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Photochromic properties of TiO_2-doped Keggin-type silicon-Molybdenum-Tungsten ternary heteropoly acid composite film

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A series of TiO_2/$SiMo_{11}W$/polyvinyl alcohol (TSP) composite films were prepared by TiO_2-doping as the third component in Keggin-type silicon-molybdenum-tungsten acid ($H_4SiMo_{11}W$)/polyvinyl alcohol (PVA). The microstructure of TSP was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). The results showed that the heteropoly acid and doping components were well dispersed in the organic network, and the basic structures of $H_4SiMo_{11}W$ and PVA in the composite film were undecomposed. TiO_2 doping enhanced the non-chemical bond interaction between the heteropoly acid and polymer. Under ultraviolet light (UV) irradiation, the TSP composite film changed from light yellow to blue. With the increase of TiO_2 addition, the color generation efficiency was significantly improved, which affected the microstructure of the composite film and resulted in different photochromic properties of the composite film.

Keywords: photochromic film, Keggin-type heteropolyacid, tungsten-molybdenum-silicic acid, polyvinyl alcohol, TiO_2.

УДК 54.04

Фотохромные свойства легированной TiO_2 композитной плёнки типа Кеггина на основе молибден-вольфрам-кремниевой гетерополикислоты

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Серия композитных плёнок TiO_2/$SiMo_{11}W$/поливиниловый спирт (TSP) была приготовлена путём легирования TiO_2 в качестве третьего компонента в вольфрам-молибден-кремниевую кислоту типа Кеггина ($H_4SiMo_{11}W$)/поливиниловый спирт (PVA). Микроструктура TSP была охарактеризована с помощью инфракрасной спектроскопии с преобразованием Фурье (FTIR) и рентгеновской дифракции (XRD). Результаты показали, что гетерополикислота и легирующие компоненты были хорошо диспергированы в органической сетке, а основные структуры $H_4SiMo_{11}W$

и PVA в композитной плёнке были не разложены. Легирование TiO_2 усилило нехимическое взаимодействие связей между гетерополикислотой и полимером. Под воздействием ультрафиолетового света композитная плёнка TSP изменила цвет со светло-жёлтого на синий. С увеличением содержания TiO_2 эффективность генерации цвета значительно улучшилась, что повлияло на микроструктуру композитной плёнки и привело к изменению фотохромных свойств композитной плёнки.

Ключевые слова: фотохромная плёнка, гетерополикислота типа Кеггина, вольфрам-молибден-кремниевая кислота, поливиниловый спирт, TiO_2.

Heteropoly acids (HPA) is a class of homogeneous inorganic polymers with M_3O_{13} trimetallic oxygen cluster structure, which are widely used in many fields because of their strong acidity, strong oxidation and high electron transfer ability [1–5]. In particular, one of the applications of HPA, as green and eco-friendly catalysts [4], is the treatment of wastewater from organic pollutants by photocatalysis. Due to its high efficiency, simplicity and easy control this method is finding increasing application in the degradation and destruction of organic pollutants [5]. To prevent HPA easy dissolution in water and recombination of hole-electron pairs HPA was carried on semiconductors as TiO_2 which increased the HPA specific area and synergy resulting in enhanced photocatalytic degradation [4].

In the trimetallic oxygen cluster structure M_3O_{13}, an octahedron (MO_6) composed of coordination atoms (represented by M) and oxygen atoms forms a polynuclear coordination structure containing oxygen bridges, which makes it have excellent electron acceptance ability. It can accept not only 1–2 electrons to form heteropoly blue, but also multiple electrons to form heteropoly brown, indicating that heteropoly acid has excellent photochromic properties. With the development of the information age, photochromic materials have attracted more and more attention due to their applications in optical information storage, optical conversion devices and optical switches. Over the past two decades, in order to improve the chromogenic efficiency of heteropoly acid photochromic materials and the mechanical processing performance of heteropoly acids, Keggin-type heteropoly acids as the molecular-based materials was used to construct inorganic-organic photochromic materials has become a research hotspot through hydrogen bonds and covalent bonds interacting with organic polymer macromolecules. Among them, the heteropoly acid composite films prepared using water-soluble polymer with active groups as the substrate, such as polyvinyl alcohol [6], polyvinylpyrrolidone [7], polyacrylamide [8] polyvinylidene [9], and so on, have the advantages of good film-forming property, high photoreduction efficiency, mild preparation conditions and simple preparation methods. Some research results show that the electrons in organic molecules can be transferred to heteropoly acid through the charge transfer bridge formed by hydrogen bond under UV light, which causes heteropoly acid to undergo photoreduction reaction and change color to produce heteropoly blue. The charge intensity of the surface of different organic functional group is different, and their activity in the photoreduction process is also different. The interaction between heteropoly acid and organic substrate has a significant effect on the photochromic properties and microstructure of the composite films. The aforementioned research contents involved the influence of component and the structure of thin film materials on the photochromic performance, and the study of reaction mechanism, which was mainly concentrated in the Keggin structure binary heteropoly acid compounds. Generally speaking, tungsten heteropoly acid is acidic, molybdenum heteropoly acid oxidation is strong, by changing its composition, can adjust the acidity and oxidation of heteropoly acid, which is conducive to the exploration of photochromic properties [10–12]. At present, there are few studies on the preparation of ternary substituted heteropoly acids by tungsten and molybdenum substitution and the modulation of photochromic properties of heteropoly acids [13, 14].

