Preparation of mesoporous potassium phosphotungstate/silicon dioxide photocatalyst and study on degradation of chlorothalonil

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ABSTRACT

Mesoporous potassium phosphotungstate/silicon dioxide photocatalysts (KPW/SiO_2) were prepared by the sol-gel method using cetyl trimethyl ammonium bromide (CTAB), tetraethoxysilane (TEOS) as raw materials and prepared insoluble potassium phosphotungstate. The structures of KPW/SiO_2 were characterized by using XRD, BET, IR and TG. The photocatalytic activities were evaluated by using the organic pesticide chlorothalonil as a model reactant. The results indicate that the degradation rate reaches 86.04% when the illumination time is 120 min under 100 W mercury lamp, the dosage of KPW/SiO_2 is 0.01 g, the concentration of chlorothalonil is 5 mg/L, pH = 5. Mesoporous SiO_2 effectively enhanced the photocatalytic activity of KPW (70%).

Keywords: Mesoporous; Potassium phosphotungstate; Silicon dioxide light; Photocatalysts; Chlorothalonil

1. Introduction

Pesticide is the indispensable means of production in modern agriculture; it does guaranteed the harvest of agricultural products. The use of a large number of pesticides not only guarantees agricultural production and income but also brings an abundance of environmental problems at the same time. Such as the Lipton tea pollution incident in 2012, Pesticide pollution accident in Guangzhou on the Pearl river [1], pesticide fish poisoning incident in EnShi, Hubei, etc. Water pollution caused by pesticides has attracted widespread attention. Reducing or eliminating the hazards of pesticides and secondary pollution is also an important direction of environmental chemistry research at this stage. Chlorothalonil is a widely used substitutive benzene fungicide. Not only used in agriculture to prevent and control diseases of vegetables, melons and fruits, peanuts, rice, wheat and other crops but also used in industry as mildew-proof coatings and additives [2]. Chlorothalonil

is a low-toxic fungicide [3,4], which annual output in China exceeds 8,000 t, the solubility in water is 0.9 mg/L, and the half-life period in water is 8–9 d. Under normal conditions, chlorothalonil powder acute transoral LD50 in both rats and rabbits is greater than 10,000 mg/kg. Rats with acute inhalation LD50 > 4.7 mg/L. However, some studies have shown that chlorothalonil should pay attention to the harm of the environment. For instance, Tang et al. [5] found that chlorothalonil had the effect of inducing cell mutation and could induce the exchange of sister chromatids of mouse bone marrow lymphocytes. And Juárez et al. [2] found that chlorothalonil could make genetic mutations in aquatic organisms, amphibians and plant cells. Chauhan and Bhattacharya [6] found that chlorothalonil had sensitization effect on human body. Mozzachio et al. [7] observed that chlorothalonil has certain connection with cancer incidence. The United States Environmental Protection Agency (USEPA) has listed the chlorothalonil as one of the possible inducements of human cancer, and it has a potential threat to environmental and

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food safety [8–10]. So it is imperative to eliminate the harm of chlorothalonil residues in water which is harm to environment and human body.

Biodegradation, hydrolysis and photochemical degradation were the main degradation pathways of chlorothalonil in water environment. Although biodegradation is environmentally friendly, it has a long degradation cycle. And hydrolysis is greatly affected by the pH and temperature of water. In addition, studies have shown that chlorothalonil can be removed by effective degradation under the illumination of nano-TiO_2 [11]. The photochemical degradation of chlorothalonil has a significant effect under sunlight and high pressure mercury lamps [12]. It has also been pointed out that chlorothalonil can also be effectively degraded under the sunlight and xenon illumination, and can be effectively proved by the shortening of half-life [13]. Photochemical degradation is best; however, photosensitizers can greatly affect efficiency. Therefore, the selection of suitable photocatalyst is the key to degradation of chlorothalonil in water [14]. Heteropoly acid compound is a kind of polynuclear inorganic macromolecule compound containing oxygen bridge. It consists of heteropoly anions and cations (including metal cationic, protons and other organic cations) and crystalline water or organic molecules [15]. Its unique structure and spectral properties make it a highly efficient photocatalyst [16,17]. About the synthesis and application of heteropoly acid photocatalyst, some scholars at home and abroad have carried out the related research, such as Chen et al. [18] made CsCl react with $H_3PW_{12}O_{40}$ to generate $Cs_3PW_{12}O_{40}$, which can rapidly degrade n-methylpyrrolidone under 254 nm ultraviolet light [19]. However, traditional heteropoly acid photocatalysts has a strong water solubility, it is easy to dissolve in water and oxygen-containing organic solvents. Moreover, low reuse efficiency, small specific surface area and difficulty in recycling limit its application. Therefore, the preparation of water-insoluble photodegradation catalysts for organic pesticides has great theoretical and practical significance.

