H$_4$SiW$_{12}$O$_{40}$/polymethylmethacrylate/polyvinyl alcohol sandwich nanofibrous membrane with enhanced photocatalytic activity

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**Highlights**

- H$_4$SiW$_{12}$O$_{40}$/PMMA/PVA sandwich nanofibrous membranes were prepared by electrospinning.
- The Keggin structure of H$_4$SiW$_{12}$O$_{40}$ has not been destroyed in the sandwich nanofibrous membrane.
- The sandwich nanofibrous membrane exhibited enhanced photocatalytic activity in the degradation of methyl orange (MO).
- The sandwich nanofibrous membrane could be easily separated and reused.
- The photocatalytic degradation of MO by the sandwich nanofibrous membrane was driven by the reductive pathway.

**Abstract**

Nanofibrous membranes of H$_4$SiW$_{12}$O$_{40}$/polymethylmethacrylate (PMMA)/polyvinyl alcohol (PVA) were prepared by electrospinning technique. The sandwich structure and element composition of the membranes were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier transformation infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS). The characterization indicated that H$_4$SiW$_{12}$O$_{40}$ has been successfully loaded into the upper and bottom layers of the sandwich nanofibrous membrane, while the Keggin structure of H$_4$SiW$_{12}$O$_{40}$ was preserved. The as-prepared H$_4$SiW$_{12}$O$_{40}$/PMMA/PVA sandwich nanofibrous membranes exhibited greatly enhanced photocatalytic efficiency (≥94.0%) in the degradation of methyl orange (MO) under ultraviolet irradiation, outperforming H$_4$SiW$_{12}$O$_{40}$ powder (4.6%) and H$_4$SiW$_{12}$O$_{40}$/PMMA composite nanofibrous membrane (13.8%). Notably, the sandwich nanofibrous membrane could be easily separated from aqueous MO solution and the photocatalytic efficiency of the membrane had little change after three photocatalytic cycles. The great performance of the as-prepared membrane may be attributed to the water tolerance of the sandwich nanofibrous membrane and the stability of H$_4$SiW$_{12}$O$_{40}$ in the membrane. The photocatalytic mechanism of the sandwich nanofibrous membrane was also discussed.

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1. Introduction

Contaminations of ground water by organic dyes pose a serious environmental threat [1]. Within the category of dyestuffs, azo dyes (e.g., methyl orange, acid orange 7 and naphthol blue black) constitute a significant portion and cannot be readily degraded by conventional chemical and biochemical treatment processes [2,3]. As a green technology, photocatalytic treatment of polluted water has been considered as one of the most attractive approaches to solve this environmental issue [4]. Polyoxometalates (POMs) are well-defined transition metal–oxygen clusters with unique structure characteristics and can function as photocatalysts through the photoexcitation of the oxygen-to-metal charge transfer bands to separate the electron-hole pair used for reductive and oxidative reactions with surrounding molecules [5]. Earlier investigation has illustrated that POMs possess similar photochemical characteristics of semiconductor photocatalysts [6–8]. Due to a number of featured advantages such as optical stability, adjustable oxidizability, more stable chemical structure, low toxicity and inexpensiveness [4], in recent years there are increasing interests in studying POMs as photocatalysts and applying them for degrading organic dyes [1,9].