TiO_2 is a semiconductor conductive material with stable chemical properties and green environmental protection. It has photoreducing activity similar to heteropoly acid. When added to heteropolyacid as the third component, TiO_2 will induce the photochemical activity of heteropolyacid and enhance its photochromic performance. In this paper, an inorganic-organic composite film was prepared, which composed of nano-TiO_2 doping the ternary substituted heteropoly acid $H_4SiMo_{11}W$ and polyvinyl alcohol (PVA). Photochromic properties and affecting factors of the film were studied.

Objects and methods of research

$Na_2WO_4 \cdot 2H_2O$, $Na_2MoO_4 \cdot 2H_2O$ was purchased from Shanghai Sinopharm Chemical

Reagent Co., Ltd., $Na_2SiO_3 \cdot 9H_2O$ was purchased from Shenyang Xindong Reagent Factory, and P25 nano titanium dioxide TiO_2 was obtained from Aladdin Reagent Co., Ltd. Vinyl alcohol (PVA 1799) is the product of Beijing Xinguang Chemical Reagent Factory. The reagents used above are all analytically pure, and the water is deionized water.

The infrared spectrum was collected by WRF-510 FT-IR spectrometer and the scanning range was between 400 and 4000 cm^{-1}. The UV-visible spectrum was obtained by TU-1950 Ultraviolet-visible spectrophotometer. X-ray diffraction pattern was obtained by Rigaku D/max-rB X-ray diffractometer.

Keggin-type $H_4SiMo_{11}W$ was synthesized according to the reported literature [15, 16]. The $SiMo_{11}W$ was added to deionized water with stirred at 65 °C and 10 mg/mL $SiMo_{11}W$ aqueous solution was obtained. The aqueous solution of $SiMo_{11}W$ was added to an equal volume of 1 wt% PVA solution with stirring under dark condition at 65 °C for 2 hours. After cooling to room temperature, a $SiMo_{11}W$/PVA yellow transparent composite liquid was obtained. The TiO_2 powder was added to deionized water under ultrasonic at room temperature for 30 min to prepare 1 wt% suspension. 5μL, 10μL, 20μL and 30μL of the TiO_2 suspension were added to 20 mL of the $SiMo_{11}W$/PVA composite liquid under ultrasonic for 1 hour at dark condition to obtain $TiO_2/SiMo_{11}W$/PVA composite liquid. Then 10 μL of $TiO_2/SiMo_{11}W$/PVA composite liquid was coated on the glass substrate by spin coating method and dried at room temperature, and then a pale yellow transparent composite film having a film thickness of about 2 μm was obtained. The composite films were named as I – $TiO_2/SiMo_{11}W$/PVA, II – $TiO_2/SiMo_{11}W$/PVA, III – TiO_2/ $SiMo_{11}W$/PVA and IV – $TiO_2/SiMo_{11}W$/PVA, respectively. The detailed content of composite film is in Table 1.

The film photochromic performance test was carried out using a PLS-SXE300 UV400W xenon lamp as the ultraviolet light source, and the main emission wavelength was 365 nm. The distance between the sample and light source was 10 cm and light exposure time was 1–2 min. The UV-visible absorption spectrum was obtained by scanning with TU-1950 UV-Vis spectrophotometer in the wavelength range of 300–900 nm until the absorption peak intensity of the test was consistent with the previous one, and the absorbance intensity reaches saturation, the coloring process of the composite film was finish.