In this paper, chlorothalonil is used as target degradant, and the potassium phosphotungstate (KPW) is prepared by the reflux adsorption method. Mesoporous potassium phosphotungstate/silicon dioxide (KPW/SiO_2) is prepared by the sol-gel method to load the potassium phosphotungstate on mesoporous silica. Then the photocatalytic activities of KPW/SiO_2 for chlorothalonil, the affect factors of degradation and the mechanism of KPW loaded on SiO_2 were investigated.

2. Experimental

2.1. Instruments and reagents

D/Max-38 X-ray Diffractometer (CuK α as incident light source target, incident wavelength $\lambda = 0.154$ nm, voltage 40 kV, current 40 mA), NICOLET IS10 Fourier Infrared Spectrometer (resolution 4 cm^{-1}, wave number range 4,000–400 cm^{-1}, KBr wafer method), QUANTA 200 Electron Microscope, UV-2550 Spectrophotometer (with diffuse reflection measurement device integrating sphere, Testing wavelength is 200–900 nm, Use calcium sulfate as a reference. XPA Photochemical Reaction Instrument (Light source is 100 W mercury lamp).

Trace 1300 Gas Chromatograph (ECD detector, TR-5 chromatographic column). Phosphotungstic acid, potassium chloride, ethyl acetate are all analytically pure. Florisil solid-phase extraction small column (500 mg/6 mL), chlorfenuron (purity is 98.2%) are provided by the National Pesticide Quality Supervision and Testing Center (5 Guanghua East Street, Qinhuai District, Nanjing, Jiangsu, China).

2.2. Preparation of KPW/SiO₂

CTAB was added in distilled water, stirring was continued in water bath at 40°C temperature to clarify, then absolute ethyl alcohol was added and agitated for 10 min, ammonia was added drop by drop and stirred for another 10 min, TEOS was added when the solution turns milky and cloudy, stirring was continued for 2 h. Finally, potassium phosphotungstate, which was prepared by reflux adsorption method [20], was added and agitated for 2 h. After washing in distilled water till Cl$^-$ free, the precipitate was dried at 105°C and then vacuum dried at 70°C overnight. In the end, the white powder was ground and calcined in muffle furnace for 3 h, KPW/SiO_2 composite was obtained.

2.3. Structure characterization of KPW/SiO₂

D/max-38 X-ray diffractometer (CuK α as incident light source target, the incident wavelength λ is 0.154 nm, 40 kV voltage, electric current 40 mA, scanning rate is 10°/min; the 2θ range from 5° to 70°), NOVA 2000 Specific surface tester (Test in 7 K, Use N_2 as adsorbent. Degassing conditions: degassing phase, heating rate is 10°C/min, final temperature is 90°C, degassing the sample at 363 K for 3 h before we do the analysis), NICOLET IS10 type Fourier infrared spectrometer (resolution 4 cm^{-1}, wave number range 4,000–400 cm^{-1}, KBr wafer method), STA-449F3 thermogravimetric analyzer (heating rate 20°C/min, heating range is 23–800, nitrogen as carrier gas). And use UV-2550 spectrophotometer to characterize (test wavelength 200–900 nm, with calcium sulfate as reference).

2.4. Photocatalytic activity analysis

The photocatalytic performance of KPW/SiO_2 was carried out on the XPA-7 photochemical reactor, using 100 W mercury lamp as the light source. 0.1 g of immobilized potassium phosphotungstate catalyst was mixed with 10 mL of chlorothalonil solution, and stirred for 30 min in the dark to reach the adsorption equilibrium. After the lamp was irradiated for 15 min, the sample was sampled once every 15 min. After centrifugation, 100 samples were measured. Chlorothalonil was determined by the method which has been shown in this article [21]. The retention time of chlorothalonil was 2.28 min and the detection limit was 0.0035 mg/L.

