Mesoporous titania-based H$_3$PW$_{12}$O$_{40}$ composite by a block copolymer surfactant-assisted templating route: Preparation, characterization, and heterogeneous photocatalytic properties

Jinhuan Li, Wanli Kang, Xia Yang, Xiaodian Yu, Leilei Guo, Yihang Guo, Hongbo Fang, Shaodong Zhang

Abstract

Mesoporous H$_3$PW$_{12}$O$_{40}$/TiO$_2$ composite with H$_3$PW$_{12}$O$_{40}$ loading from 3.2 to 16.6% was prepared by the combination of sol–gel chemistry, templated self-assembly, and solvothermal treatment in the presence of a triblock copolymer surfactant. At relatively low solvothermal treatment temperature (80 to 120 °C), as-prepared composite exhibited an anatase phase structure. Bulk and surface sensitive probe testing results indicated that the primary Keggin structure remained intact after formation of the composite, and strong interaction between the Keggin unit and TiO$_2$ network existed in the composite. Nitrogen gas porosimetry, low-angle XRD, and TEM testing results suggested the composite exhibited three-dimensionally interconnected pore structure with pore diameter of 3.3–4.0 nm, BET surface area of 151.5–195.1 m$^2$ g$^{-1}$, and pore volume of 0.17–0.26 cm$^3$ g$^{-1}$. The composite was used as a heterogeneous photocatalyst to degradation of dyes with azoic (methyl orange), heteropolyaromatic (methylene blue), triarylmethane (crystal violet), and fluorescent (rhodamine B) structures; at the same time, adsorption behaviors of dyes on mesoporous H$_3$PW$_{12}$O$_{40}$/TiO$_2$ composite are tested. Finally, photodegradation pathway of dye crystal violet over mesoporous H$_3$PW$_{12}$O$_{40}$/TiO$_2$ was tentatively put forward based on the identified intermediates generated during the photocatalytic degradation process. The results shown in Fig. 9 demonstrate that PW12/TiO2 with higher H$_3$PW$_{12}$O$_{40}$ loading has higher photocatalytic activity.

1. Introduction

Titania-based nanocomposite materials are expected to have a significant impact on the field of photocatalysis, especially for environmental-related applications. Purpose for development of this kind of composite materials is to improve the photocatalytic efficiency of TiO$_2$. As a photocatalyst, TiO$_2$ exhibits excellent ability in photocatalyzing the degradation of various organic contaminants, at the same time, it is chemically and photocatalytically stable [1–8]. However, low quantum efficiency and high bandgap of TiO$_2$ limit its photocatalytic activity [9]. So far, many attempts have been made to further improve the photocatalytic activity of TiO$_2$, among which utilizing doping metals, nonmetals, and other semiconductors with wide or narrow bandgap, reducing the size and changing the morphology of TiO$_2$, and adding hole scavengers are the most prevalent means [10–13]. Thus the photocatalytic activity of TiO$_2$ was enhanced owing to the improved properties of TiO$_2$-based composite materials such as decreased bandgap, nanometer sizes, new surface compositions and structures, enhanced quantum efficiency, and high crystallinity.

Recently, polyoxometalates (POMs) have been applied to TiO$_2$ photocatalytic systems as electron scavengers to retard the fast charge recombination with h$^+$ in TiO$_2$ and, consequently, enhance the photocatalytic redox processes [14–19]. In some of the above POM–TiO$_2$ systems, POMs (e.g. PW$_{12}$O$_{40}^-$, SiW$_{12}$O$_{40}^-$, or W$_{18}$O$_{49}^+$) were in the homogeneous phases thereby dissolved in the reaction systems, thus separation them for recycling applications is very difficult [20]. In other heterogeneous POM–TiO$_2$ systems, Keggin-type POMs used were in lacunary ([X$^m$W$_{11}$O$_{39}$]$^{12−m}$, X$^m$=Si, Ge, or P) or substituted ([M(H$_2$O)PW$_{11}$O$_{39}$]$^{13−}$, M=Mo, or W) structure, and their photocatalytic activity is lower than that of saturated ones [21]. Therefore, these POM–TiO$_2$ systems only showed UV-light (rather than visible-light) photocatalytic activity towards degradation of aqueous organic pollutants. Furthermore, BET surface areas and porosities of these...
POM–TiO₂ composites need to be improved further [22]. More recently, we have prepared micro-meso bimodal porous TiO₂-based POM nanocomposites by combining sol–gel chemistry and solvothermal treatment, here POM selected was saturated Keggin or Wells–Dawson unit. The composites exhibited visible-light photocatalytic activity towards degradation of an aqueous parathion-methyl. This high photocatalytic activity is explained by the synergistic effect between the POM and TiO₂ [23–27], which retarded fast recombination of charge-carriers. The disadvantages of this kind of materials is their uneven distributed pore sizes and aggregation among particles, which were resulted from the preparation route used [28]. The results motivated us to further improve the photocatalytic activity of this POM–TiO₂ system by developing a new preparation method since the photocatalytic activity is highly sensitive to the synthetic route used in their preparation, which results in the materials with different surface physicochemical properties, phase structures, surface chemical compositions, and morphology. All of these factors control the activity of the photocatalysts.

