

# Preparation and Characterization of 9-Phosphotungstic Acid Photochromic Glass Coatings

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**Abstract:** WO<sub>3</sub>-Polymer hybrid sol was prepared from self-prepared 9-Tungstophosphate acid based on polyvinylpyrrolidone (PVP) by alcoholysis at a certain temperature. Coatings on glass substrates were obtained by spraying technique and subsequently dried at room temperature. The transparent WO<sub>3</sub>-Polymer coatings could be transformed to blue after exposed to the sun light for less than 10 s. X-ray diffractometer (XRD) and scanning electron microscope (SEM) analysis were employed to characterize the crystal structure and surface morphology of these coatings. Changes in the visible light transmittance of the thin films were measured with spectrometer irradiated under UV light. The results indicate good photochromic and decoloration behavior of the coatings.

**Key words:** photochromic; 9-phosphotungstic acid; glass coatings

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Photochromic phenomenon has been found for over a century. Most of photochromic materials are organic such as woad, triphenylmethane, azobenzene, and so on<sup>[1]</sup>. Inorganic photochromes offer only a limited colour range and are not suitable for treating organic polymeric substrates as there exists no coating material for such an application, but photochromic polymeric lenses have been obtained with organic photochromic dyes by thermal transfer technique (high processing costs)<sup>[2]</sup>. Soft polymers are not applicable because of the poor mechanical properties. In order to fulfill these antagonistic demands, some general approaches of a nanocomposite material with ceramic nanoparticles in an organic-inorganic matrix were chosen for the development of photochromic coatings with a great variety of colors for glass and plastic substrates<sup>[3]</sup>. Since the first report on the photochromic properties of  $\alpha$ -WO<sub>3</sub> by Deb in 1973, the preparation, microstructure and photochromic properties of the WO<sub>3</sub> have been studied in these years<sup>[4]</sup>. Silicone doping WO<sub>3</sub> thin films was prepared by sol-gel<sup>[4]</sup> and Keggin type 12-Tungstophosphate acids based on Polyvinyl Pyrrolidone (PVP) was also prepared<sup>[5]</sup>. 9-Tungstophosphate acid was prepared at first and then WO<sub>3</sub>-Polymer hybrid sol was prepared with 9-Tungstophosphate acid based on polyvinylpyrro-

lidone (PVP) by alcoholysis at a certain temperature. Coatings on the glass substrate were obtained by the spraying technique. Coatings were dried at room temperature. The coating structure and hybrid sol characteristic have been analyzed and discussed.

## 1 Experimental

9-Tungstophosphate acid was prepared at first. Polyvinylpyrrolidone (PVP) dissolved in alcoholic solution. And then WO<sub>3</sub>-Polymer hybrid sol was prepared with 9-Tungstophosphate acid based on polyvinylpyrrolidone (PVP) by alcoholysis at a certain temperature.

Coatings on the glass substrate were obtained by the spraying technique or dip coating. Coatings were dried at room temperature

The corresponding structure, surface morphology, constituent phase and photochromic behavior of coatings were investigated with FTIR-8300PCS infrared spectrometer (Shimadzu), D8 X-ray diffraction (Germany), S-3400N (II) scanning electron microscope (Japan) and UV-2501PC spectrometer (Shimadzu).

## 2 Results and Discussions

### 2.1 Transmittance

Average transmittance of the glass substrate before

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light exposure is 89% (Fig.1 curve a) and average transmittance of the coating before light exposure is 87.5% (Fig.1 curve b). Fig.2 gives two conclusions. First, the main absorption of visible light of the WO<sub>3</sub>-polymer coating are from 550 nm to 580 nm olivine light area, 580 nm to 600 nm yellow light area, 600 nm to 650 nm orange light area, and 650 nm to 700 nm red light area. Second, decrease rate of the coating, which has been irradiated in different time, is faster during the first 10 min than the last 20 min. In the first 10 min, average transmittance decrease is 1.4 nm/min at 550, 1.7 nm/min at 600 and 2.2 nm/min at 650 nm and in last 20 min, average transmittance decrease is 0.7 nm/min at 550, 0.8 nm/min at 600 and 0.8 nm per minute at 650 nm. Transmittance of the coating increases quickly when the coating is laid in the room after irradiation for 45 min. Average transmittance increase during 40 min is 1 nm/min at 700 nm (Fig.3). Photo responsive rate is faster than that of the WO<sub>3</sub>-SiO<sub>2</sub> thin films<sup>[4]</sup>.