Prepare a certain concentration of chlorothalonil solution, divide it into two parts, one part without photocatalyst, the other part with a certain amount of photocatalyst. Then, the two samples were placed in a photochemical reactor, and the time of irradiation with a 100 W UV lamp was taken out from the centrifuge and detected by a gas chromatograph. The degradation rate of chlorothalonil was calculated by using the following formula:

$$D = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

Here D (%) is the degradation rate of chlorothalonil, C_0 (mg/L) is the sample concentration of photocatalyst, C_t (mg/L) is the concentration of photocatalyst.

3. Results and discussion

3.1. Characterization of KPW/SiO₂

3.1.1. BET analysis

The main function of mesoporous SiO_2 is to effectively increase the specific surface area of KPW/SiO_2, pore volume and uniform pore distribution of KPW/SiO_2. The N_2 adsorption–desorption isotherms of SiO_2 and KPW/SiO_2 are shown in Fig. 1. It can be seen from the figure that the hysteresis loop caused by capillary condensation is obvious in the range of 0.25–1.0 relative pressure. It belongs to the IV Langmuir adsorption–desorption isotherm and it is a unique isotherm for multi-layer adsorption of porous materials. Meanwhile, the hysteretic loop on the desorption branch was between H_2 and H_3 types, indicating the existence of mesopore structure of the catalyst [22,23].

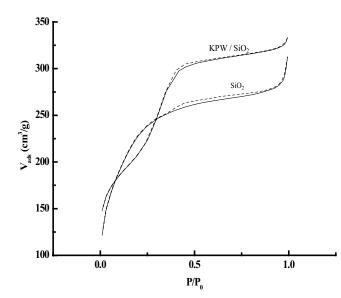According to Table 1 and Fig. 2, compared with SiO_2, the specific surface area, pore diameter and pore volume of KPW/SiO_2 has been increased. Combined with the isothermal adsorption curve (Fig. 1), which the KPW does not change the mesoporous structure of SiO_2. On the contrary, when the KPW combine with mesoporous SiO_2, the specific surface pore diameter and pore volume of KPW/SiO_2 are increased effectively. The advantages of mesoporous SiO_2 structure are well utilized.

3.1.2. Small-angle XRD analysis

It can be seen from the small-angle XRD spectrum (Fig. 3) that when 2θ is in the range of 2–3 and 4–6, respectively. Both SiO_2 and KPW/SiO_2 have a strong diffraction peak and a weak diffraction peak, corresponding to characteristic crystal peak (200) and (210). It is further explained that the KPW does not destroy the mesoporous structure of mesoporous SiO_2. However, the intensity of the diffraction peak of KPW/SiO_2 decreases indicating that the crystallinity of mesoporous SiO_2 is weakened when the KPW is existence [24].
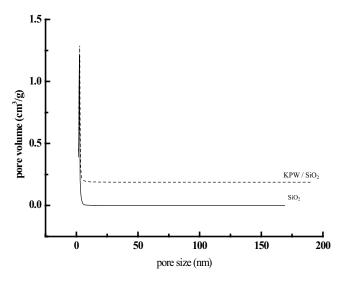

Fig. 1. Adsorption–desorption isotherm of mesoporous SiO_2, KPW/SiO_2.

Fig. 2. Pore size distribution curves of mesoporous SiO2, KPW/SiO_2.

Fig. 3. XRD spectrum of mesoporous SiO_2, KPW/SiO_2.

Table 1
BET parameters

Sample name	Specific surface area (m²/g)	Pore size (nm)	Pore volume (cm³/g)
SiO₂	840.32	2.12	0.44
KPW/SiO₂	1,536.76	3.28	1.26