In the present work, we demonstrate a new route to prepare H₃PW₁₂O₄₀/TiO₂ composite with well-distributed three-dimensionally (3D) interconnected mesostructure. The preparation is performed by the combination of sol–gel chemistry, templated self-assembly, and solvothermal treatment in the presence of a triblock copolymer surfactant. As-prepared materials are thoroughly characterized by low- and wide-angle XRD, XPS, Raman scattering spectroscopy, UV–vis/DRS, nitrogen porosimetry, and TEM. Subsequently, their heterogenous photocatalytic activity is evaluated by degradation of dyes with different chemical structures including azoic (methyl orange), heteropolyaromatic (methylene blue), triarylmethane (crystal violet), and fluorescent (rhodamine B). For comparison, pure TiO₂ and surfactant-free H₃PW₁₂O₄₀/TiO₂ are also tested. In addition, adsorption behaviors of dyes on mesoporous H₃PW₁₂O₄₀/TiO₂ composite are tested and discussed. Finally, photodegradation pathway of dye crystal violet over mesoporous H₃PW₁₂O₄₀/TiO₂ was tentatively put forward based on the identified intermediates produced during dye photocatalytic process.

2. Materials and methods

2.1. Reagents and materials

Titanium tetraisopropoxide (TTIP, Ti(OC₃H₇)₄, 98%) was purchased from J&K Chemical Inc. Pluronic P123 (MW 5800, EO₁₅PO₈EO₁₅, E₀ = ethylene oxide, PO = propylene oxide) was purchased from Aldrich. The following reagents were all AR grade and purchased from Beijing, China: methylene blue (MB, C₁₆H₁₈ClN₃S·3H₂O, pH = 7.00 ± 0.05) was purchased from Aldrich. The following reagents were all AR grade and purchased from Beijing, China: methylene blue (MB, C₁₆H₁₈ClN₃S·3H₂O, pH = 7.00 ± 0.05) was purchased from Aldrich. All reagents used were purchased without further purification. Double distilled water was used throughout the experimental procedures.

2.2. Catalyst preparation

A typical method of preparation of mesoporous H₃PW₁₂O₄₀/TiO₂ composite is described below. P123 was dissolved with i-ProH under vigorous stirring. After 1 h of stirring, TTIP was added dropwise to P123/i-ProH solution. H₃PW₁₂O₄₀ was dissolved with water and i-ProH, and then the solution was ultrasonicated for 10 min to obtain good dispersion of H₃PW₁₂O₄₀ in water/i-ProH solution. The H₃PW₁₂O₄₀ solution was added dropwise into P123/TTIP/i-ProH solution under vigorous stirring. The molar ratio of P123:TTIP:i-ProH:H₂O was controlled at 1:78:1673:194. The resulting mixture was adjusted to pH 2.0 ± 0.5 by addition of 12 mol L⁻¹ HCl, and then it was stirred at room temperature till the formation of transparent gel. The gel was transferred into a Teflon-lined stainless steel autoclave and heated to 100 °C with a heating rate of 2 °C min⁻¹, and the temperature was kept constant for 48 h. The resulting hydrogel was dehydrated slowly at 45 °C in vacuum for 24 h, and then it was suffered following thermal treatment in vacuum: 12 h at 60 °C, 2 h at 80 °C, 2 h at 100 °C, and 0.5 h at 120 °C. The product was refluxed in boiling absolute ethanol (30 mL) for 3 h, and the procedure was repeated three times. Finally, the product was calcined at 400 °C with a heating rate of 1 °C min⁻¹ till white power was formed. The final product are denoted as PW₁₂/TiO₂-x, where x is H₃PW₁₂O₄₀ loading (wt.% ) in the composite. Herein, x = 3.2, 8.3, 13.4, and 16.6 (wt.% ), respectively, with different H₃PW₁₂O₄₀ adding amounts (0.02, 0.04, 0.08, 0.12, and 0.2 mmol), which was determined by a Leeman Prodigy Spec inductively coupled plasma atomic emission spectrometer (ICP–AES).

2.3. Catalyst characterization

UV–vis diffuse reflectance spectra (UV–vis/DRS) of the composites were recorded on a Cary 500 UV–vis–NIR spectrophotometer. Low- and wide-angle X-ray diffraction (XRD) patterns of the composites were recorded on a Rigaku D/max-3c X-ray diffractometer (Cu Kα radiation, λ = 0.154 nm). Transmission electron microscopy (TEM) micrographs were obtained by a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a VG-ADG 400 instrument with Mg Kα-ADES source at a residual gas pressure of below 10⁻⁶ Pa. Raman scattering spectra were recorded on a Jobin-Yvon HR 800 instrument with an Ar⁺ laser source of 488 nm wavelength in a macroscopic configuration. Nitrogen porosimetry was performed on a Micromeritics ASAP 2010 instrument. Surface areas were calculated using the BET equation. Pore size distributions were calculated using the BJH model based on nitrogen desorption isotherm (the samples were outgassed under vacuum at 120 °C overnight).