However, most of the studies on photooxidative behavior of POMs have been carried out in homogeneous systems [10]. The major disadvantage of these systems is that the high solubility of POMs makes the collection and thus reuse of the photocatalysts difficult [11–14]. For the purpose of practical applications, it is desirable to develop a heterogeneous photocatalytic system by combining POMs with supporting materials to make them more recoverable. Driven by such desire, considerable interests have been dedicated to the coupling of POMs with many supports such as silica, activated carbons, TiO₂, mesoporous molecular sieve and polymeric membranes [15–19]. Most of the supporting substrates are inorganic or modified inorganic porous materials so that they can increase the specific surface areas of POMs (BET specific surface areas of POMs are lower than 10 m²/g [20]). Larger specific surface areas can provide sufficient contact between POMs and pollutants, increasing the catalytic activity of POMs. To date, preparation of POM-containing films is an effective way of immobilizing soluble POMs. From the standpoint of separation and recovery of catalyst in practical wastewater treatment, the POM-containing films are more predominant compared with the powdered POM materials because no separation process is needed for the films. To the best of our knowledge, while there have been some studies on the photocatalytic properties of POM-containing composite films prepared by layer-by-layer self-assembly method and sol–gel technique [11,21], few reports have been made on photocatalytic application of POM-containing composite films which are prepared by electrospinning.

Electrospinning technique is a simple, versatile and effective method for the preparation of polymer, polymer/organic hybrid and inorganic nanofibers [22,23]. The nanofibrous membrane has many remarkable characteristics, such as fine diameters ranging from submicron to several nanometers [24], large specific surface area, high porosity and high permeability [25] etc. Hence, electrospun nanofibrous membranes may be promising supports for the immobilization of photocatalysts. Briefly, the qualification of electrospun nanofibrous membranes as excellent supports includes: (i) the easy separation and thus reusability due to their non-woven mesh forms; (ii) the high level exposure of the photocatalysts due to their large surface areas [26]. Sui et al. [27] used POM as a template and prepared Ag/PVA/SiW₁₂ tri-component nanohybrids by electrospinning and photoreduction methods. The photocatalytic activity of the nanohybrids was significantly improved due to the synergistic effects of three components. Unfortunately, as a water-soluble polymer, the structure and porosity of electrospun PVA nanofibers would disappear when the membrane is immersed in water even for just a few minutes. So PVA nanofibrous membranes usually needed to be treated before its utilization in water. Crosslinking is a widely used and effective method to make PVA nanofibers insoluble, but it would alter chemical properties of PVA.

In this work, a nanofibrous membrane with a sandwich structure was designed as the supporter of POM, and its constitution and structure is illustrated in Fig. 1. The upper layer and bottom layer are H₄SiW₁₂O₄₀/poly(methylenacrylate) (PMMA) composite nanofibrous membranes having the same thickness. PMMA was chosen primarily because it is a commonly used water-insoluble polymer which has high mechanical strength and good spinnability. However, the composite nanofibrous membrane is nonwettable due to the hydrophobicity of PMMA, which hinders the contact between H₄SiW₁₂O₄₀ and pollutants. In view of this, hydrophilic polymer, PVA was selected as the intermediate layer of the sandwich nanofibrous membrane. The molecular structure and surface morphology of sandwich nanofibrous membrane were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). Photocatalytic activity and mechanism of the sandwich nanofibrous membrane were studied through the photodegradation of MO. The stability and reusability of the sandwich nanofibrous membrane were also investigated. Results presented in this report shall be useful for further study on the design of nanofibrous membrane for photocatalytic treatment of practical waste effluents.

2. Materials and methods

2.1. Materials

Analytical reagents H₄SiW₁₂O₄₀, ethanol (C₂H₅OH) and perchloric acid (HClO₄) were supplied by Sinopharm Chemical Reagent Co., Ltd. Polymethylmethacrylate (PMMA) (Mₙ = 60,000) was obtained from Simitomo Chemical (Japan), Polyvinyl alcohol (PVA) (Mₘ = 75,000) was also purchased from Sinopharm Chemical Reagent Co., Ltd. Dimethyl formamide (DMF), sodium dodecyl sulfate (SDS) and methyl orange (MO) were purchased from Aladdin Industrial Corporation. All the solvents were used without further purification, and all the aqueous solutions were prepared with deionized water.