3.1.3. IR analysis

For a better understanding, the functional groups of KPW/SiO$_2$, IR spectrum of KPW, mesoporous SiO$_2$ and KPW/SiO$_2$ were performed and shown in Fig. 4. Based on Fig. 4, we found that the characteristic peaks of KPW at 1,079 cm^{-1} belongs to the stretching vibration of P–O bond; the peak at 982 cm^{-1} belongs to the vibration of W=O bond; 891 cm^{-1} for the vibration absorption W–Oe–W; the peak at 799 cm^{-1} is attributed to the vibration absorption of W–Oc–W. The characteristic peak for SiO$_2$ at 466 cm^{-1} belongs to the stretching vibration absorption of Si–O–Si; and at 803 cm^{-1}, 953 cm^{-1} belongs to the bending vibration absorption of Si–O–Si and Si–O, respectively. Besides these bands, the peak at 1,062 cm^{-1} is the asymmetric vibration absorption peak of Si–O–Si. When KPW is combined with mesoporous SiO$_2$, the characteristic absorption peaks of KPW at 1,079 and 891 cm^{-1} are blue shifted to 1,072 and 953 cm^{-1}, respectively, the peak at 799 cm^{-1} is red shifted to 813 cm^{-1}. The characteristic absorption peaks at 958, 863 and 466 cm^{-1} of SiO$_2$ have different levels of blue shift, the broad peak at 1,072 cm^{-1} which indicate the chemical interaction between KPW and SiO$_2$ is attributed to overlap of the peak at 1,062 cm^{-1} of SiO$_2$ with the peak at 1,079 cm^{-1} of KPW, and from this broad peak, we can infer the basic structure of KPW and SiO$_2$ are still existed [25].

3.2. Degradation performance research

3.2.1. Influence of different quality

For the study, the effect of different quality KPW/SiO$_2$ on the degradation of chlorothalonil and results are shown in Fig. 5. When the dosage of KPW/SiO$_2$ is 0.01 g, the degradation effect is the best, and the degradation rate reaches 65.95%. However, when the dosage of KPW/SiO$_2$ exceeds the optimal amount, the degradation rate decreases instead, which may be the turbidity of the solution will affect the photocatalytic effect. The dosage of catalyst is larger, the more turbidity of the suspension increases, and that make the transmittance decrease, and finally the degradation effect is reduced [26].
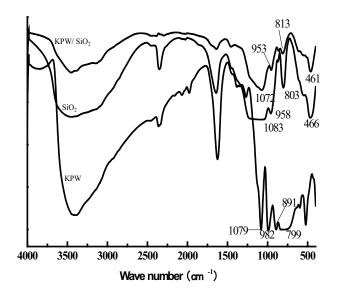
3.2.2. Effect of different degradation time

As can be seen from Fig. 6, the degradation effect of KPW/SiO$_2$ on chlorothalonil is improved with the increase of degradation time at 0 to 120 min. The degradation effect reaches the best when the degradation time is at 120 min, and the degradation rate reached 79.70%.

3.2.3. Effect of chlorothalonil initial concentration

Fig. 7 shows that the degradation rate of KPW/SiO$_2$ has been affected by different concentrations of chlorothalonil. As seen in the picture, we can see that the degradation rate of KPW/SiO$_2$ for chlorothalonil is lower with the concentration
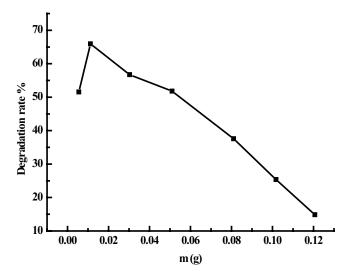

Fig. 5. Effects of KPW/SiO$_2$ with different weight on degradation of chlorothalonil.

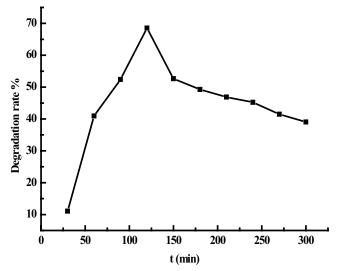Fig. 4. IR spectra of KPW, mesoporous SiO$_2$ and KPW/SiO$_2$.

Fig. 6. Effect of degradation time on degradation of chlorothalonil by KPW/SiO$_2$.

of chlorothalonil increase. This is due to the fact that the large concentrations of chlorothalonil affect the light transmittance, and then reduce the light adsorption of KPW/SiO$_2$, and ultimately lead to the degradation rate decrease. So choose 5 mg/L as the initial concentration of chlorothalonil in the following experiment.