2.4. Photocatalytic test

The photoreactor was designed with an internal light source (125 W high-pressure mercury lamp with a main emission wavelength of 313 nm) surrounded by a water-cooling quartz jacket. The suspension containing the solid catalyst (0.135 g) and an aqueous solution of dye MO, CV, RB (25 mg L⁻¹, 90 mL), or MB (50 mg L⁻¹, 90 mL) surrounded by a water-cooling quartz jacket. The suspension was ultrasonicated for 10 min and then stirred in the dark for 30 min to obtain a good dispersion, and thus adsorption–desorption equilibrium between dye molecules on the catalyst surface was established. The acidity of the suspension was neutral, and the system was open to air. Decreases of the concentrations of dyes were analyzed by a Cary 500 UV–vis–NIR spectrophotometer at their maximum wavelength (λmax, Table 1). At given intervals of illumination, fixed amounts of reaction solution were taken out, centrifuged and filtrated. Finally, the filtrates were analyzed. Intermediates generated during the process of CV degradation were identified by an Applied Biosystem liquid chromatography (C₈ column)+Q-Trap triple quadrupole mass spectrometer (LC-MS) equipped with electrospray ionization source. Other intermediates and final products were analyzed by a DX-300 ion chromatography (IC) equipped with a conductivity detector. CS12 cation column was used for analysis of NH₄⁺ ion; AS4A anion column was used for analysis of NO₃⁻ ions; and ICE-ASI anion column was used for analysis of organic acids.

3. Results and discussion

3.1. Catalyst preparation

Template synthesis is a useful method for controlling the microstructure of a material, which often results in a material with uniform pore and high porosity. Herein, mesoporous PW₁₂/TiO₂ composite is obtained by combining sol–gel chemistry and solvothermal treatment in the presence of amphiphilic block copolymer (P123) as a soft template. After solvent evaporation, the copolymer micelles
are trapped within PW\textsubscript{12}/Ti(OTi)\textsubscript{n}(OH)\textsubscript{4−n} (n = 0−4) network formed during the process of hydrolysis of TTIP in the presence of Keggin unit; the network is further fastened by successive thermal treatment in the range of 45 to 120 °C, which ensures strong combination of the Keggin unit and titania network; finally, the copolymer micelles are eliminated by boiling ethanol extraction, resulting in PW\textsubscript{12}/TiO\textsubscript{2} composite with mesoporosity (see Section 3.2.2).

Purposes of selecting nonionic surfactant P123 as a structure directing reagent are based on the following reasons. On the one hand, preparation of PW\textsubscript{12}/TiO\textsubscript{2} should perform at acidic condition so that the decomposition of the Keggin unit can be avoided [29]. On the other hand, the interaction between the surfactant and inorganic network should not be too strong, thus the mesostructure assembly can take place and the surfactant can be removed easily (e.g. ethanol extraction) without damage to the integrity of the channel walls and the Keggin structure (H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} loses all acidic protons at 465 °C [30]). Additionally, in the PW\textsubscript{12}/TiO\textsubscript{2} composite, W\textsuperscript{6+} ion (1.70, 0.060 nm) can easily substitute for Ti\textsuperscript{4+} ion (1.54, 0.0605 nm) because of the similarity in ionic radius of Ti\textsuperscript{4+} and W\textsuperscript{6+}, and the work reported by other groups also proved the same [31,32]. The other hand, the interaction between the surfactant and inorganic network should not be too strong, thus the mesostructure assembly can take place and the surfactant can be removed easily (e.g. ethanol extraction) without damage to the integrity of the channel walls and the Keggin structure (H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} loses all acidic protons at 465 °C [30]). Additionally, in the PW\textsubscript{12}/TiO\textsubscript{2} composite, W\textsuperscript{6+} ion (1.70, 0.060 nm) can easily substitute for Ti\textsuperscript{4+} ion (1.54, 0.0605 nm) because of the similarity in electronegativity and ion radius for both of ions. Therefore, the Keggin unit may interact with TiO\textsubscript{2} support through W−O−Ti bonds, which has been verified by XPS results (see Section 3.2.1). The strong interaction is expected to improve the catalytic stability of the composite catalyst. At the same time, H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} loading is controllable via changing starting H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} amount. In fact, leaching of H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} can easily happen for the supported POM-containing composite catalysts prepared by post-synthesis grafting method. This is due to the strong Brønsted acid property of H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}, and it is readily soluble in many polar solvents. Thus most of the incorporated H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} may lose during the catalytic process if the reaction performs in polar solvents.

### 3.2. Catalyst characterization

#### 3.2.1. Structural information

#### Phase structure. Wide-angle XRD patterns of PW\textsubscript{12}/TiO\textsubscript{2} obtained at different solvothermal treatment temperatures (80, 100, and 120 °C) are shown in Fig. 1. The results indicate the composites are mainly in an anatase phase with 2θ at 25.2, 37.8, 48.0, 55.1, and 62.6°, respectively (JCPDS no. 21-1272), regardless of solvothermal treatment temperatures applied. The weak peak with 2θ at 30.8° (121) is assigned to a brookite phase. Formation of some brookite phase in the composites may be induced by the preparation method used here.