Results and discussion

Figure 1 (see color insert I) displayed the FTIR spectra of pure $SiMo_{11}W$, PVA, $SiMo_{11}W$/PVA, $TiO_2/SiMo_{11}W$/PVA composite films. As shown in Table 2 and Figure 1, the characteristic peak of pure PVA was located at 3300cm^{-1} (-OH stretching vibration); 2900 cm^{-1} (C–H stretching vibration), 1425 cm^{-1} and 1320 cm^{-1} (C–H bending vibration), 1100 cm^{-1} (C–C) vibration peak. The characteristic peaks of PVA also existed in curve of $SiMo_{11}W$ and curve of $TiO_2/SiMo_{11}W$/PVA, were not damaged after recombination with heteropoly acids. Four characteristic peaks of the Keggin-type heteropoly acid $SiMo_{11}W$ [17], which were $\nu_{(M\text{-}Od)}$ at 958 cm^{-1}, $\nu_{(Si\text{-}Oa)}$ at 914 cm^{-1}, $\nu_{(M\text{-}Ob\text{-}M)}$ at 858 cm^{-1}, and $\nu_{(M\text{-}Oc\text{-}M)}$ at 773 cm^{-1}, displayed a slight shift when $SiMo_{11}W$ combined with TiO_2 and PVA. Comparing curve of $SiMo_{11}W$/PVA and curve of $TiO_2/SiMo_{11}W$/PVA, it can be seen that four characteristic stretching vibration peaks of Keggin-type heteropolyacid $SiMo_{11}W$ still exist after adding TiO_2. Furthermore, the peaks shift also occurred. This phenomenon results from the electrostatic force between two phases of polyacid anion and polymer substrate after the addition of TiO_2. That can be attributed to hydrogen bonding interaction or electrostatic force between polyacid anion and polymer substrate. It can be found that the vibration peaks position of $\nu(M\text{-}O_d)$ and $\nu(Si\text{-}O_a)$ if composite films were red shifted, and the vibration peaks of $\nu(M\text{-}O_c\text{-}M)$ weakens or even disappeared, inferring that the heteropoly acid $TiO_2/SiMo_{11}W$/PVA composite film had undergone photoreduction.

Table 1

The detail content of composite film

Name	10 mg/mL $SiMo_{11}W$	1wt% PVA	1wt% TiO_2
I – $TiO_2/SiMo_{11}W$/PVA	10 mL	10 mL	5 μL
II – $TiO_2/SiMo_{11}W$/PVA	10 mL	10 mL	10 μL
III – $TiO_2/SiMo_{11}W$/PVA	10 mL	10 mL	20 μL
IV – $TiO_2/SiMo_{11}W$/PVA	10 mL	10 mL	30 μL

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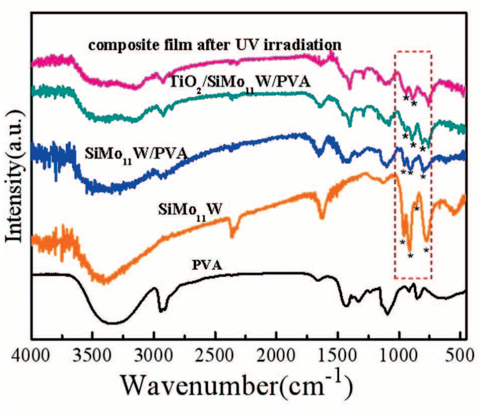

Fig. 1 FTIR spectra of different samples. Asterisk indicates major peaks (see text)