3.2.4. Effects of pH

The effect of different pH values on the degradation of chlorothalonil by KPW/SiO$_2$ is shown in Fig. 8. We can see from Fig. 8 that KPW/SiO$_2$ has the best degradation effect on chlorothalonil when the pH is 5, and the degradation rate reaches 58.08%. The acidity is too high or too low, and the degradation effect is not good. This may be due to the fact that different pH values affect the structure of mesoporous silica, the stability and dispersibility of KPW/SiO$_2$ in chlorothalonil solution, which affects its degradation.
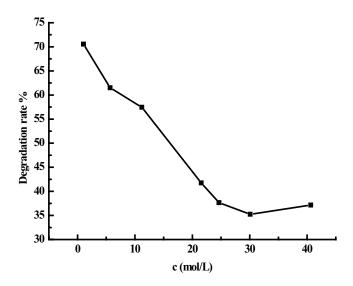

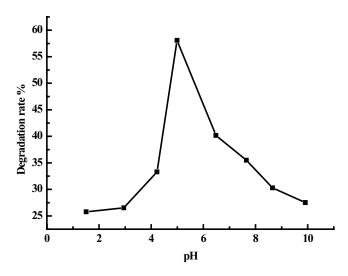Fig. 7. Effect of different chlorothalonil concentration on the degradation rate of KPW/SiO$_2$.

Fig. 8. Effect of different pH on the degradation of chlorothalonil by KPW/SiO$_2$.

3.2.5. Comparison of degradation effects of KPW/SiO$_2$

The degradation effects of KPW and KPW/SiO$_2$ are shown in Fig. 9. The degradation rate of chlorothalonil was significantly improved after SiO$_2$ was loaded on KPW, and the degradation rate increases from 72.06% to 86.40%.

3.2.6. Comparison of degradation properties of materials prepared by different methods

As shown in Table 2, the effects of materials prepared by different methods on the degradation of chlorothalonil were compared. It can be seen that the degradation of KPW/SiO$_2$ has been improved 2%–20%, and the removal rate of chlorothalonil can reach 86.04%. Moreover, the degradation activity of the photocatalyst is effectively improved by preparing the mesoporous material KPW/SiO$_2$. Therefore, photocatalytic degradation of chlorothalonil by mesoporous material KPW/SiO$_2$ is of great significance.

3.2.7. Changes in COD$_{cr}$ values

The changes of COD$_{cr}$ before and after chlorothalonil degradation are shown in Table 3. It can also be seen from the data that the COD$_{cr}$ change value of the samples degraded by KPW/SiO$_2$ was 33.93, 21.49 higher than that of KPW (12.44).

3.2.8. Study on degradation kinetics

According to the photocatalytic degradation effect of KPW/SiO$_2$ on chlorothalonil, the degradation process was fitted by using the pseudo-first-order, second-order kinetic models and the particle internal diffusion model. The fitting parameters are shown in Table 3. As can be seen from Table 4, the degradation of chlorothalonil by KPW/SiO$_2$ conforms to the first-order kinetic model, the correlation coefficient is 0.9913, and the Q_e value which was calculated by the first-order kinetic model is 15.89 mg/g, which is more consistent with the experimental value (15.32 mg/g).
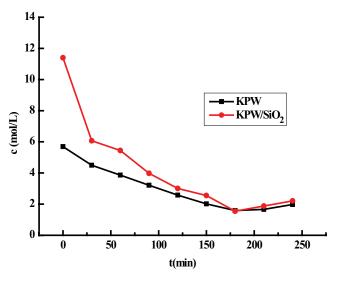

Fig. 9. Study on degradation of chlorothalonil by KPW and KPW/SiO$_2$.

3.2.9. Analysis of degradation products

3.2.9.1. GC-MS analysis

The degradation production of chlorothalonil in water samples was extracted three times with 5 mL of chloroform, ethyl acetate, toluene and *n*-hexane, respectively. The organic phases were combined, and then evaporated by rotary evaporator, finally, dissolved with 1 mL toluene and analyzed by using GC-MS, the spectrum is shown in Fig. 10, the peak at 7.67 min is identified as 1,2,3-trimethylbenzene which is the most intermediate product.

3.2.9.2. IC analysis

In order to compare the photocatalytic activity of KPW and KPW/SiO$_2$, ion chromatogram (IC) was chosen for

Table 2
Comparison of degradation properties of materials prepared by different methods

References	Degradation rate of chlorothalonil
[27]	60.40%
[28]	84.2%
[29]	85.39%
[30]	71.88%
[31]	73.62%
This article	86.04%

Table 3
COD$_{cr}$ values of chlorothalonil degradation before and after SiO$_2$ loaded on KPW

COD$_{cr}$ (mg/L)	KPW	KPW/SiO$_2$
Before	32.98	89.34
After	20.54	55.41
Changing value	12.44	33.93