#### Evolution of surface species. The nature of the surface species of as-prepared composites is explored by surface spectroscopy (XPS). Evaluation of the surface tungsten, oxygen, and titanium environments are described below (Fig. 2).

Fig. 2a shows the Ti2p XPS lines of pure TiO\textsubscript{2}, and PW\textsubscript{12}/TiO\textsubscript{2} composites. The reference TiO\textsubscript{2} sample exhibits spin-orbit lines Ti2p\textsubscript{3/2} and Ti2p\textsubscript{1/2} at 458.7 and 464.4 eV, respectively, characteristic of the Ti (IV) oxidation state. After introduction of the Keggin unit into TiO\textsubscript{2} network, both lines become asymmetry together with shifts of the peaks towards lower binding energies (BES, Table 2). This behavior implies the increasing presence of intermediate formal oxidation states of Ti (<IV), except for metallic titanium.

Fig. 2b demonstrates the O1s XPS lines of pure TiO\textsubscript{2}, starting H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}, and PW\textsubscript{12}/TiO\textsubscript{2} composites. The O1s XPS line of starting H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} shows one peak at 529.8 eV [denoted as O1s(1)], originating from lattice oxygen species of anatase TiO\textsubscript{2} [33]. The O1s XPS line of starting H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} displays one peak at 531.6 eV, attributed to lattice oxygen species of the Keggin unit [denoted as O1s(2)] [34]. After incorporation of the Keggin unit into TiO\textsubscript{2} network, both O1s(1) and O1s(2) species are found, and the peak intensity of O1s(2) species increases with H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} loading. As for PW\textsubscript{12}/TiO\textsubscript{2} − 16.6 composite, a new oxygen species is observed with BE of 533.5 eV, assigned to adsorbed oxygen species at the surface of the composite [denoted as O1s(3)] [35]. Existence of the adsorbed oxygen species at the surface of the composite is due to oxygen vacancies originated from substitution of W\textsuperscript{6+} ion for Ti\textsuperscript{4+} ion in the composite, which is a very active group and can easily combined with other atoms or groups to become stable [36].

Fig. 2c shows W4f XPS lines of the starting H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}, and PW\textsubscript{12}/TiO\textsubscript{2} composites. The resulting W4f XPS are characteristic of the highest oxidation state of tungsten [W (VI)] [37]. The W4f XPS lines of the starting H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} show two peaks at 35.8 and 37.8 eV, respectively [denoted as W (VI)]. After incorporation of the Keggin unit into TiO\textsubscript{2} network, BEs of W4f shift towards lower values. Moreover, higher POM loading results in lower BE value (Table 2). This result implies that the increasing presence of intermediate formal oxidation states of W (<VI) at the surface of the composite except for W (VI).

Based on the above XPS results and similarity of electronegativity and ionic radius of Ti\textsuperscript{4+} and W\textsuperscript{6+}, and the work reported by other groups [38,39], we tentatively infer that the terminal W=O groups within the Keggin unit coordinate to the surface Ti−OH groups within TiO\textsubscript{2} network via Ti−O−W bonds and form (≡Ti−OH\textsubscript{n})\textsubscript{n}−PW\textsubscript{12}O\textsubscript{40} species at the interface of the composites.

#### Chemical structure. Fig. 3 shows Raman spectra of pure TiO\textsubscript{2}, starting H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}, and PW\textsubscript{12}/TiO\textsubscript{2} composites with different H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} loadings. A well-resolved Raman scattering peak of anatase TiO\textsubscript{2} is
observed at 141.2 cm\(^{-1}\) \((E_g)\) for pure TiO\(_2\). Moreover, other scattering peaks at 390.2 \((B_{1g})\), 516.6 \((A_{1g})\), and 637.2 cm\(^{-1}\) \((E_g)\) are also present, indicating the anatase phase of as-prepared TiO\(_2\) [40]. After incorporation of the Keggin unit into TiO\(_2\) framework, the sharpest and strongest scattering peak \((E_g)\) became broader and weaker and positively shifted by 26.7, 30.6, and 32.0 cm\(^{-1}\), respectively, with H\(_3\)PW\(_{12}\)O\(_{40}\) loading of 8.3, 13.4 and 16.6\% (Insert of Fig. 3). The result suggests increasing crystalline defects within the framework [41], which could be ascribed to the distortion of anatase crystalline lattice induced by the Keggin unit. Additionally, some brookite phase in the composite may also lead to this crystalline defect. The other information derived from Raman spectra is an evidence to confirm the structure integrity of the Keggin unit in the composites. The Raman scattering peaks found in the range of 1100–900 cm\(^{-1}\) are assigned to the starting Keggin unit, which correspond to stretching vibrations of P–O bonds of the PO\(_4\) sites (1009.5 cm\(^{-1}\)), W=O bonds (993.9 cm\(^{-1}\)), and W–O–W bonds (912.4 cm\(^{-1}\)) of the Keggin unit, respectively [42]. After incorporation of H\(_3\)PW\(_{12}\)O\(_{40}\) into anatase TiO\(_2\) crystal lattice, the scattering peaks corresponding to W–O–W, W=O, and P–O bond vibrations are broadened, therefore, only one wide peak is observed in the range of 957.8 to 994.5 cm\(^{-1}\). The changes are due to strong interactions between the Keggin unit and anatase TiO\(_2\) framework, which resulted in the decrease of the symmetry of either TiO\(_2\) or the Keggin unit.

