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Photochemical preparation of SnO₂ nanoparticles for application in alcohol sensor

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Abstract. SnO₂ nanoparticles were prepared by a photochemical method with different concentrations of PVP as surfactant. The PVP can put regular impact on the size of the particles and the corresponding sensing response to alcohol gas. The optimized sensor of the SnO₂ nanoparticles could exhibit a response of ~21 to 50 ppm alcohol at 270 °C, which is more than 2-folds of that without PVP. The sensor also had excellent stability, repeatability and concentration linear, exhibiting good practicality in alcohol detection. The method is easily-manipulated, low-cost and green for obtaining a gas sensing material.

1. Introduction

The alcohol sensor which can be used for the detection of alcohol concentration in air has been widely applied to checking drunk drivers or monitoring ethanol vapor leakage. Various semiconductors or modified semiconductors, including SnO₂, ZnO-Ag, In₂O₃-NiO et al [1-3], have been applied to improve the performance of alcohol response in the recent years. SnO₂ materials, which have high chemical stability, easy preparation and nontoxicity, have a dispensable role in commercial alcohol sensor. The performance of SnO₂-based materials has been improved by preparing method, morphology control, doping, and composite [4]. Meanwhile, the SnO₂-based gas sensors have been used not only in alcohol sensing, but also in other volatile organic compound (VOC) and toxic gases [5].

Tin dioxide (SnO₂), a commercial and multifunctional n-type semiconductor material with direct band gap up to 3.6eV, has been widely applied to different research fields and commercial applications, such as catalysis, solar cells, lithium ion batteries, gas sensor and so on [6-9]. In the recent years, the wet chemistry and chemical vapor deposition methods have been extensively studied and applied in preparation of SnO₂ materials [4, 10]. However, very high temperature or high pressure are required, Shipu Xu et. reported a photochemical method to prepare ordered porous SnO₂ monolayer film under UV light (254nm, 8W) at room temperature [11].

In this work, we report a facile photo-chemical method for the synthesis of SnO₂ nanoparticles stabilizing with PVP in aqueous system. The shape and size of SnO₂ nanoparticles are controlled by



the hydrophilic PVP. The reaction is fast and finishes within 1 h under a low power UV lamp (254 nm, 8 W) at room temperature. The performance of SnO₂ nanoparticles based sensor was remarkably improved by adding PVP surfactant. In addition, this photochemical method for the produce of SnO₂ nanoparticles is extremely simple and scalable, and the eco-friendly, low cost, and simple operation enable manufacture. We believe this facile approach for the preparation of SnO₂ opens a new avenue for SnO₂ materials applying into to other diverse fields.

2. Experimental

2.1. Reagents

All chemicals were analytic grade without further purification. The polyvinylpyrrolidone (PVP) (Mr. about 1000) and tin dioxide were purchased from damao chemical reagent factory and Guangzhou chemical reagent factory, respectively.

2.2. Synthesis of SnO₂ sphere-like nanoparticles

A precursor solution was formed by dissolving SnSO₄ (0.1 mol/L) and PVP (0.01 wt%, 0.1 wt%, 1 wt%, 2 wt%, 10 wt%) into 3 % H₂SO₄ solution of 50 ml with magnetic stirrer. And then the precursor solution was illuminated with magnetic stirrer for 1h under two UV lamps (8 W, 254 nm, Philips) in a darkroom. And the lamp is 5 cm away from the liquid level. After product was washed with deionized water and ethanol for several times, and dried at 60 °C for 6 h.

2.3. Characterization

The morphology and structure of SnO₂ with different concentration PVP was observed by using the scanning electron microscopy (SEM, ZEISS Gemini 500, Carl Zeiss, Germany). In order to further analyze characterization, the x-ray diffraction (XRD, UltimaIV, Rigaku, Japan) was using with Cu K α radiation.

2.4. Gas-sensing measurements

The alcohol gas sensors based on SnO₂ sphere-like nanoparticles were tested through operating static gas-sensing system (WS-30A, Weisheng Instruments Co., Ltd., Zhengzhou, China). Firstly, a paste was formed by stirring the mixture of SnO₂ powers and deionized water, coated onto ceramic tube to cover its two gold electrodes, and a Ni-Cr alloy heating wire was inserted into ceramic tube inside to control and adjust operating temperature during gas sensing. And then the sensor device was aged at 400 °C until the testing system displayed a stable value. The sensitivity of gas sensor was defined as $S=R_{\text{air}}/R_{\text{gas}}$, R_{air} and R_{gas} are the resistance of sensor in air and in target gas, respectively. And the response time or recover time is 90% of the corresponding whole change time.