**2.2 Surface morphology**

Fig.4 is the surface morphology of WO<sub>3</sub>-polymer. The surface of the coating, which has not been irradiated under mercury lamp, is uniform. The surface of the coating, which has been irradiated for 45 min and then laid for 40 min in the room, is also uniform (Fig.5). Thus, the coatings are very uniform when these coatings are

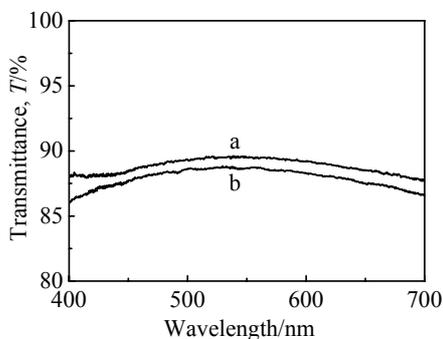


Fig.1 Transmittance of the non-coating glass substrate (a) and the WO<sub>3</sub>-Polymer coating (b) before light exposure

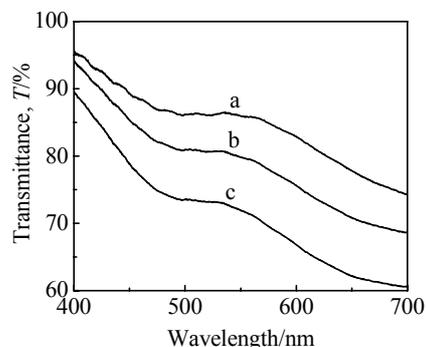


Fig.2 Transmittance of the WO<sub>3</sub>-polymer coating irradiated by 60 W mercury lamps for 10 min (a), 20 min (b), and 30 min (c)

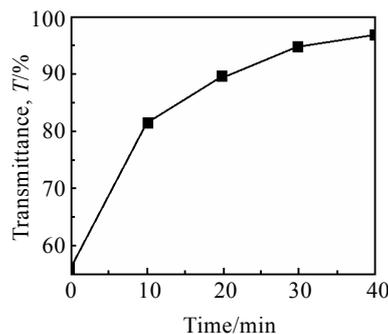


Fig.3 Decoloration transmittance of the WO<sub>3</sub>-Polymer coating irradiated at 700 nm by 60 W mercury lamps for 45 min

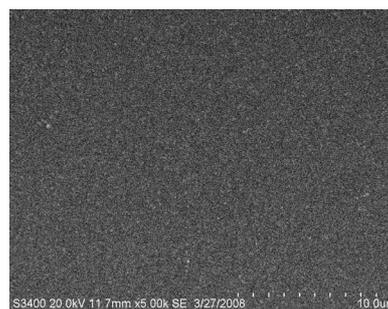


Fig.4 SEM image of the WO<sub>3</sub>-polymer coating before irradiation

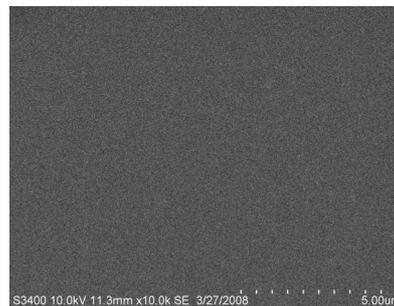


Fig.5 SEM image of the WO<sub>3</sub>-polymer coating irradiated for 45 min and laid for 40 min in the room

prepared by the spraying technique or dip coating process. 9-tungstophosphate acid and polyvinylpyrrolidone (PVP) form the compact network structures through reacting with the alcoholic solution. This structural network makes the coating stable and uniform.