### 3.2.2. Mesostructure, morphology, and porosity

#### Mesostructure

Low-angle XRD patterns of as-prepared PW\(_{12}\)/TiO\(_2\) obtained at 100 °C solvothermal treatment temperature is shown in Fig. 4. In the range of 0.90–0.96°, one reflection peak (100) is detected.

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ti2p 3/2</th>
<th>Ti2p 1/2</th>
<th>O1s (1)</th>
<th>O1s (2)</th>
<th>O1s (3)</th>
<th>W4f 7/2</th>
<th>W4f 5/2</th>
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</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>458.7</td>
<td>464.4</td>
<td>529.8</td>
<td>531.5</td>
<td>–</td>
<td>35.8</td>
<td>37.8</td>
</tr>
<tr>
<td>H(<em>3)PW(</em>{12})O(_{40})</td>
<td>–</td>
<td>–</td>
<td>531.6</td>
<td>–</td>
<td>–</td>
<td>35.3</td>
<td>37.0</td>
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<td>458.6</td>
<td>464.3</td>
<td>529.9</td>
<td>531.4</td>
<td>–</td>
<td>35.3</td>
<td>37.0</td>
</tr>
<tr>
<td>PW(_{12})/TiO(_2)-16.6</td>
<td>458.4</td>
<td>464.2</td>
<td>529.8</td>
<td>531.8</td>
<td>533.2</td>
<td>34.9</td>
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</table>

Fig. 2. XPS survey spectra for the pure TiO\(_2\), starting H\(_3\)PW\(_{12}\)O\(_{40}\), and PW\(_{12}\)/TiO\(_2\) composites in the (a) Ti2p; (b) O1s; and (c) W4f binding energy regions.

Fig. 3. Raman scattering spectra of pure TiO\(_2\), starting H\(_3\)PW\(_{12}\)O\(_{40}\), and PW\(_{12}\)/TiO\(_2\) composites.

Fig. 4. Low-angle XRD patterns of PW\(_{12}\)/TiO\(_2\) composites.
for the two tested samples. The result is in good agreement with the materials prepared by using a neutral template (P123), indicative of a sponge like unordered mesoporous structure of the composite [43,44].

**Morphology.** The morphology of the composites is studied by TEM (Fig. 5). TEM images reveal that as-prepared PW12/TiO2 composites are random and lack discernible long-range order in the pore arrangement with 3D interconnected or sponge-like pore-network structure; and moreover, porosity increased with H3PW12O40 loadings. It is reported that this interconnected pore-network structure would be much more attractive than a 2D hexagonal phase for applications in photocatalysis requiring diffusion of species into and out of the pore network [45]. Formation of this morphology is associated with the role of triblock copolymer surfactant; in addition, the preparation route applied is different from the standard method for ordered materials [46].

**Nitrogen gas porosimetry.** The mesoporosity of as-prepared PW12/TiO2 is characterized by nitrogen gas porosimetry, and the results are shown in Fig. 6 and Table 3. All of the isotherms for the tested materials are Type IV with H2-type hysteresis (Fig. 6a and c), which is an indicator of 3D interconnected porous structure of the samples [43,44]. As increasing H3PW12O40 loading from 0 to 16.6%, the onset of the capillary condensation step occurs at lower relative pressures, which suggests pore shrinkage to some extent with H3PW12O40 loading increasing. The conclusion is supported by the pore size distribution profiles (Fig. 6b) and the calculated pore diameters according to BJH method on the desorption branch of the N2 sorption isotherms (Table 3). After the steps including hydrolysis, polycondensation, solvothermal treatment, dehydration, and thermal treatment, the Keggin unit is entrapped by the TiO2 network, resulting in PW12/TiO2 composite with smaller pore size with respect to pure TiO2. Fig. 6b also indicates that the pores of the composites are well-distributed. Additionally, increasing H3PW12O40 loading from 0 to 16.6%, BET surface area of the composite increased from 110.8 to 195.1 m2 g⁻¹, whereas the pore volume decrease from 0.26 to 0.18 cm³ g⁻¹ (Table 3).

Fig. 6b and d demonstrate nitrogen gas sorption isotherms and pore size distribution profiles of PW12/TiO2 composites obtained at different molar ratios of P123 and TiTP (0, 1:1560, 1:78 and 1:52). Together with data summarized in Table 3 it is found that the influence of P123 adding amount on BET surface area, pore volume, and pore diameter of the composites is improved.

### 3.2.3. Optical absorption properties

The optical absorption properties of as-prepared PW12/TiO2 with different PW12 loadings (8.3–16.6%) are evaluated by UV-vis/DRS spectra (Fig. 7). Compared with pure TiO2, a slight blueshift is observed after formation of PW12/TiO2 composites. Moreover, the absorption threshold onset gradually shifts to lower wavelength with increasing PW12 loading from 8.3 to 16.6%. Nevertheless, all PW12/TiO2 exhibited strong absorption in the range of 200 to 400 nm. For the PW12/TiO2 composites, both W5d and Ti3d orbital contribute to the CB band, which results in a slight difference of bandgap between pure TiO2 and PW12/TiO2 composite. Additionally, no separated absorption peak originated from the starting PW12 was found, implying homogenous dispersion of the Keggin unit throughout the composite.

