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Sol-Sol Doping WO_3 Gasochromic Thin Films with Improved Hydrogen-Sensing Properties

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Abstract: WO_3-TiO_2-SiO_2 sol was prepared for dip coating room-temperature optical hydrogen-sensing thin films. SEM, AFM, TEM, FT-IR, XPS and UV-VIS-NIR spectroscopy were used to study the composite films and their gasochromic properties. Though TiO_2 is not doped into the film, it can form WO_3 particles during the doping stage in sol. These particles are well distributed on the films and improve the roughness of the films. The results of hydrogen sensing test prove that TiO_2-doped films show better sensitivity than WO_3-SiO_2 films. The improvement of sensitivity may be assigned to the existence of WO_3 particles and high roughness of the films.

Key words: sol-gel; WO_3 film; coating; hydrogen sensing properties

Hydrogen is considered as one of the most promising clean and renewable energy carriers for use in industry[1]. Unfortunately, H_2 has a wide explosive limit (4%~74.4%) and it is easy to leak because of its small molecule. Therefore, hydrogen sensors which can sensitively and safely respond to H_2 are key for the development of "hydrogen economy". For now, hydrogen sensor can be divided into thermal conductivity, semiconductor, electrochemical and optical sensor[2], which mainly work under the electrical circuits. However, the possibility of electrical spark still threats the safety of these sensors.

The optical sensor, which can detect hydrogen through optical fibers and keep measurements electrical circuits away from hydrogen, has received much attention [3-7]. Remote measurements ensure the safety of the sensor even when the measure devices produce electrical sparks accidently. Optical sensor could base on gasochromic devices such as $WO_3/PdCl_2$ thin films[5,8-10], which can dramatically change its transmittance reversibly when exposed to H_2 even at room temperature. Unfortunately, pure WO_3 films' low sensitivity and transmittance changing speed restrict their applications. Therefore, many of works focus on improving WO_3 gasochromic properties, including changing catalysts[11,12] or coating methods[5,13,14] and adjusting WO_3 microstructures[8,15,16].

Doping is also an important method to improve gasochromic properties[17,18]. D. Li et al[19] presents a gasochromic performance with ultrafast coloring-bleaching rates and totally reversibility and stability by doping SiO_2, which are attributed to the silica matrix providing an excellent porous structure for WO_3[20]. Our group reports a WO_3-TiO_2 hydrogen sensing films but they still need more improvements[21].

In this work, we synthesized a Sol-Gol doped WO_3-TiO_2-SiO_2 films with improved hydrogen sensing property based on WO_3-SiO_2 films via sol-gel methods. The improvement of sensitivity was due to the increase of the surface roughness.

1 Experiment

All of the chemical reagents used in experiment are of analytical grade except acetylacetone (AcAc) and tetrabutyl titanate (TBOT) are chemical pure. The preparation routes of WO_3[22] and TiO_2[23] sol are seen in Ref.[22,23]. Metal tungsten was used as precursor and oxide by H_2O_2; after centrifugal and reflux, the WO_3 sol was obtained; for TiO_2 sol, the TBOT were mixed with EtOH to form solution A, and the mixture of EtOH, HCl, AcAc and H_2O was solution B. The solution B was added dropwise to solution A, and reacted for 1 h. Then the solution was refluxed and the TiO_2 sol was obtained.

The doping sol was prepared as followed: 1 mL of TiO_2 sol was added dropwise to the 50 mL WO_3 sol; after stirring, 11.3 mL TEOS was added into the sol. Then the solution was centrifuged for removing large particles. After that, the WO_3-TiO_2-SiO_2 sol was synthesized. In contrast, WO_3-SiO_2 sol was prepared alike without TiO_2 doping and centrifugation.

FESEM (Philips-XL-30FEG) and AFM (Bruker Edge) were used to determine the surface morphologies of films; the sol were investigated by TEM (JEOL-1230); the chemical

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structure of the film were studied by FTIR (TENSOR27, Bruker OpTik Gmbh) and XPS (PHI5300); the XRD (D/MAX2550) was used to analyze the phase of TiO_2; UV-VIS-NIR spectrophotometer (V-570, Jasco) was used for transmittance measurements.

2 Result and Discussion

2.1 Phase of the TiO_2

XRD patterns of the TiO_2 xerogel is shown in Fig.1. According to the JCPDF: 21-1272, TiO_2 xerogel are anatase. The crystalline TiO_2 was formed in the reflux process[24].