2.2. Preparation of sandwich nanofibrous membrane

Preparation of upper layer (H₄SiW₁₂O₄₀/PMMA layer): electrospinning solution was prepared by dissolving 1.0 g PMMA in 6.0 mL DMF at 30 °C. The solution was stirred until PMMA completely dissolved, and then 4.0 mL C₂H₅OH containing 1.0 g H₄SiW₁₂O₄₀ was added to the solution. Stirring was continued for additional 40 min at 30 °C. After cooling to room temperature, the electrospinning solution prepared above was added to a 5 mL glass syringe with a needle tip (0.5 mm diameter). The flow rate of the solution was 0.5 mL h⁻¹, which was controlled by a micro syringe pump.

Fig. 1. Scheme of H₄SiW₁₂O₄₀/PMMA/PVA sandwich nanofibrous membrane.
The used voltage was 15 kV and the collection distance between the needle tip and aluminum foil was 15 cm. When the electrospinning solution with appointed volume (0.25 mL, 0.5 mL, 1.0 mL respectively) was consumed, the electrospinning of intermediate layer was started.

Preparation of intermediate layer (PVA layer): 1.2 g PVA was added to 15.0 mL deionized water at 80°C. After PVA completely dissolved, 0.2 g SDS was added to the solution while the stirring was kept on for additional 1 h. After cooling to room temperature, 2.5 mL of the as-prepared electrospinning solution was added to a 5 mL glass syringe with a needle tip (0.5 mm diameter). The flow rate was 0.6 mL h⁻¹, the applied voltage was 20 kV and the collection distance was 13 cm.

The preparation of bottom layer (H₄SiW₁₂O₄₀/PMMA layer) was in accord with the preparation of the upper layer. The three-layer nanofibrous membranes were compressed for two minutes at room temperature before being peeled off from the aluminum foil.

2.3. Photocatalytic activity test

The photocatalytic activity of the sandwich nanofibrous membrane was evaluated for decomposition of harmful methyl orange (MO) aqueous solution. A 300 W high pressure mercury lamp with a double walled quartz glass tube (for water cooling) was suspended vertically (the distance between quartz glass reactor and lamp was 10 cm). Photodegradation of MO was carried out at atmospheric pressure and room temperature. In a typical experiment, 50 mL MO aqueous solution (10 mg L⁻¹, pH was adjusted to 1.0 using HClO₄) was placed in the reactor, and the sandwich nanofibrous membrane was immersed in the solution. Prior to the irradiation, the reactor was shaken dark for 30 min to establish adsorption–desorption equilibrium between the organic molecules and the catalyst surface. Decreases in the concentrations of MO were analyzed by UV–vis spectrophotometer at λ = 510 nm. At given intervals of illumination, the samples (5.0 mL) of the reaction solution were taken out and analyzed.

2.4. Instruments and characterization

The injection rate of electrospinning solution was controlled by a 78–9100C syringe pump (Cole Palmer Instrument Company). The nozzle was connected to a high-voltage regulated DC power supply (DW-P503-4ACCD, Tianjin Dongwen High Voltage Power Supply Plant). FT-IR spectra were recorded using a Nicolet-380 spectrometer, which were obtained at a resolution of 4 cm⁻¹.
Microstructure of the sandwich nanofibrous membranes were analyzed using a Hitachi S-4800 field emission-scanning electron microscope (FE-SEM) and an energy dispersive X-ray spectrometry (EDX, Noran7 EDX spectrometer). XPS measurement was carried out with a ESCALAB 250Xi spectrometer, with the non-monochromatized Al Kα X-radiation (hv = 1486.6 eV) and a power of 1500 W (10 mA × 150 W). Concentrations of the MO solutions were measured by a Specord S-600 UV–vis spectrophotometer (Analytik Jena AG Company) over the wavelength range of 200–800 nm.