### 3.3. Photocatalytic test

**As-prepared novel PW12/TiO2 nanocomposite with unique surface physicochemical properties and morphology has the potential for the application in the photocatalytic degradation of organic pollutants.** Herein, the heterogeneous photocatalytic activity of mesoporous PW12/TiO2 composite is evaluated via UV-light photocatalytic degradation of aqueous textile dyes including MO, MB, RB, and CV.

#### 3.3.1. Adsorption of dyes on mesoporous TiO2 or PW12/TiO2 composites

It has been reported that the dye molecules adsorbed on TiO2 nanoparticles is excited by absorbing light energy transferring an electron to the conduction band of the TiO2. The process results in enhanced quantum efficiency thereby photocatalytic activity. The efficiency of the charge injection process is strongly dependent on the type of binding of dye molecule to the TiO2 [47]. This suggests that the surface-anchoring form of dye plays an important role in the photocatalytic activity. Therefore, investigation of dye adsorption on the PW12/TiO2 surface is the first step to understand its photocatalytic behaviors. Herein, four types of dyes with different chemical structures are chosen to test their adsorption behaviors on the PW12/TiO2 composites, and the results are shown in Fig. 8. Fig. 8a indicates that adsorption of dye MO molecule on the pure TiO2 or PW12/TiO2 composites with various H3PW12O40 loadings results in a redshift of λmax of MO (from 464 to 480 nm). Additionally, the adsorption ability of TiO2 to MO is stronger than that of PW12/TiO2 composites, which results in a significant decrease of MO concentration after adsorption for 30 min. However, decrease of MO concentration is insignificant after its adsorption on the PW12/TiO2 composites regardless of H3PW12O40 loading. In the cases of other three dyes (MB, RB, and CV), their adsorption behaviors on pure TiO2 and PW12/TiO2 composites are the same. That is, the adsorption process doesn’t shift the chromophore of MB, RB, or CV; dye adsorption on pure TiO2 is the weakest, while PW12/TiO2 composite with higher PW12 loading exhibits stronger adsorption ability to dye molecule (Fig. 8b-d).

![Fig. 5. TEM images of (a) pure TiO2; (b) PW12/TiO2-8.3; and (c) PW12/TiO2-16.6.](image-url)
The above results suggest that MO adsorption at the surface of pure TiO$_2$ or PW$_{12}$/TiO$_2$ composite results in chemical bond formation via interaction between the sulfonate groups (–SO$_3$H) of MO molecule and Ti (IV) ion of TiO$_2$ (chemisorption) [48]. The adsorption ability of TiO$_2$ to MO molecule decreases after incorporation of the Keggin unit. The results also suggest the dye CV, RB, or MB adsorption at the surface of pure TiO$_2$ or PW$_{12}$/TiO$_2$ is in physisorption via hydrogen bonding, which is formed by interacting of protons of the Keggin unit with nitrogen or oxygen atoms of dye molecules. Physisorption is mainly determined by the specific surface area of the catalysts, therefore, PW$_{12}$/TiO$_2$ composite with higher H$_3$PW$_{12}$O$_{40}$ loading exhibits higher adsorption ability to CV, RB, or MB molecule.

### 3.3.2. Photocatalytic degradation of dyes over mesoporous TiO$_2$ or PW$_{12}$/TiO$_2$ composite

At first, direct photolysis of dyes in the absence of catalyst is examined via UV-light irradiation of aqueous dye solutions. The results show that degradation of dye MO (25 mg L$^{-1}$) and CV reach to 83.1 and 96.8% respectively over PW$_{12}$/TiO$_2$ composite. The higher degradation efficiency of MO is mainly attributed to the higher adsorption ability, which facilitates the contact between dye molecule and catalyst surface. The results also indicate that the presence of PW$_{12}$ unit in the composite increases the charge separation efficiency, thus facilitating the photo-degradation of dyes. The photocatalytic activity of PW$_{12}$/TiO$_2$ composite is found to be superior to that of pure TiO$_2$, which is due to the synergistic effect of the Keggin unit and TiO$_2$ nanotubes. The PW$_{12}$/TiO$_2$ composite is found to be an efficient photocatalyst for the degradation of a wide range of organic dyes, making it a promising candidate for wastewater treatment applications.