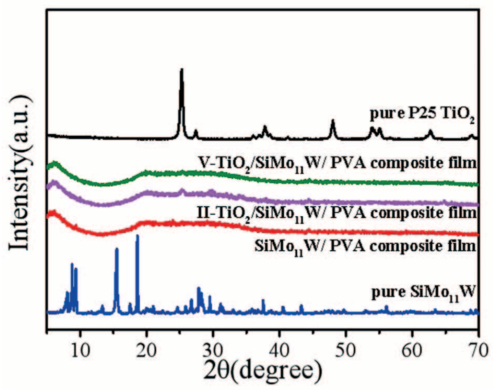

Fig. 2 XRD patters of different samples

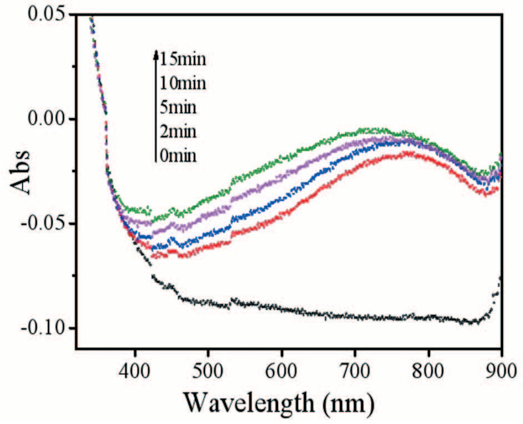

Fig. 3. UV-Vis adsorption spectra of $SiMo_{11}W/PVA$ composite film

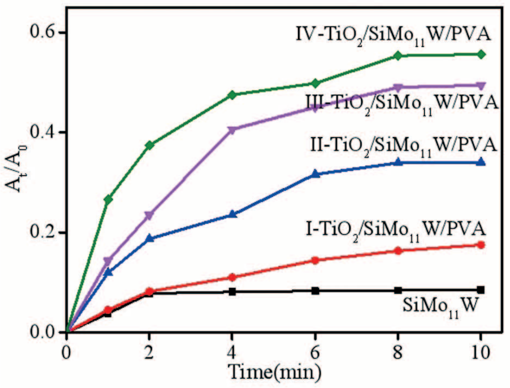

Fig. 4. The change of absorbency for the $TiO_2/SiMo_{11}W/PVA$ composite films containing different TiO_2 content *vs* UV irradiation time at 764 nm

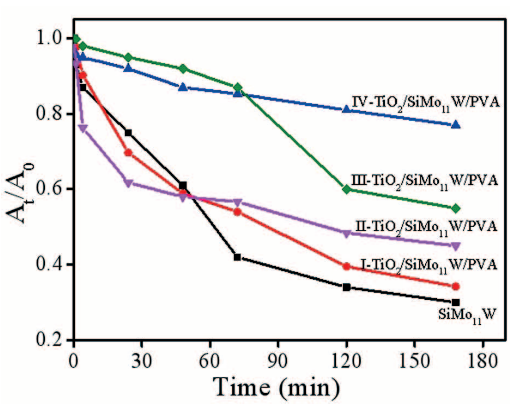

Fig. 5. The change of absorbency for the $TiO_2/SiMo_{11}W/PVA$ composite films containing different TiO_2 content *vs* bleaching time at 764 nm

Table 2

The detail IR spectra of compounds at 1000–700 cm^{-1}

Indicator	ν_{as}(M-O_d)	ν_{as}(Si-O_a)	ν_{as}(M-O_d-M)	ν_{as}(M-O_c-M)
$TiO_2/SiMo_{11}W$/PVA(UV)	937	891	–	–
$TiO_2/SiMo_{11}W$/PVA	943	893	–	809
$SiMo_{11}W$/PVA	951	907	–	800
$SiMo_{11}W$	958	914	858	773

Note: a dash indicates no peaks.

Figure 2 (see color insert I) demonstrated XRD patterns of pure $SiMo_{11}W$, TiO_2, $SiMo_{11}W$/PVA, II-$TiO_2/SiMo_{11}W$/PVA composite film and IV-$TiO_2/SiMo_{11}W$/PVA composite film. A series of characteristic diffraction peaks at 6–12°, 16–22°, 22–30°, and 32–38° suggested the Keggin-type structure and crystalline state of pure $SiMo_{11}W$ [18], which was in accordance with that of FTIR. Some weak diffraction peaks in the heteropoly acid composite film can be found in the range of 2θ=6–10°, corresponding to the diffraction peaks of $SiMo_{11}W$. That indicated the primary structure of the heteropoly acid anion still existed in the structure of composite films. The sharp characteristic diffraction peaks of heteropoly acid and TiO_2 disappeared instead of broad dispersion peaks in the range of 2θ=15–70°, suggesting that heteropoly acid and TiO_2 were dispersed in the PVA network uniformly, and the diameter of dispersed particles was small enough so that the crystal features disappeared, thus the composite films exhibited an amorphous state. With the increase of TiO_2 addition, the XRD pattern of IV-$TiO_2/SiMo_{11}W$/PVA composite film showed a diffraction peak at 2θ=25°, manifesting the existence of TiO_2 in the composite film.

The composite film formed on the activated glass wafer by the drop film method was transparent light yellow when unirradiated by ultraviolet light. However, the film changed from light yellow to blue after a few minutes under ultraviolet light.