3. Results and discussion

3.1. Characterization of the sandwich nanofibrous membrane

Fig. 2a and b shows typical SEM images of pure PMMA nanofibers and H₄SiW₁₂O₄₀/PMMA composite nanofibers (upper layer), respectively. It can be observed that these randomly oriented fibers have smooth and uniform surface. The diameters of pure PMMA nanofibers range from 120 nm to 300 nm, while the diameters of H₄SiW₁₂O₄₀/PMMA composite nanofibers range from 380 nm to 450 nm. The diameters of nanofibers increased after blending with H₄SiW₁₂O₄₀, yet the diameter distribution became narrow at the same time. As is apparent from Fig. 2c, the sandwich nanofibrous membrane has three layers, and the upper layer and the bottom layer are much thinner than the intermediate layer. Composition of the sandwich nanofibrous membrane was confirmed by EDS spectrum analysis, as shown in Fig. 2d, in which C, O, Si and W elements exist in the sandwich nanofibrous membrane, supporting the presence of H₄SiW₁₂O₄₀ in the membrane.

The FT-IR spectra of PMMA, H₄SiW₁₂O₄₀, and H₄SiW₁₂O₄₀/PMMA composite nanofibrous membrane are shown in Fig. 3. For PMMA, the peak at 1727 cm⁻¹ is typical of C=O stretching in the ester group. The peak at 2946 cm⁻¹ corresponds to C–H stretching of alkyl group. For H₄SiW₁₂O₄₀, the characteristic absorption peaks of Keggin unit at 1017 cm⁻¹, 980 cm⁻¹, 922 cm⁻¹ and 792 cm⁻¹ are attributed to the νₚ(Si–O₅), νₚ(W=O=O=O), νₚ(W=O=O=W) and νₚ(W=O=W=O), respectively [27]. The FT-IR spectrum of H₄SiW₁₂O₄₀/PMMA composite nanofibrous membrane has nearly all the key features of PMMA and H₄SiW₁₂O₄₀ with minor shifts of some peaks. It is obvious that the composite sample displays four discernible peaks between 790 cm⁻¹ and 1100 cm⁻¹, agreeing with Keggin unit well, which suggests that the Keggin structure of H₄SiW₁₂O₄₀ remains intact in the H₄SiW₁₂O₄₀/PMMA composite membrane [28].

To further investigate the surface chemical composition and the valence state of W in the sandwich nanofibrous membrane, XPS measurement was carried out. Fig. 4a shows the survey spectrum of the H₄SiW₁₂O₄₀/PMMA composite nanofibrous membrane (upper layer), indicating the presence of W, C and O. For W 4f XPS spectrum, as shown in Fig. 4b, the shape of the spectrum suggests the presence of two different forms of W. The spin-orbit doublet with binding energies for the W 4f₇/₂ and W 4f₅/₂ core levels of 35.7 and 37.9 eV account for approximately 94.8% of the total spectral area. These values demonstrate the presence of W (VI) centers, which is assigned to H₄SiW₁₂O₄₀ in the membrane. A second doublet at 34.3 eV (4f₂/₅ component) accounts for the remaining area. This value may represent the partial decomposition of H₄SiW₁₂O₄₀ and the formation of an oxide of the type WO₃ in which W has an oxidation state lower than VI or, more likely, the existence of perturbed tungstate environments resulting from interactions of H₄SiW₁₂O₄₀ with the support [29]. The O 1s spectrum of the sample can be deconvoluted into three components (Fig. 4c). The peak at 530.6 eV is attributed to the lattice oxygen in the Keggin structure (W–O–W), in good agreement with the results reported elsewhere [30]. The components with higher binding energies at 531.8 and 533.3 eV can be assigned to C=O and C–O respectively, arising from PMMA. The C 1s spectrum can also be deconvoluted into three components (Fig. 4d), corresponding to C–C (284.8 eV), C–O–C (286.3 eV) and O–C=O (288.6 eV) of PMMA, respectively.