3. Results and Discussion

3.1. Structural and morphological characterization

The SnO₂ nanoparticles were prepared with varied wt% PVP as surfactant, named as SnO₂-PVP. The various SnO₂ nanoparticles by adding different concentration PVP surfactant, displayed in SEM images of Figure 1. The pure SnO₂ has a wide size range of 280-850 nm and the particles aggregated severely as shown in Figure 1a. The aggregation is slightly improved by adding 0.1 wt% PVP as seem in Figure 1b. A quantity of small particles emerged, with $d \sim 170$ nm. Interestingly, when the PVP increased to 1 wt%, the particles formed into two sizes, $d \sim 30$ nm and ~ 200 nm. Outstandingly, when PVP further increased to 10 wt%, very uniform SnO₂ formed with $d \sim 200$ nm (Figure 1d). The particles have a roughness surface of raspberry-like.

The crystalline structure of SnO₂ nanoparticles was investigated by XRD. The SnO₂ samples were calcined at 400 °C for 30 min before the XRD in order to simulate the operation condition of gas sensor device. The SnO₂ nanoparticles stabilized by varied amount of PVP shows similar XRD patterns (Figure 2a), which are recognized as tetragonal rutile (JCPDS file card NO. 77-0452). The diffraction peaks of SnO₂ nanoparticles with stabilizer are much stronger and sharper than that of pure

SnO_2 , which indicate that the order of crystalline structures are significantly enhanced by adding stabilizer, even at a very low amount of 0.1 wt%. In addition, the half peak width of diffraction peaks of SnO_2 with PVP is much smaller than the pure SnO_2 , which reveals that SnO_2 with PVP has a bigger grain size than pure SnO_2 based on the Scherrer formula. We suppose that the hydrophilic PVP with long chain provide more growth sites for SnO_2 crystal, which results in the formation of bigger grains.

Under UV illumination with a wavelength of 254 nm, the Sn^{2+} ions capture photons to produce Sn and Sn^{4+} . Sn is quickly oxidized into SnO_2 by O_2 in air [11]. The growing crystal of SnO_2 aggregate easily, which hinders the further growing of grains and leads to low crystalline, as shown in Figure 2b.

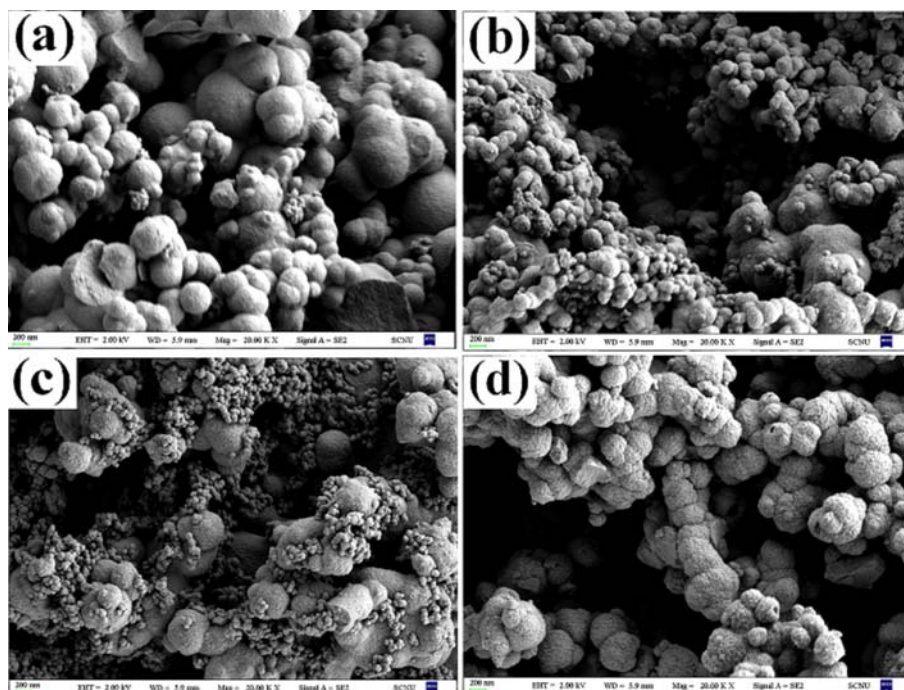


Figure 1. The SEM images of (a) pure SnO_2 , (b) SnO_2 -0.1 wt% PVP, (c) SnO_2 -1 wt% PVP, and (d) SnO_2 -10 wt% PVP.