Figure 3 (see color insert I) was UV-Vis adsorption spectra of $SiMo_{11}W$/PVA and $TiO_2/SiMo_{11}W$/PVA composite film. For the light-yellow composite film, no adsorption peak appeared in the wavelength range of 300–900 nm without any irradiation. After ultraviolet-light irradiation, a broad absorption peak at 720–800 nm emerged following irradiation time. Meanwhile, the blue color of the composite film was gradually deepened. With the increased of the irradiated time and the amount of TiO_2 added, the absorption peak in the visible light region undergoes a blue shift. This phenomenon can be attributed to the IVCT (intervalence charge transfer) transition of single electron transfer, which can be considered as the characteristic absorption band of Heteropoly blue which formed by $SiMo_{11}W$ electron reduction. From Figure 4 (see color insert I), it can be found that the $SiMo_{11}W$/PVA film reached saturation after being exposed to light for 15 min. Nevertheless, only UV irradiating 10 min, TiO_2 /$SiMo_{11}W$/PVA composite film was achieved saturation (Figure 3). During the UV-light irradiation process, O–H and W=O bonds gradually disintegrate, and the heteropoly acid was reduced (Mo(VI)→Mo(V)). Along with the duration of UV-light irradiation time, the number of Mo(VI) atoms decreased while the number of Mo(VI) atoms increased. After addition of TiO_2, the interaction between $SiMo_{11}W$ and PVA was enhanced, correspondingly improving the oxidizing property of the heteropoly acid.

It can be seen from Figure 4 that the maximum absorbance of the $TiO_2/SiMo_{11}W$/PVA composite film tends to saturate with the extension of the UV light time. Moreover, the peak absorption strength of the composite film increases with an increase in the amount of TiO_2 in the same conditions and the absorbance of the composite film reached 0.10, 0.176, 0.33, 0.50 and 0.553, respectively with an increase in TiO_2 content at saturation. As a result, the light absorption efficiency of the composite film was improved, and the photochromic effect of the ternary composite film was enhanced with the addition of TiO_2. From the UV–Visible spectrum of TiO_2/SiWo11W/PVA composite film, with the increasing of the TiO_2 addition, the absorption peak underwent a blue shift. That can be attributed to the intervalence charge transfer (IVCT) of the single electron transfer, which indicates the characteristic heteropoly blue absorption formed due to the electron reduction of $SiMo_{11}W$.

Figure 5 (see color insert I) displayed the fading process for the TiO_2 / $SiMo_{11}W$ / PVA composite film. After the UV light source was turned off, the composite film was gradually fade in a dark place. If the TiO_2 / $SiMo_{11}W$ / PVA composite film was stored in nitrogen or vacuum after UV-light irradiation, the color of the film can be maintained for about three days. Then the fading process will be continued as the film was placed in dark with air or oxygen. This phenomenon suggested that the oxygen in the air played an important role in the discoloration of the composite film. From the plots of I – $TiO_2/SiMo_{11}W$/PVA, II – $TiO_2/SiMo_{11}W$/PVA and $SiMo_{11}W$/PV in Figure 5, the composite film with TiO_2 addition, the color removal rate showed a significant acceleration. However, the decolorization rates of curves for III – $TiO_2/SiMo_{11}W$/PVA and IV – $TiO_2/SiMo_{11}W$/PVA was rather slow with increase of the TiO_2 addition amount increasing. The rate of color fading of the film was related to the rate of oxygen intake and transmission. The addition of TiO_2 made the composite film structure loose, improving its permeability and enhancing the speed of oxygen participating in the oxidation reaction. As the amount of TiO_2 increasing, the coverage ability of TiO_2 nanoparticles enhanced, reducing the oxygen transmission speed and resulting in a slower fading speed. On the other hand, TiO_2 nanoparticles had the ability to capture oxygen, which resulted in the amount of oxygen cut down during the oxidation reaction of Mo(V). Therefore, the decolorization speed decreased as the addition of TiO_2 nanoparticles increased.

Conclusion

A series of novel composite films was obtained by doping TiO_2 in $H_4SiMo_{11}W$/PVA composite films. Heteropoly acid and TiO_2 were well dispersed in the PVA organic network, and TiO_2 showed amorphous in composite films. Composite films exhibited reversible photochromism. The peak absorption strength of the composite film increases with an increase in the amount of TiO_2 under the same conditions. The photochromic efficiency of the heteropolyacid composite film is significantly higher than the undoped composite film. However, the discoloration speed of the composite film decreases significantly as the doping amount increases. Thus, photochromic efficiency of the composite films effectively improved and discoloration speed slowed down by doping TiO_2.

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