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Preparation and properties of antimony doped tin oxide nanopowders and their conductivity

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ABSTRACT

Antimony doped tin oxide (ATO) nanopowders were prepared by solid-liquid heterogeneous coprecipitation reaction, using $SnCl_4{\cdot}5H_2O$ and $SbCl_3$ as the raw materials, NH_4HCO_3 as the neutralizing agent, CH_3COOH as the cosolvent, and C_2H_5OH as the reaction medium. The ATO nanopowders were prepared into waterborne transparent antistatic coatings. The structure and properties of ATO powders were characterized by X-ray diffraction (XRD), energy dispersive spectrometer (EDS), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area measurement and resistance tester. The results show that ATO nanopowders, whose primary particle size is about 5–8 nm and specific surface area is 92.75 $m^2\,g^{-1}$, have a structure of tetrahedral rutile and a uniform shape of approximately sphere, and the resistivity of ATO nanopowders reaches 1.0 Ω cm. The ATO coating is applied on the surface of polyethylene terephthalate (PET) film by roller coating method, the test shows that the ATO film has excellent physical properties. When the visible light transmission rate is more than 80%, the surface resistance of coating film is about $10^5\,\Omega$, which is completely satisfied with the requirement of the anti-static electricity field.

1. Introduction

ATO nanopowders are a kind of n-type semiconductor materials with wide bandgap, having optical performances and physical properties that the substances with macroscopic size do not possess [1]. By the means of dispersing and adding ATO nanopowders to various types of coatings, the transparent multifunctional film materials with thermal insulation and conduction are prepared [2–4], which can be widely applied in the field of Environmental Care and Anti-static, such as building, electrommunication and packaging materials.

The methods of preparing ATO nanopowders with tin salt and antimony salt mainly include co-precipitation [5–8], hydrothermal [9–11], sol-gel method [12–15] and so on. Among them, the method of liquid co-precipitation is the most common and mature method for preparing ATO nanopowders. The purity of nanopowders prepared by the above methods is not high, moreover, most of the processes are using water as the reaction medium, which leads to that nanopowders particles are easy to agglomerate. On the one hand, due to the surface tension of water and other factors, there exist hydrogen bond and capillarity between the precursor particles, what's more, a large number of OH^- are attached on the surface of the particles, resulting in prone agglomeration between the particles. On the other hand, in order to ensure that tin and antimony exist in the solution medium in the form of ionic, it is required to add a certain amount of compounding ingredient and dispersant in the preparation of mixed solution, which can reduce the hydrolysis of Sn^{4+} and Sb^{3+}, however, at the same time, a large number of impurities are brought in, which affects the performance of products.

To overcome these problems, in this paper, antimony salt and tin salt were used as the raw materials, NH_4HCO_3 as the neutralizing agent, CH_3COOH as the co-solvent, C_2H_5OH as the reaction medium, through the reaction of solid-liquid heterogeneous coprecipitation, and after filtering, washing, dehydration, drying and calcination, the blue grey ATO nanopowders were obtained. The product is with small particle size in a narrow distribution range, less agglomerate, and doping uniformity, in

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addition, it has high specific surface area and better electrical performance. In order to further test its photoelectric properties, ATO nanopowders were prepared into waterborne transparent antistatic coating, and the coating is applied on the surface of PET film by roller coating method. The test shows that the physical properties of ATO film is excellent, and ensures that the transmittance of visible light up to more than 80%, at the same time, the surface resistance down to $10^5\,\Omega$, its fully meet the requirements of the field of anti-static market.

2. Experimental

2.1. Preparation of ATO nanopowders and aqueous antistatic coatings

20.67 g $SnCl_4·5H_2O$ and 1.72 g $SbCl_3$ were dissolved in 50 mL ethanol solution, then 32.63 g NH_4HCO_3 was mixed with 100 mL ethanol solution, followed by the addition of 3.54 g CH_3COOH and dispersal, and the solid-liquid suspension mixed solution was obtained. Under the condition of stirring, the resulting colorless and transparent tin-antimony mixed salt solution was added dropwise into the solid-liquid suspension solution to react. During the reaction, kept the reaction temperature is 15 °C, pH value from 6.5 to 7.5 and the reaction time is about 4.0 h. After the reaction, the white emulsion mixture precipitation including $Sn(OH)_4$, $Sb(OH)_3$ and NH_4Cl was got. After filtration, vacuum drying under 70 °C and recycling ethanol at the same time, 30 g deionized water was added into the residue to dissolve and disperse, then, the solution was filtered again and washed with deionized water until the ions of chloride could not be detected any more. And then, the resulting residue was dehydrated with 30 mL ethanol and dried under vacuum at least 3.0 h to get the white powdery ATO precursor. After calcination under 550 °C and smash, the blue gray ATO nanopowders were prepared.