3.2. Photocatalytic property

3.2.1. Photocatalytic activity

The photocatalytic activities of H₄SiW₁₂O₄₀/PMMA/PVA sandwich nanofibrous membranes were tested by degrading aqueous methyl orange (MO) under UV illumination. Fig. 5a shows the absorption spectra of MO vs. irradiation time in the presence of sandwich nanofibrous membrane in the solution. Here, both the upper layer and bottom layer were prepared with 0.25 mL electrospinning solution. Hence, there is 0.05 g H₄SiW₁₂O₄₀ in this sandwich nanofibrous membrane according to the mass ratio of PMMA to H₄SiW₁₂O₄₀ in the electrospinning solution. The major absorption peaks of MO at around 510 nm declined rapidly under UV light irradiation, while the color of the aqueous MO solution changed from red to nearly colorless after 30 min, indicating a nearly complete degradation of MO.

As a comparison, photocatalytic performances of H₄SiW₁₂O₄₀ powder, H₄SiW₁₂O₄₀/PMMA composite nanofibrous membrane, and H₄SiW₁₂O₄₀/PMMA/PVA composite nanofibrous membrane (the electrospinning solution was prepared by mixing H₄SiW₁₂O₄₀ powder, PMMA emulsion and PVA solid together in deionized water) were also evaluated. As shown in Fig. 5b, in the absence of photocatalyst, no obvious degradation of MO was observed under UV irradiation. In the presence of the photocatalysts, the absorbance of MO solution decreased in time. After 30 min UV light irradiation, the degradation efficiency of MO were calculated as about 4.6%, 13.8%, 95.1% and 94.0% for the H₄SiW₁₂O₄₀ powder, H₄SiW₁₂O₄₀/PMMA composite nanofibrous membrane, H₄SiW₁₂O₄₀/PMMA/PVA composite nanofibrous membrane (C) and H₄SiW₁₂O₄₀/PMMA/PVA sandwich nanofibrous membrane (S), respectively. Clearly, H₄SiW₁₂O₄₀/PMMA/PVA composite and sandwich nanofibrous membranes exhibit much higher photocatalytic activities than that of H₄SiW₁₂O₄₀ powder and H₄SiW₁₂O₄₀/PMMA composite membrane at the same conditions. The possible reason was that H₄SiW₁₂O₄₀ powder had low specific surface areas. Meanwhile, a completely different photocatalytic mechanism took place in the presence of PVA, resulting in the synergetic enhancement of the degradation rate (see below).

For further investigation, sandwich nanofibrous membranes with different H₄SiW₁₂O₄₀/PMMA layer thickness were prepared and evaluated. Their photocatalytic activities are shown in Fig. 5c, where 94.0%, 97.6% and 94.2% degradation of MO was observed after 30 min irradiation for the sandwich nanofibrous membranes that the H₄SiW₁₂O₄₀/PMMA layers were prepared by 0.25 mL(0.25/2.5/2.5), 0.5 mL(0.5/2.5/0.5) and 1.0 mL(1.0/2.5/1.0) electrospinning solutions, respectively. Among the three samples, 0.5/2.5/0.5 sandwich nanofibrous membrane displayed the best photocatalytic activity. As seen from the curves, for the 0.5/2.5/0.5 sandwich nanofibrous membrane, the degradation of MO has reached 95.5% after only 15 min irradiation. The photocatalytic activity of the sandwich nanofibrous membrane decreased when the electrosprining solution used to prepare H₄SiW₁₂O₄₀/PMMA layer was increased from 0.5 mL to 1.0 mL. When the H₄SiW₁₂O₄₀/PMMA layer was too thick, it could not be wetted adequately. MO dye molecules cannot penetrate into the membrane and contact with H₄SiW₁₂O₄₀ inside the membrane [21]. Although the total amount of H₄SiW₁₂O₄₀ increased, most of them was embedded inside the membrane and could not contact with MO. As a result, the photocatalytic activity of 1.0/2.5/1.0 sandwich nanofibrous membrane decreased slightly. On the basis of the above experimental results, we infer that the thickness of the
Fig. 4. (a) XPS spectra of H₄SiW₁₂O₄₀/PMMA composite nanofibrous membrane (upper layer). (b) W 4f scan. (c) O 1s scan. (d) C 1s scan.

