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PVDF modified Pd-SnO_2 hydrogen sensor with stable response under high humidity

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ABSTRACT

We deposited polyvinylidene fluoride (PVDF) microporous membrane on the surface of palladium loaded tin dioxide (Pd-SnO_2) gas-sensitive film by phase separation to reduce the sensitivity loss of Pd-SnO_2 gas-sensitive film at high humidity. The sensitivity loss of the PVDF-Pd-SnO_2 gas-sensitive film to 50 ppm H_2 at 100 RH% is 22% which is almost one-third of the Pd-SnO_2 film (70%). At 100 RH%, the sensitivity loss of Pd-SnO_2 film is direct proportional to the H_2 concentration, but it become inversely after PVDF microporous membrane deposition. PVDF microporous membrane significantly improved the stability of Pd-SnO_2 film under high humidity, and verified the feasibility of non-conductive polymer materials improving the performance of gas-sensitive materials.

1. Introduction

Hydrogen has been attracting attention as a potential energy currency in the transportation, residential, and industrial sectors [1]. But the flammable and explosive properties of hydrogen require stable and reliable gas sensors during storage and transportation. Pd-SnO_2 gas sensors is one of the most widely used H_2 sensors, and humidity seriously deteriorates the sensitivity of Pd-SnO_2 gas sensor [2–4]. But the existing water vapor adsorbs on the SnO_2 surface will decrease the sensitivity of SnO_2 to reducing gas by decreases the electric resistance of the gas sensors in a similar way to reducing gas. Therefore, prevent the water vapor adsorbs on the surface of SnO_2 is the feasible way to improve the gas sensing properties of SnO_2 based gas sensors in humidity environment. Due to the optimal working temperature of Pd-SnO_2 gas sensor is above 100 °C and the request of H_2/water vapor separation, the material used on the surface of gas sensors to prevent water vapor should have outstanding performances in thermal stability, hydrogen flux and hydrophobicity.

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer material and widely used in the field of gas separation, microporous separation, mesoporous separation and membrane distillation since the 1880s [5–7]. Compared with other commercial macromolecules, such as polystyrene (PS), polyethersulfone (PES), polyimide (PI), polyvinylidene fluoride has high mechanical strength, good thermal stability, chemical resistance and high hydrophobic characteristics. PVDF has a melting point of 140–170 °C and 1% weight loss temperature in the air at 357 °C. Due to the sufficient fluorine atom in its molecular chain, PVDF has excellent hydrophobicity, and distillation and separation PVDF membranes are often added other hydrophilic polymers or surface modification to increase their hydrophilicity. Different from other fluorocarbon materials and crystalline polymers (such as polytetrafluoroethylene, polypropylene, etc.), PVDF have better process ability and can form a stable multi-form film by phase inversion process. Based on the above performance, PVDF can meet the requirements of Pd-SnO_2 gas-sensitive film surface hydrophobic material.

In this work, PVDF membrane was deposited on the surface of the Pd-SnO_2 nanoparticles gas sensing film by water/NMP/PVDF phase inversion system which effectively enhanced the reliability of Pd-SnO_2 gas sensitive film in high humidity environment.

2. Material and methods

The preparation process of Pd-SnO_2 nanoparticles can be described as follow: dropping 1 g SnO_2 nanoparticles (particle size: 50–70 nm, Mackin Biochemical Co.) and 0.0835 g $PdCl_2$ (Sigma-Aldrich) into 50 ml distilled water, and ultrasonic dispersing the mixture 24 h to get homogeneous $PdCl_2$-SnO_2 suspension. $PdCl_2$-SnO_2 suspension was dried at 90 °C to remove water and then calcined the $PdCl_2$-SnO_2 particles at 800 °C to get Pd-SnO_2 nanoparticles.

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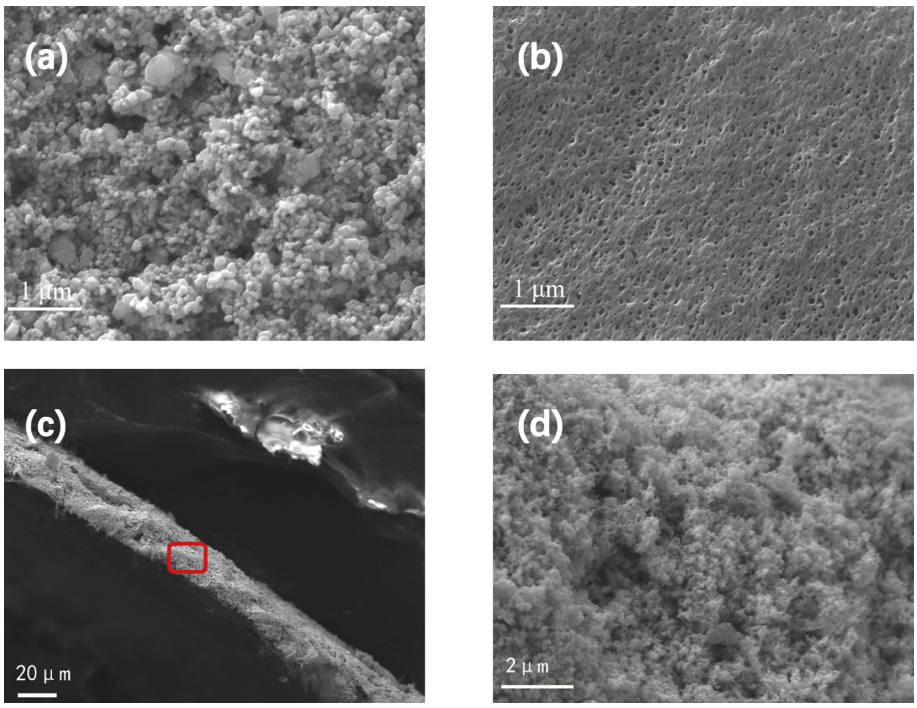