Then, 30 g ATO nanopowders were mixed with 100 g deionized water and added the mixtures into bead mill to mill with 0.5 mm zirconia beads for 2.0 h, at the same time adjust the pH of dispersion to 6–8, then we get the 20% nano ATO aqueous slurry with stable performance. The 7.14 g nano ATO aqueous slurry and 2.86 g waterborne polyurethane emulsion with solid content of 35% were mixed, and then add a few drops of leveling agent, antifoaming agent and thickener. Through the high shearing and dispersing emulsifying machine, the waterborne transparent antistatic coating is prepared.

2.2. Characterizations of ATO nanopowders

The morphology, dispersion and particle size of nanoparticles was directly observed through the transmission electron microscope (TEM, Tecnai G^2 F30, American FEI Company). The structure and morphology of ATO nanopowder were studied by X-ray diffraction (XRD, Smart Lab, Japanese Neo Confucianism), and then utilizing the Scherer formula

$$D = k\lambda/(\beta\cos\theta)$$

to calculate the grain size of nanopowder. (In the above formula, k is the shape factor, which is 0.89, λ is the wavelength of X-ray, 0.15406 mm, β is the full width at half maxima, θ is the Bragg angle). The surface composition of the sample is determined by energy dispersive spectrometer (550i, IXRF Systems, Inc.). Automatic surface area and porosity analyzer (Tristar II 3020, American Micromeritics Instrument Corporation), the specific surface area of ATO nanopowders was obtained according to the nitrogen adsorption-desorption curve of the nanopowders at liquid nitrogen temperature, and then the particle size of the nanopowders was calculated by using the formula

$$D = 6/(\rho S_w)$$

in which, ρ is the particle density, S_w is the specific surface area of the nanopowders. 1.0 g ATO nanopowders were weighed to put into the forming cavity of the powder resistivity tester (FZ-2006, Ningbo Rooko Company), and measured the resistivity of the ATO nanopowders at the condition of 2.0 MPa.

2.3. Characterizations of waterborne antistatic coatings

Using the roll coating method, the waterborne transparent antistatic coatings were applied on the PET thin films which had been pretreated, the surface of the coating film dried at room temperature, and then cured at 80 °C for 3.0 h, the surface of the coating film was solidified into a film. Transmittance in the visible light region was measured by the LS-102 type optical transmittance measuring instrument. The surface resistance of coated film was determined to judge the film's anti-static performance by hammer type surface resistance tester. In order to further study the comprehensive performance of the film, we measured other physical properties, mainly includes: the coating films appearance, hardness, adhesion, water resistance, heat resistance and alkali resistance.

3. Results and discussion

3.1. Solid-liquid heterogeneous coprecipitation reaction mechanism

In the co-precipitation reaction of the tin-antimony mixed salt ethanol solution with NH_4HCO_3, since NH_4HCO_3 is insoluble in ethanol, the hydrolysis reaction occurs in the solid-liquid interface, and the generated $Sn(OH)_4$ and $Sb(OH)_3$ are easy to deposit on the surface of unreacted NH_4HCO_3 solid particles. As the reaction proceeds, the NH_4HCO_3 surface is gradually coated with the hydroxide precipitation completely, which prevents the further decomposition of NH_4HCO_3 and the hydrolysis reaction. In the interphase co-precipitation reaction, a small amount of CH_3COOH is added to the NH_4HCO_3 suspension solution of ethanol, which can improve the coated phenomenon, thus, the reaction process is easier to control and the reaction can react completely. The reason may be that the presence of CH_3COOH changes the reaction pathways and promotes the decomposition of NH_4HCO_3. The specific reaction mechanism is as follows (Fig. 1):

$$CH_3COOH_{(aq)} + NH_4HCO_{3(s)} \rightarrow CH_3COONH_{4(aq)} + CO_2\uparrow + H_2O \quad (1)$$

$$SnCl_{4(aq)} + 4H_2O \rightarrow Sn(OH)_{4(s)} + 4HCl_{(aq)}$$

$$SbCl_{3(aq)} + H_2O \rightarrow SbOCl_{(s)} + 2HCl_{(aq)}$$

$$SbOCl_{(s)} + H_2O \rightarrow Sb(OH)_{3(s)} + HCl_{(aq)} \quad (2)$$

$$HCl_{(aq)} + CH_3COONH_{4(aq)} \rightarrow CH_3COOH_{(aq)} + NH_4Cl_{(s)} \quad (3)$$

The below is the overall reaction equation:

$$SnCl_{4(aq)} + SbCl_{3(aq)} + 7NH_4HCO_{3(s)} \rightarrow Sn(OH)_{4(s)} + Sb(OH)_{3(s)} + 7NH_4Cl_{(s)} + 7CO_2\uparrow$$