2.2 Characterization of the sol

Fig.2 is the TEM images of the sol. The WO_3 are amorphous in sol, and there is no significance difference between WO_3-TiO_2-SiO_2 sol and WO_3-SiO_2 sol. According to the EDX, there is no signal of TiO_2 in WO_3-TiO_2-SiO_2 sol.

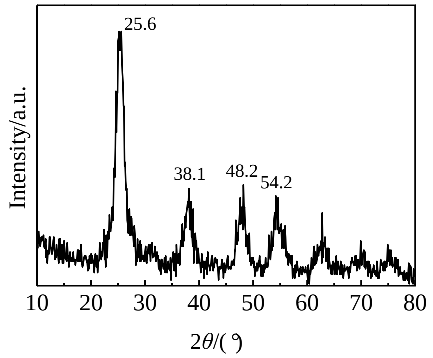

Fig.1 XRD pattern of the TiO_2

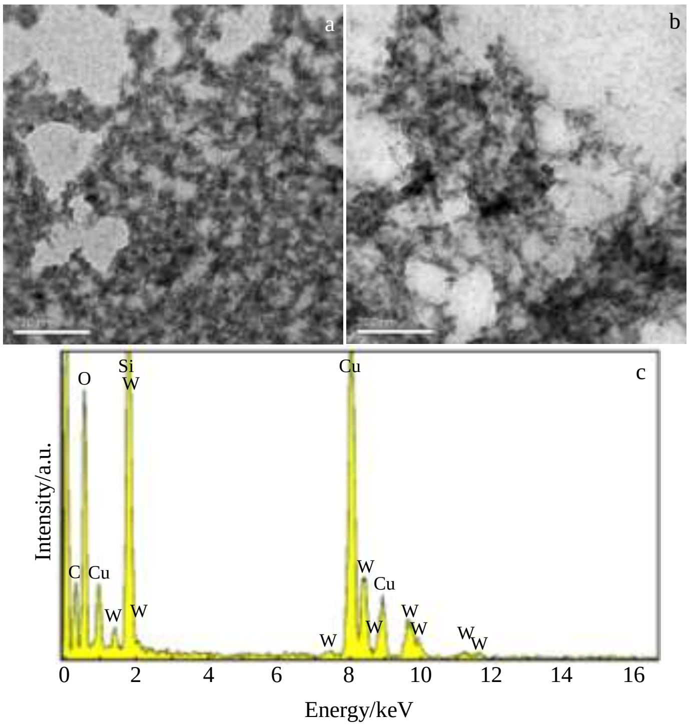

Fig.2 TEM images (a, b) and EDX results (c) of sol: (a) WO_3-SiO_2 sol, (b) WO_3-TiO_2-SiO_2 sol, and (c) WO_3-TiO_2-SiO_2 sol's EDX result

2.3 Characterization of the thin films

Fig.3 are the FTIR spectra of the films. Peak at 800 cm^{-1} may be assigned to edge-sharing W-O-W stretching, while the band around 960 cm^{-1} is ascribed to terminal W=O stretching[25]. The most intense 1076 and 1182 cm^{-1} bands are assigned to the transverse optic (TO) and longitudinal optic (LO) modes of the asymmetric Si-O-Si stretching vibrations, respectively[26]. Peaks around 3070, 3240 and 3450 cm^{-1} are related to OH with hydrogen bond, coordinated H_2O and crystal water, respectively. A small peak at 890 cm^{-1} may be contributed from Si-O^- in-plane stretch[27].

Fig.4 is the FESEM images of the films. Comparing with two films, it is obvious that the surface of the WO_3-TiO_2-

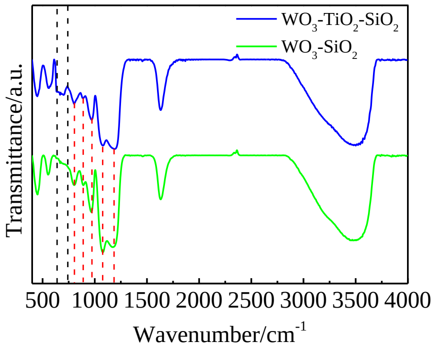

Fig.3 FTIR spectra of the films

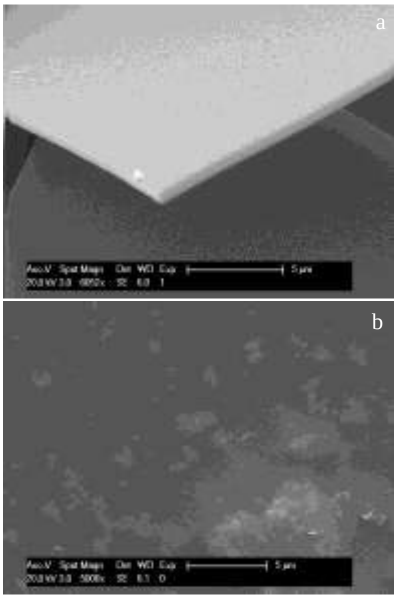

Fig.4 FESEM images of the films: (a) WO_3-SiO_2 and (b) WO_3-TiO_2-SiO_2

SiO_2 films present large particles, and the WO_3-SiO_2 films only have a smooth surface. However, same as TEM, the EDX shows no signal of TiO_2 in WO_3-TiO_2-SiO_2 films.