Fig. 1. SEM image of a) P-S film, b) P-P-S film, c) the cross-section image of PVDF membrane and d) the enlarge view of the red box area in image c).

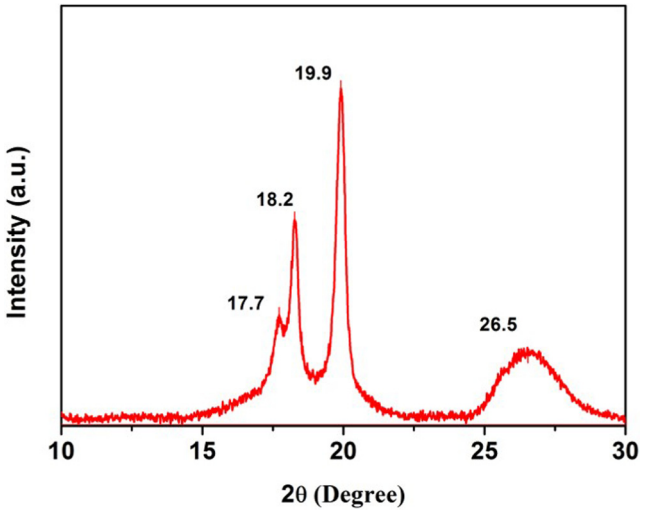

Fig. 2. XRD pattern of the PVDF membrane.

PVDF-Pd-SnO_2 gas sensors are prepared as follow. Firstly, mixing the Pd-SnO_2 nanoparticles and terpineol (Heowns Biochemical Co.) in a weight ratio of 1:2 to form the Pd-SnO_2 paste. Then 20 mg Pd-SnO_2 paste coasted on the interdigitated Ag-Pd alloy electrode (Beijing Elite Tech Co., Ltd, Pd content: 5 wt%, electrodes spacing: 0.15 mm, electrode width: 0.18 mm, electrodes pairs: 8 pairs). Next, the wet Pd-SnO_2 film was dried at 120 °C 6 h to remove terpilenol and get Pd-SnO_2 film (named P-S film).

PVDF membrane was deposited on the surface of Pd-SnO_2 gas sensors by immersion precipitation. In this procedure, a casting solution was prepared by dissolving PVDF in NMP (N-Methyl-2-pyrrolidone) at 60 °C (5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% polymer, concentration used in main paper is 10 wt%) followed by standing for 24 h to remove air bubble present in the solution. Then the casting solution was coated on the Pd-SnO_2 gas sensors by spin coating. The spin coating conditions were set as followed: rotation speed: 3000 r/min, spin coating time: 100 s, acceleration: 100 r/s^2. After spincoating, the gas sensor immersed in 5%–25% NMP water solution bath or DI water to form the PVDF membrane (concentration used in main paper is 5%). In the process, NMP will quickly transport from the coating solution into the water, resulting in PVDF precipitation film. After film formation, the gas sensors were washed by distilled water twice to remove residual solvent. At last, the gas sensors were dry at 150 °C 24 h to complete remove the water. The PVDF-Pd-SnO_2 film named P-P-S film.

The gas sensing properties of the P-P-S films and P-S films were operated on a CGS-4TPs intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd., China). In order to maintain a balanced mixing ratio of highly purified test gases (1000 ppm in air), wet air (100 RH%) and dry air, the concentration of gases is controlled by mass flow controllers. The total flow rate was set at 1000 sccm and humidity was stable before the measurement.

The sensitivity is defined as: $S = R_a/R_g$, where the R_a is the sensor resistance in the air, and R_g is the sensor resistance in the target gas. The sensitivity loss is defined as the ratio of the difference between the sensitivity of the dry environment and the humid environment to the sensitivity of the drying environment.

3. Results and discussion

The microstructure of the P-S film and P-P-S film were investigated by SEM. Fig. 1 is the SEM picture of P-S film, it could see in the picture that P-S gas-sensitive film shown a loose structure which mainly composed by large number nanoparticles. Fig. 1b shows upper surface of the P-P-S gas-sensitive film is a space-like structure with an average pore size of 95 nm. Fig. 1cd is the cross-sectional view of the PVDF membrane and the enlargement of the red frame area. It shows that PVDF membrane have a thickness about 20 μm and accumulated by polymer particles.

Fig. 2 is the XRD pattern of the PVDF membrane. In comparison with literatures [8], the peaks at 17.7, 18.2, 19.9 and 26.5 show the