### Table 3

<table>
<thead>
<tr>
<th>P123:TTIP molar ratio</th>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p$ (cm$^3$ g$^{-1}$)</th>
<th>$D_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PW$_{12}$/TiO$_2$-16.3</td>
<td>151.5</td>
<td>0.15</td>
<td>2.9</td>
</tr>
<tr>
<td>1:1560</td>
<td>PW$_{12}$/TiO$_2$-17.6</td>
<td>166.7</td>
<td>0.17</td>
<td>3.3</td>
</tr>
<tr>
<td>1:78</td>
<td>TiO$_2$</td>
<td>110.8</td>
<td>0.26</td>
<td>6.8</td>
</tr>
<tr>
<td>1:78</td>
<td>PW$_{12}$/TiO$_2$-8.3</td>
<td>158.9</td>
<td>0.21</td>
<td>4.0</td>
</tr>
<tr>
<td>1:78</td>
<td>PW$_{12}$/TiO$_2$-13.4</td>
<td>189.3</td>
<td>0.20</td>
<td>3.9</td>
</tr>
<tr>
<td>1:78</td>
<td>PW$_{12}$/TiO$_2$-16.6</td>
<td>195.1</td>
<td>0.18</td>
<td>3.3</td>
</tr>
<tr>
<td>1:52</td>
<td>PW$_{12}$/TiO$_2$-15.9</td>
<td>154.1</td>
<td>0.17</td>
<td>3.5</td>
</tr>
</tbody>
</table>

$^a$ BET surface area.  
$^b$ Pore volume.  
$^c$ Median pore diameter.
96.4%, respectively, after 90 min UV-light irradiation. As for dyes RB (25 mg L\(^{-1}\)) and MB (50 mg L\(^{-1}\)), their degradation is negligible after 120 min UV-light irradiation. However, significant degradation of dye is observed after UV-light irradiation of the suspension including TiO\(_2\), PW\(_{12}/\)TiO\(_2\), or H\(_3\)PW\(_{12}\)O\(_{40}/\)SBA-15 and aqueous dye solutions (Fig. 9).

From the results shown in Fig. 9 it is found that pure TiO\(_2\) or PW\(_{12}/\)TiO\(_2\) composites shows different degradation behaviors to dye MO compared with the other three tested dyes, then H\(_3\)PW\(_{12}\)O\(_{40}/\)SBA-15 shows only different adsorption behaviors to four dyes (Fig. 9f). Pure TiO\(_2\) demonstrates the highest UV-light photocatalytic activity to MO degradation, and total degradation of MO needs 20 min UV-light irradiation. In the cases of PW\(_{12}/\)TiO\(_2\) composites, the UV-light photocatalytic activity to MO degradation decrease with increasing H\(_3\)PW\(_{12}\)O\(_{40}\) loading (Fig. 9a). As for the other three model dyes, all tested PW\(_{12}/\)TiO\(_2\) composites show higher photocatalytic activity than that of pure TiO\(_2\); moreover, the photocatalytic activity increases with H\(_3\)PW\(_{12}\)O\(_{40}\) loading, e.g. complete decomposition of MB, CV, or RB needs ca. 20 min UV-light irradiation in the presence of PW\(_{12}/\)TiO\(_2\)-13.4 (Fig. 9b–d).

Photocatalytic activity of PW\(_{12}/\)TiO\(_2\)-16.6 composites obtained with different P123 and TTIP molar ratios (0, 1:1560, 1:156, 1:78 and 1:52) is also studied. From the results shown in Fig. 9e it is found that all tested PW\(_{12}/\)TiO\(_2\)-16.6 composites prepared in the presence of P123 show higher photocatalytic activity compared to surfactant-free PW\(_{12}/\)TiO\(_2\) sample. Moreover, PW\(_{12}/\)TiO\(_2\)-16.6 obtained with P123:TTIP molar ratio at 1:78 shows the highest photocatalytic activity towards RB degradation.

Photocatalytic activity of PW\(_{12}/\)TiO\(_2\)-16.6 composites prepared with different P123 and TTIP molar ratios (0, 1:1560, 1:156, 1:78 and 1:52) is also studied. From the results shown in Fig. 9e it is found that all tested PW\(_{12}/\)TiO\(_2\)-16.6 composites prepared in the presence of P123 show higher photocatalytic activity compared to surfactant-free PW\(_{12}/\)TiO\(_2\) sample. Moreover, PW\(_{12}/\)TiO\(_2\)-16.6 obtained with P123:TTIP molar ratio at 1:78 shows the highest photocatalytic activity towards RB degradation.

Based on the above catalytic data and physicochemical properties of as-prepared mesoporous PW\(_{12}/\)TiO\(_2\) composites, their photocatalytic behaviors are explained below. Considering little influence of introduction of the Keggin unit on the optical absorption property of anatase TiO\(_2\), the influence of the optical absorption property on the photocatalytic activity of PW\(_{12}/\)TiO\(_2\) is excluded in this discussion.

Firstly, adsorption behaviors of the catalyst to dye molecules play the most important role in the photocatalytic activity since the photocatalytic reaction performs at the surface of the catalyst. Pure TiO\(_2\) shows the strongest adsorption to dye MO molecule among all tested catalysts, therefore, it exhibits the highest photocatalytic activity to MO degradation. As for the other three dyes including MB, CV, and RB, the adsorption on the PW\(_{12}/\)TiO\(_2\) composites increases with H\(_3\)PW\(_{12}\)O\(_{40}\) loading, e.g. complete decomposition of MB, CV, or RB on pure TiO\(_2\) is the weakest thereby the lowest photocatalytic activity of TiO\(_2\) is obtained.

