photocatalytic oxidation of benzyl alcohol to benzaldehyde performance was achieved.
- Enhanced selective photocatalytic performance can be owing to the synergistic effect between MoP particles and MoO₃ nanowires.

Originality and Novelty



The selective oxidation of small molecules to high-value-added products is regarded as a promising approach to alleviating the worldwide energy crisis. In this work, heterogenous non-noble-metal molybdenum(III) phosphide (MoP) catalysts were anchored onto MoO_{3-x} nanowires ($MoP@MoO_{3-x}$) via a facile phosphorization method using various amounts of phosphorus precursor. Because of the combined attributes of the MoP and the MoO_{3-x} nanowires, the novel $MoP@MoO_{3-x}$ nanowire catalysts not only provide more active sites but also enhance electron–hole separation efficiency. The results show that the selective transformation of benzyl alcohol to benzaldehyde was achieved with 67% selectivity. A comprehensive study including field-emission transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, Brunauer–Emmett–Teller analysis, X-ray diffraction analysis, UV–vis diffuse reflectance spectrum, electron-spin resonance, photocurrent measurements, electrochemical

Journal Pre-proofs

impedance spectroscopy, and density functional theory (DFT) computations was conducted. The selective photocatalytic oxidation results and the DFT calculations indicate that the MoP particles anchored onto the MoO_{3-x} substrate display an important role in enhancing the selective photocatalytic oxidation of benzyl alcohol.