Fig.5 is the AFM results of the films. The AFM also shows the large particles on the WO_3-TiO_2-SiO_2 films, which fit with the FESEM results. It leads to a larger surface roughness (1.8 nm) of the WO_3-TiO_2-SiO_2 film than that of WO_3-SiO_2 films (0.628 nm).

The XPS results of films are shown in Fig.6. The box in Fig.6a shows the Ti peak's position. One can conclude that there has no evidence of TiO_2 in WO_3-TiO_2-SiO_2, and it fit with the EDX results. The spectra of W 4f level are shown in Fig.6b, 6c, and the fitting results are listed in Table 1. The results are fitted with previous research[28].

2.4 Optical properties

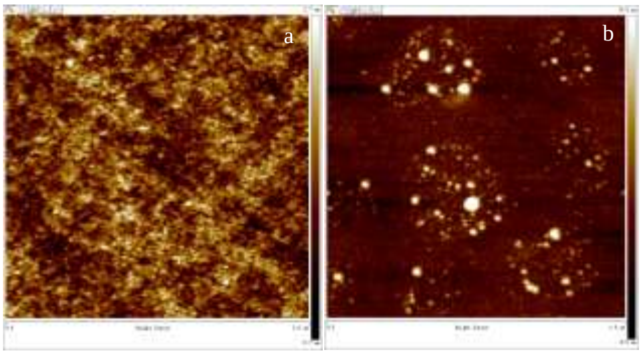

Fig.5 AFM images of the films: (a) WO_3-SiO_2 and (b) WO_3-TiO_2-SiO_2

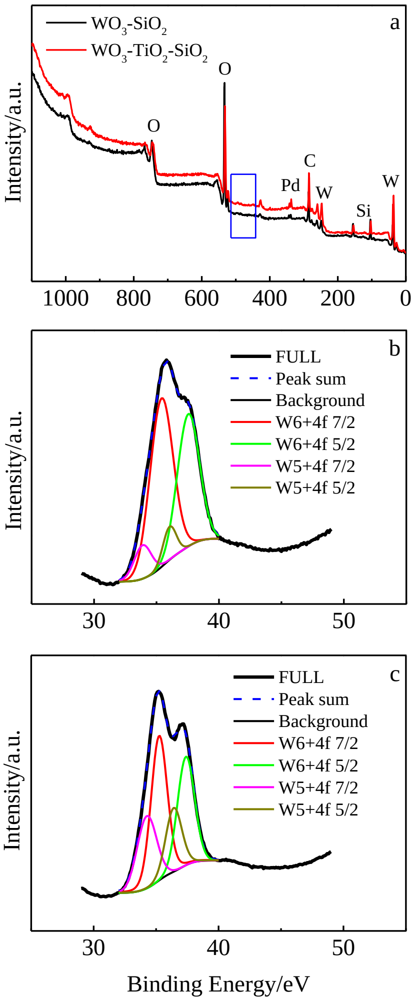

Fig.6 XPS spectra of the films: (a) full spectrum; W 4f level XPS spectra for WO_3-SiO_2 film (b) and WO_3-TiO_2-SiO_2 film (c)

Fig.7 Shows the gas sensing properties of WO_3-TiO_2-SiO_2 films and WO_3-SiO_2 films. The test was performed in a 600 mL chamber. After pump to vacuum, a certain volume of 10% H_2/Ar gas was injected into the chamber, and then the transmittance difference of the films was measured. At 30 mL, both of films have a large transmittance difference; at 20 mL, the WO_3-SiO_2 film's transmittance difference decreases to 35%, but WO_3-TiO_2-SiO_2 film still has a similar transmittance difference as 30 mL; when the hydrogen drops to 10 mL, the WO_3-TiO_2-SiO_2 film shows a smaller transmittance difference but can't remain at colored state. It may be assigned to the competition of remained oxygen inside the chamber.