Secondly, in PW\(_{12}/\)TiO\(_2\) system, H\(_3\)PW\(_{12}\)O\(_{40}\) can assist in the generation of the photogenerated oxidizing species because of its effective electron scavenging from the CB of TiO\(_2\), consequently, enhancing the photocatalytic redox processes. In addition, crystalline defects within TiO\(_2\) framework due to introducing the Keggin unit may also favor capturing photoelectrons and inhibiting charge recombination [10]. Both cases increase quantum efficiency of the photocatalysts.

Finally, pore texture also has an influence on photocatalytic activity of PW\(_{12}/\)TiO\(_2\) composites. For surfactant-free PW\(_{12}/\)TiO\(_2\) composite, the pores are formed due to aggregation among the particles, and their pore...
size is smaller and uneven distribution. As for the surfactant-templated mesoporous PW12/TiO2 composites, the pores are formed due to the structure directing function of the template, which creates the pores with 3D sponge like mesostructure and larger pore size. This pore morphology would minimize diffusion problems of large dye molecules and increase pore accessibility. Accordingly, their photocatalytic activity is higher than that of the surfactant-free PW12/TiO2.

3.3.3. Photodegradation pathway of dye CV catalyzed over the PW12/TiO2 composite

In order to investigate UV-light photodegradation pathway of dye catalyzed over mesoporous PW12/TiO2 composite, the intermediates and final products yielded during the process of dye CV photodegradation are analyzed by LC-MS and IC at various time intervals. The intermediates analyzed by LC-MS are identified by interpretation of their molecule-ion peaks based on determined values of \((M+H)/z\), where \(M\) is molecular weight of the intermediates. Accordingly, two parallel photodegradation pathways of dye CV catalyzed over the PW12/TiO2 composite are tentatively put forward (Scheme 1).

For both of the pathways, Cl− ion is firstly released into the reaction system and yields Compound 2. In Pathway I, photodegradation of CR catalyzed over the PW12/TiO2 composite starts from the cleavage of C–C bond between the aromatic ring and the center carbon of CV molecule, which leads to benzophenone (Compound 3 in Scheme 1) due to attack of •OH radicals. •OH radicals are produced at the surface of the composite under UV-light irradiation of the PW12/TiO2 composite. Compound 3 is further oxidized by •OH radicals and generates its demethylated and deaminated products, successively (Compounds 4–7 in Scheme 1).
Pathway I

\[ \text{M 408} \quad \text{(1)} \]

\[ \text{M 372} \quad \text{(2)} \]

\[ \text{M 269 detected M+H 269.3} \]

\[ \text{M 255 detected M+H 255.3} \]

\[ \text{M 138 detected M+H 138.3 detected M+H 124} \quad \text{(15)} \]

\[ \text{M 122 detected M+H 124} \quad \text{(14)} \]

\[ \text{OH} \]

\[ \text{C}_n \text{ acid (n<6)} \quad \text{(16)} \]

\[ \text{CH}_3 \text{COOH} \quad \text{(17)} \]

\[ \text{HCOOH} \quad \text{(18)} \]

\[ \text{CO}_2 + \text{H}_2\text{O} \quad \text{(19)} \]

Pathway II

\[ \text{M 372} \quad \text{(2)} \]

\[ \text{M 358 detected M+H 358.5} \quad \text{(8)} \]

\[ \text{M 344 detected M+H 344.51} \quad \text{(9)} \]

\[ \text{M 330 detected M+H 330.5} \quad \text{(10)} \]

\[ \text{M 138 detected M+H 138.3 detected M+H 124} \quad \text{(15)} \]

\[ \text{M 122 detected M+H 124} \quad \text{(14)} \]

\[ \text{OH} \]

\[ \text{C}_n \text{ acid (n<6)} \quad \text{(16)} \]

\[ \text{CH}_3 \text{COOH} \quad \text{(17)} \]

\[ \text{HCOOH} \quad \text{(18)} \]

\[ \text{CO}_2 + \text{H}_2\text{O} \quad \text{(19)} \]

Scheme 1. Photodegradation pathway of dye CV catalyzed over the PW_{12}/TiO_2-13.4 composite. Initial concentration of CV (50 mg L^{-1}); catalyst amount 0.135 g.
Continuing UV-light irradiation results in total cleavage of CV chromophore into Compounds 14 and 15 and then quinone (Compound 16 in Scheme 1). At this time (UV-light irradiation for 45 min), decolorization of CV is ended up and the reaction solution is colorless. However, disappearance of CV doesn’t mean its total degradation. It requires a reaction time longer than for destruction of its chromophore due to the successive cleavage of carbon-chain. Via IC analysis we observe that intermediates follows the same route with Pathway I. At last, total cleavage of CV chromophore occurs, at this step, Compounds 14–16 are produced. Further degradation of these intermediates follows the same route with Pathway I.

4. Summary

The present work demonstrated a novel PW12/TiO2 composite photocatalyst with well-distributed 3D interconnected mesopore structure. The composite exhibited significantly high UV-light photocatalytic activity to aqueous dye degradation. This excellent photocatalytic performance of as-prepared composite is mainly attributed to adsorption behaviors of dye molecules on the photocatalyst; the synergetic effect existed between the Keggin unit and TiO2 network; crystalline defects within TiO2 framework; and unique pore morphology of the composite.

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References