Fig. 5. (a) UV–vis spectra of MO vs. photoreaction time catalyzed by sandwich nanofibrous membrane; (b) photodegradation of MO over different catalysts against irradiation time; photodegradation of MO against irradiation time (c) and kinetic linear fitting curves (d) of sandwich nanofibrous membranes with different H₄SiW₁₂O₄₀/PMMA layer thickness.
H$_4$SiW$_{12}$O$_{40}$/PMMA layer in the sandwich nanofibrous membrane is also an important factor influencing its photocatalytic activity.

The kinetics linear simulation curves of MO photocatalytic degradation over different sandwich nanofibrous membranes are displayed in Fig. 5d. The results show that the above degradation reactions follow a Langmuir-Hinshelwood apparent first-order kinetics model due to the low initial concentrations of the reactants [31]. In this experiment, the initial concentration of MO is 10 mg L$^{-1}$, so the model can be expressed by the following equation:

$$-\ln \left( \frac{C}{C_0} \right) = k_{app} t$$

where $C_0$ is the initial concentration of the reactant (mg L$^{-1}$), $C$ is the concentration of the reactant at time $t$ (mg L$^{-1}$), $t$ is the UV-light illumination time, and $k_{app}$ is the apparent first-order rate constant (min$^{-1}$) [32]. The determined $k_{app}$ is 0.097, 0.183 and 0.133 for the 0.25/2.5/0.25, 0.5/2.5/0.5 and 1.0/2.5/1.0 sandwich nanofibrous membranes, respectively. It is clearly demonstrated that the 0.5/2.5/0.5 sandwich nanofibrous membrane have better performance than that of other two samples, which further confirm the conclusion studied above.

3.2.2. Stability and reusability

Cycling uses as well as maintaining high photocatalytic activity was a critical issue for long-term use in practical applications of the

Fig. 7. SEM images of H$_4$SiW$_{12}$O$_{40}$/PMMA/PVA sandwich nanofibrous membrane (a) and H$_4$SiW$_{12}$O$_{40}$/PMMA/PVA composite nanofibrous membrane (b) after three-time cycling uses.
catalyst. In view of this, two factors were needed to be considered: one was how easy the catalyst could be separated from the reaction system; the other was the stability of the catalyst to maintain its high activity over time [33]. In this work, the sandwich nanofibrous membrane could be directly separated from the aqueous MO solution without any sophisticated separation technique. To examine the stability of the sandwich nanofibrous membrane, the membrane was used for three times. As shown in Fig. 6a, after three-cycle experiments, there was no obvious decrease in the photocatalytic activity of the sandwich nanofibrous membrane (0.25/2.5/0.25). As a comparison, the H2SiW12O40/PMMA/PVA composite nanofibrous membrane was also reused for three times under identical conditions, in which the photocatalytic activity decreased obviously (Fig. 6b).

To find out the reason, the leakage of H2SiW12O40 from the two membranes was tested in water (50 mL, pH 1.0) within 3 h. Each experiment was carried out with shaking and without UV irradiation. The degree of the leakage of H2SiW12O40 was measured by the absorbance at a wavelength of 260 nm, corresponding to one of the absorption peak of H2SiW12O40. The results are shown in Fig. 6c and d. The absorbance of 0.05 g H2SiW12O40 (equal to the mass of H2SiW12O40 in the two membranes) in 50 mL water was 1.26. Other three curves were derived from the absorbance of the water when stability experiments were conducted for 1 h, 2 h and 3 h, respectively. As seen in Fig. 6c, the absorbance of the water after stability experiment at 260 nm was all very low, indicating that the loss of H2SiW12O40 from the sandwich nanofibrous membrane was very little under the investigated conditions. However, as shown in Fig. 6d, the leakage of H2SiW12O40 from the composite nanofibrous membrane was relatively more serious. Fig. 7 shows the morphologies of two membranes after photocatalytic degradation of MO with three-time cycling uses. It is clear that the structure of H2SiW12O40/PMMA/PVA composite nanofiber disappeared, while the morphology of the H2SiW12O40/PMMA layer of sandwich nanofibrous membrane was almost unchanged. The above results demonstrate that the dissolution of PVA during the photocatalytic process affected the photocatalytic activity of H2SiW12O40/PMMA/PVA composite nanofibrous membrane more seriously than that of H2SiW12O40/PMMA/PVA sandwich nanofibrous membrane, owing to the different structure of the two membranes.