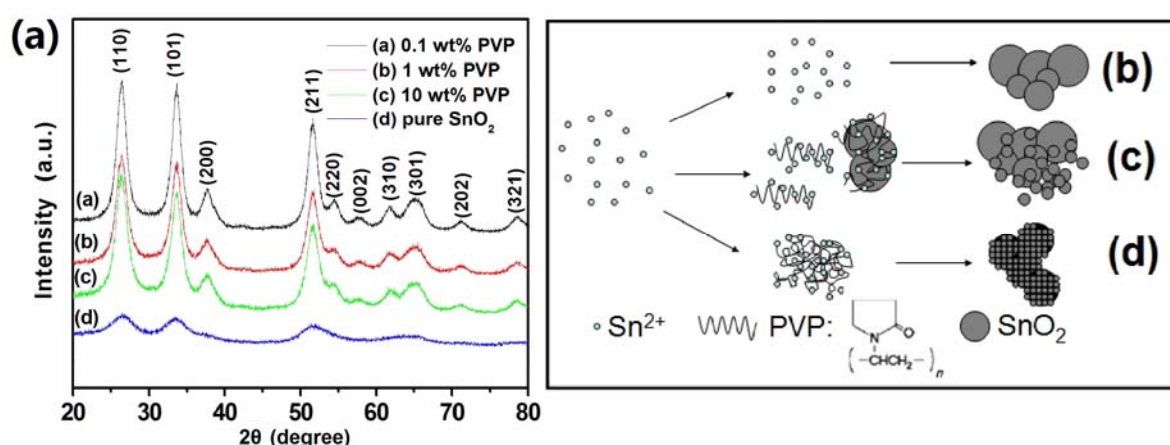


Figure 2. (a) The XRD patterns of SnO_2 with different concentration PVP. The formation schematic diagram of SnO_2 with (b) no PVP, (c) moderate PVP, (d) excessive PVP.

When PVP was added as surfactant, the long hydrophilic polymer chains absorbed to the surface of growing SnO_2 particle, which prevented the aggregation of the growing crystal. Besides, the pyrrolidone groups of PVP chains absorb Sn^{2+} ion from the aqueous solution by coordination [12, 13],

which provided much more growing sites for SnO₂ nanocrystals, resulting in bigger grain size and higher crystalline, displayed in Figure 2c. When adding 10 wt% PVP, the long polymer chains twined each other which results in the aggregation of SnO₂ nanocrystals formed into bigger nanoparticles. However, it has no effect on the growth of grain as the growth sites were exposed (Figure 2d). So the final SnO₂ nanoparticles has bigger grain and higher crystalline.