2.5 Discussion

According to Fig.3, different films' FTIR are basically the same except the band between 630~730 cm^{-1}. Though TiO_2 may have peaks in this range, the EDX and XPS show no evidence of TiO_2, which may be ascribed to the large WO_3 particles[29].

The XPS results show significant difference in valence of W between two films, WO_3-SiO_2 film has a W^{6+}/W^{5+} at 6.61

Table 1 Peak synthesis for XPS-spectrum of W 4f-level

Sample	Tungsten oxidation states	Spin separation	Position/eV	ΔE(4f5/2-4f7/2)/eV	Width/eV	Area/%
WO_3-SiO_2	W^{6+}	W 4f5/2	37.55	2.15	2.08	37.23
		W 4f7/2	35.4	2.15	2.17	49.64
	W^{5+}	W 4f5/2	36.04	2.15	1.25	5.62
		W 4f7/2	33.89	2.15	1.63	7.50
WO_3-TiO_2-SiO_2	W^{5+}	W 4f5/2	37.39	2.15	1.62	27.35
		W 4f7/2	35.24	2.15	1.53	36.47
	W^{5+}	W 4f5/2	36.41	2.15	1.52	15.51
		W 4f7/2	34.26	2.15	1.83	20.68

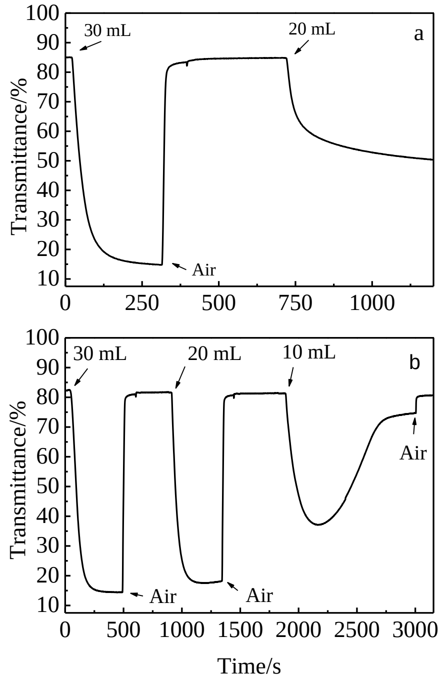

Fig.7 Gas sensing properties of the films: (a) WO_3-SiO_2 and (b) WO_3-TiO_2-SiO_2

and $W^{6+}/W^{5+} = 1.76$ for WO_3-TiO_2-SiO_2 film. The change of the valence of W indicates that the reaction of WO_3 on TiO_2 doping process. It may be assigned to TiO_2 reaction with WO_3 causing the forming of the large WO_3 particles.

Combined with AFM results, the FESEM images confirm there are large WO_3 particles on the WO_3-TiO_2-SiO_2 film's surface, which dramatically increase the surface roughness of the WO_3-TiO_2-SiO_2 films.

For gas-sensing devices, high surface roughness is a valuable property[30-33]. High surface roughness can lead to the large reaction area and is considered to have more adsorption site, with which the devices can absorb enough hydrogen modules for gas-sensing reaction even at low hydrogen partial pressure. For WO_3-TiO_2-SiO_2 film, though there is no TiO_2 in final thin films, the reaction during sol doping forms WO_3 particles which are attached on the films' surface, and it contributs the surface roughness. The high surface roughness improves the gas-sensing property of the WO_3-TiO_2-SiO_2 film.

3 Conclusions

Sol-sol doping forms large WO_3 particles, which are attached on the surface of the WO_3-TiO_2-SiO_2 films. Though without TiO_2, the WO_3 particles increase the surface roughness and cause the improvement of the hydrogen sensing property compared with WO_3-SiO_2 films.

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溶胶复合提高 WO_3 气致变色薄膜氢敏特性

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摘　要：制备了一种 WO_3-TiO_2-SiO_2 溶胶，通过浸渍提拉法制备了适用于室温下的光学氢敏薄膜。采用 FT-IR、SEM、TEM、AFM、XPS 以及紫外-可见-近红外光谱对复合薄膜的结构及气致变色性能进行了表征。尽管 TiO_2 并没有复合到薄膜中，但其在溶胶中引导了新的 WO_3 颗粒的生成。结果表明，这种颗粒分布在薄膜表面使得其表面粗糙度得到提高；气敏测试显示复合薄膜较未复合薄膜拥有更好的气敏性能。这种提升应当来源于 WO_3 颗粒带来的更高的表面粗糙度。

关键词：溶胶-凝胶法；WO_3 薄膜；镀膜；气致变色性能

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