3.2.3. Photocatalytic mechanism of the sandwich nanofibrous membrane

The photooxidative degradation of azo dyes by POM has been reported in earlier studies. The process involved excitation of POM by UV–vis light, which led to the charge transfer from an O2− ion to WO6 ion at W−O−W bonds and the formation of a strongly oxidizing excited state of POM (POM*) or POM (h+ + e−). Photooxidation of the azo dye took place via the reaction through OH radicals or direct reaction of the excited POM with the substrate [7,10]. This photocatalytic processes is in analogy to TiO2 [34]. However, studies [11,35–37] have proved that in the presence of alcohol (methanol, ethanol and isopropanol) as sacrificial electron donor, the whole process was driven by the reductive pathway with much faster degradation rate. Along this direction, the effect of PVA on the photocatalytic activity of H2SiW12O40 powder was carried out in Fig. 8, where 72.9% degradation of MO was observed after 30 min irradiation for H2SiW12O40 (powder) + PVA redox system, while only 4.6% degradation for H2SiW12O40 powder was seen in the absence of PVA. The experimental findings suggest that PVA could significantly enhance the photocatalytic activity of H2SiW12O40. According to the literature [9] and the experimental results, the possible mechanistic scheme for the degradation of MO on the sandwich nanofibrous membrane under UV irradiation is proposed as the following:

\[
\text{H}_2\text{SiW}_{12}\text{O}_{40} + h\nu \leftrightarrow \text{H}_2\text{SiW}_{12}\text{O}_{40}^* \tag{1}
\]

\[
\text{H}_2\text{SiW}_{12}\text{O}_{40} + \text{PVA} \rightarrow \text{H}_2\text{SiW}_{12}\text{O}_{40} + \text{oxidation products} \tag{2}
\]

\[
\text{H}_2\text{SiW}_{12}\text{O}_{40} + \text{MO} \rightarrow \text{H}_2\text{SiW}_{12}\text{O}_{40} + \text{reduction products} \tag{3}
\]

H2SiW12O40 absorbs light and mediates the electron transfer from PVA, the sacrificial donor, to MO. Reactions (1) and (2) describe the photocatalytic oxidation of PVA and the simultaneous formation of H2SiW12O40, while Reaction (3) describes a fast reoxidation of H2SiW12O40 in the presence of MO molecules. PVA, like other alcohols, which possess readily abstractable α-H atoms may play an important role in the rate of H2SiW12O40 production and hence, in the degradation rate of azo dyes.

4. Conclusions

H2SiW12O40/PMMA/PVA sandwich nanofibrous membranes were prepared by electrospinning technique. IR, EDX and XPS characterization confirmed that H2SiW12O40 existed in the upper and bottom layers of the sandwich membrane. The Keggin structure of H2SiW12O40 was not destroyed in the process. The investigation of photocatalytic ability indicated that the sandwich nanofibrous membrane exhibited greatly enhanced photocatalytic activity in the decomposition of MO, which may be attributed to the large specific surface area of nanofibrous membrane and the photoreduction mechanism owing to the presence of PVA (intermediate layer). More importantly, the sandwich nanofibrous membrane containing H2SiW12O40 was stable in water, so that they could be easily separated and reused without any separation process. In view of this, H2SiW12O40/PMMA/PVA sandwich nanofibrous membranes exhibit attractive properties for potential applications in removing organic pollutants from wastewater.

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