Table 4
Parameters of KPW/SiO$_2$ pseudo-first-order and second-order kinetics model and particle internal diffusion model for the degradation of chlorothalonil

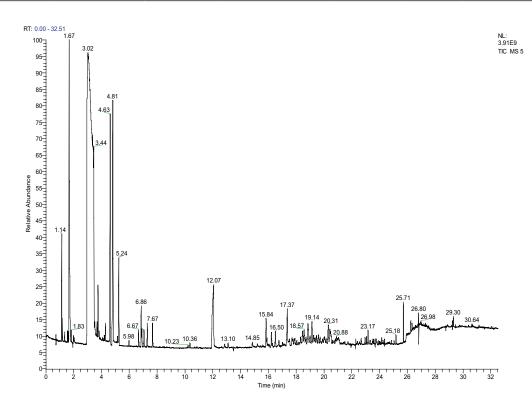| First-order kinetic model			Second-order kinetic model			Particle internal diffusion model	
k_1 (min^{-1})	Q_e (mg/g)	R	k_2 (g/(kg mg min))	Q_e (mg/g)	R	k_3 (g/(kg min$^{0.5}$))	R
0.01727	15.89	0.9913	0.005589	17.12	0.9884	1.033	0.9144
Fitting equation	lg(Q_e-Q) = –0.0075t + 1.201		t/Q = 0.0584 t + 0.6103			Q = 1.033 $t^{0.5}$ + 3.136	

Fig. 10. GC-MS of degradation intermediates of chlorothalonil.
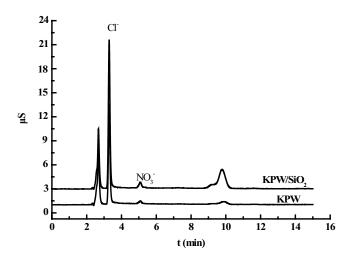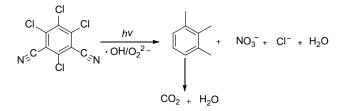
Fig. 11. IC diagram of degradation products of chlorothalonil.

detection of the degradation products of Cl^- and NO^{3-}, the result is shown in Fig. 11. As can be seen from the spectrogram, the concentration of Cl^- and NO^{3-} of KPW is 11.97 and 06446 mg/L, respectively. After combination with SiO_2, the concentration of Cl^- is increased to 20.17 mg/L, and the concentration of NO^{3-} is also increased to 1.3708 mg/L. It is evident that the photocatalytic degradation activity of KPW is improved by SiO_2 which has large specific area and multi-lacuna.

3.2.10. Degradation mechanism analysis

Based on the analysis of degradation products of chlorothalonil, it can be preliminarily inferred that KPW/SiO$_2$ photocatalytic degradation of chlorothalonil was a surface photocatalytic reaction triggered by the attack of $\cdot OH$. When ultraviolet light is irradiated on the photocatalyst surface, electron-hole pairs will be generated on the photocatalyst surface. The hole oxidizes the OH^- and H_2O adsorbed on the catalyst surface to form $\cdot OH$, which promotes the oxidation of chlorothalonil. The process of degrading the chlorothalonil is derived as follows. The enhanced degradation activity of SiO_2 on KPW was attributed to the fact that mesoporous SiO_2 by taking advantage of its large specific area and pore channel was able to adsorb bacteria to its surface, thereby increasing the contact surface between $\cdot OH$ and chlorothalonil, and finally improving the photocatalytic degradation performance [32].

4. Conclusions

Mesoporous potassium phosphotungstate/silicon dioxide photocatalyst (KPW/SiO$_2$) was synthesized by using hexadecyl trimethyl ammonium bromide ethyl orthosilicate as raw material, adding water-insoluble ammonium phosphotungstate in alkaline alcohol water system and using sol-gel one-step synthesis method. The result shows that the prepared KPW/SiO$_2$ was a mesoporous material by BET and small-angle XRD, and IR characterization indicated that KPW retained the Keggin structure of phosphotungstic acid and the mesoporous structure of SiO_2 after loading on SiO_2. In addition, when the dosage of KPW/SiO$_2$ was 0.01 g, under the condition of 5 mg/L and pH = 5 and the light exposure was 120 min, the degradation rate of KPW/SiO$_2$ reached 86.04%. And the degradation kinetics accords with the first order kinetic equation. Therefore, mesoporous SiO_2 effectively enhanced the photocatalytic activity of KPW (70%).

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