**2.3 Phase structure**

The phase structure of the xerogels prepared from colloid solutions with different temperatures was analyzed by XRD (Fig.6). It can be seen that hybrid xerogel which had been heated for 24 h at 80 °C and 30 min at 165 °C have an amorphous peak near 25° (Fig.6). Thus, the hybrid xerogel is amorphous at a lower temperature. The xerogel whose heat-treatment temperature is below 150 °C is amorphous and the crystallization begins when treated at 450 °C<sup>[6]</sup>.

## 2.4 Structure

The structures of the hybrid xerogel are analyzed by infrared spectrometer (Fig.7). The hybrid xerogel have  $\nu(\text{P-O}_a)$ ,  $\nu(\text{W-O}_d)$ ,  $\nu(\text{W-O}_b\text{-W})$  and  $\nu(\text{W-O}_c\text{-W})$  expansion and contraction vibration peak near 1079, 970, 890 and 800  $\text{cm}^{-1}$  which belong to Polyvinylpyrrolidone showing that phosphotungstic acid retains Keggin type heteropolyacid structure. The hybrid has  $\nu\text{N-H}$  bending vibrations peak near 1508  $\text{cm}^{-1}$ , indicating that PVP combine with proton and salt form with heteropoly anion built between the two charge-transfer bridges<sup>[5]</sup>.

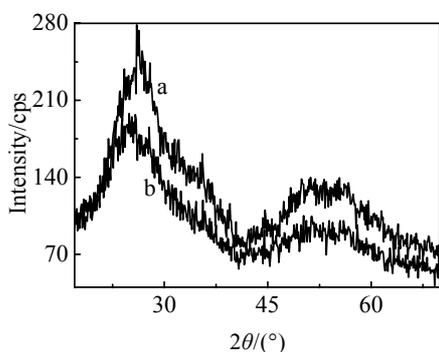


Fig.6 X-ray diffraction patterns of the  $\text{WO}_3$ -polymer xerogel heat-treated at 165 °C (a) and 80 °C (b)

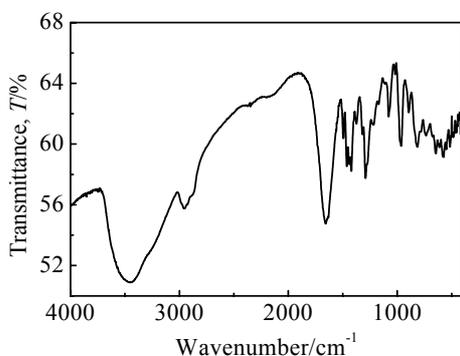


Fig.7 Transmittance of the  $\text{WO}_3$ -Polymer hybrid xerogel heat-treated at 100 °C for 60 min

ion and contraction vibration peak near 1079, 970, 890 and 800  $\text{cm}^{-1}$  which belong to Polyvinylpyrrolidone showing that phosphotungstic acid retains Keggin type heteropolyacid structure. The hybrid has  $\nu\text{N-H}$  bending vibrations peak near 1508  $\text{cm}^{-1}$ , indicating that PVP combine with proton and salt form with heteropoly anion built between the two charge-transfer bridges<sup>[5]</sup>.

## 3 Conclusion

Organic-inorganic composite of  $\text{WO}_3$ -Polymer coating was prepared by a sol-gel method. It was observed that the addition of alcoholic solution and polymer could bring good photochromic and decoloration behavior to the coating.

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## 9-磷钨酸光致变色玻璃涂层的制备与表征

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**摘要:** 自制的 9-磷钨酸与高聚物如聚乙烯吡咯烷酮、聚乙烯醇等在一定温度下的醇溶液中醇解得到混合溶胶样品, 采用喷涂法或浸渍涂布法在玻璃基板上成膜, 常温干燥得到具有光效应的涂层。透明的玻璃涂层在日光照射下 10 s 变蓝色。用 XRD、SEM、UV-可见分光光度计、红外光谱分析仪等对薄膜以及粉末的特性进行了测试。实验结果表明该涂层具有良好的光致变色消色特性。  
**关键词:** 光致变色范; 9-磷钨酸; 玻璃涂层

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