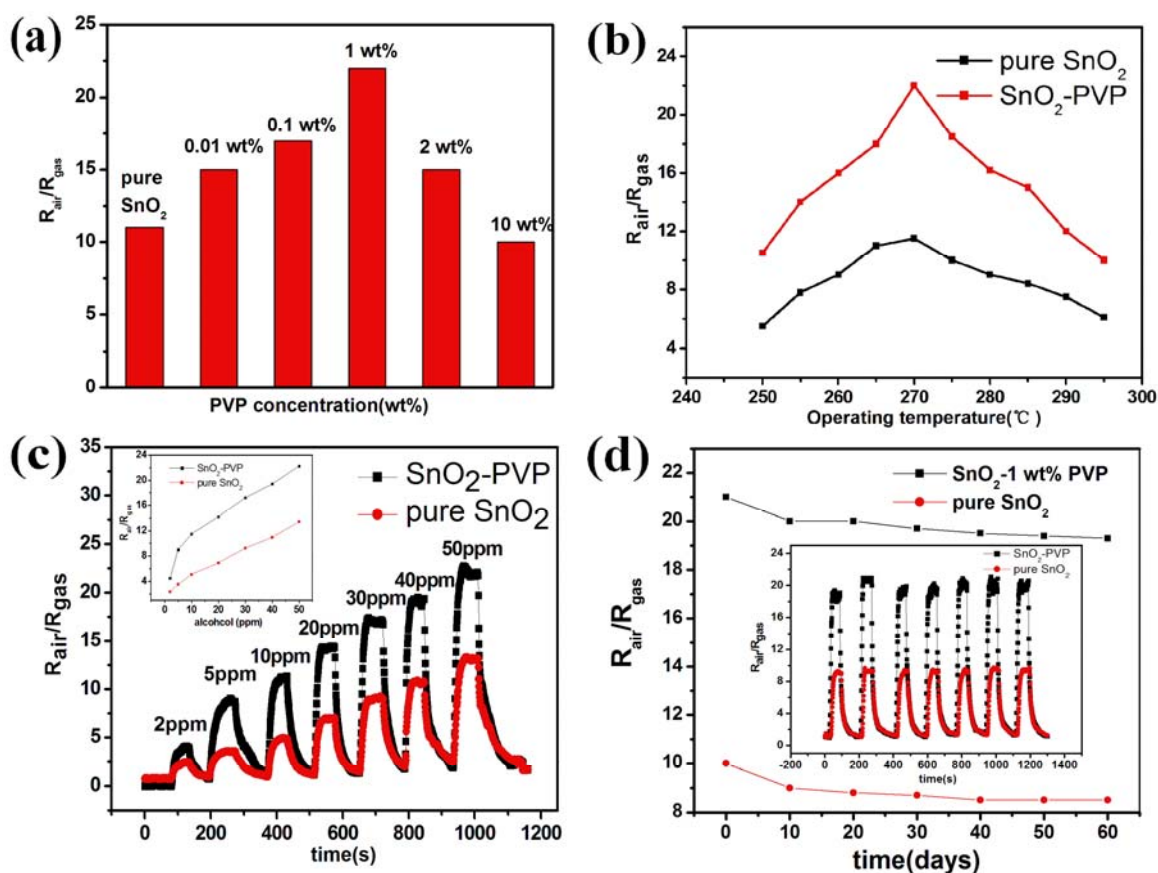


Figure 3. (a) Sensitivity of SnO₂ with different concentration PVP respond to 50 ppm alcohol at 270 °C. Gas sensor based on pure SnO₂ and SnO₂-1 wt% PVP, (b) responding to 50 ppm alcohol at different operating temperature, (c) responding to different concentration alcohol at 270 °C and their linear graph (inset), (d) keeping long-term stability and repeatability (inset).

3.2. Alcohol gas-sensing properties

The performance of SnO₂-PVP based alcohol sensor can be enhanced and improved by the morphology control. Fig. 3 shows the alcohol sensing behavior of SnO₂ based sensor in 50 ppm alcohol at 270 °C. The sensitivity increased from 9 to 22 as PVP stabilizer increased from 0 to 1 wt%, however decreased as PVP further increased. The sensors exhibit a temperature-dependence performance, which have an optimal sensitivity at 270 °C for the case of both pure SnO₂ and PVP modified SnO₂ as shown in Figure 3b. The sensitivity increased almost linearly with increasing alcohol concentration, from $S = 4$ to $S = 22$ corresponding to 2 ppm and 50 ppm alcohol. Moreover, the sensors show an excellent stability that the sensitivity is well preserved after a long-term storage, with $S = 19$ after two months compared to $S = 21$ at the beginning as seen in Figure 3d. Outstandingly, fast response time and recovery time are maintained after long-term storage (inset in Figure 3d).

3.3. Mechanism of the SnO₂ sensors

The mechanism of SnO₂ based gas sensors are explained as following [14-16]: when SnO₂ nanoparticles are exposed to the air, the oxygen molecules are absorbed at certain temperature and the

oxygen molecules can capture the free electrons of SnO₂ conduction band to form oxygen ions (O₂⁻, O₂²⁻, O⁻). When SnO₂ is exposed in air at 200-300 °C, O⁻ is mainly absorbed on the surface of SnO₂ [14]. The adsorbed O⁻ captures free electrons on the SnO₂ surface, which resulted in the formation of an electron depletion layer and thus a stable resistance in air. When the alcohol is injected and gasified, O⁻ react with alcohol molecules resulting in the free electrons is released back to the conduction band of SnO₂. The resistance of SnO₂ thus decreases in the alcohol gas atmosphere and decreases with increasing alcohol concentration atmosphere. The resistance of SnO₂ recovers to the initial level in air when the reductive alcohol is removed.

The alcohol sensitivity of SnO₂ based sensor is enhanced and improved by adding PVP as stabilizer for SnO₂ nanoparticles. The SnO₂ nanoparticles with 1 wt% PVP gives the highest sensitivity. The SnO₂ samples at 1 wt% PVP have many small size of nanoparticles attached to the bulks, which which contributes much higher surface area with more absorption sites for O⁻ than other SnO₂ samples. More absorbed O⁻ react with alcohol, resulting in more electrons release back to the conduction band.

4. Conclusion

In summary, we have used a low power 254nm UV light at room temperature to one step prepare the different size of SnO₂ sphere-like nanoparticles with surfactant PVP, increasing its crystalline and grain size. The sensitivity of alcohol sensor based on SnO₂ with 1 wt% PVP is double that of no PVP, which respond to 50 ppm alcohol at 270 °C is 21. The excellent stability and repeatability of sensor based on SnO₂ is still kept. The sensitivity of alcohol sensor based on SnO₂ has better linear relationship with alcohol concentration. Moreover, the photochemical-based SnO₂ with surfactant PVP can be applied to other fields.

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