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One-step synthesis of antimony-doped tin dioxide nanocrystallites and their property

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Abstract: Antimony-doped tin dioxide(ATO) nanoparticles with primary diameter in the range of 9−10 nm were rapidly synthesized via a novel combustion technique, starting with antimony trichloride and tin tetrachloride as metal sources and self-assembly compounds as fuels. The combustion phenomena and characteristics of products were controlled by assembling components in fuel compounds according to appropriate molar ratio. The as-synthesized products were characterized by XRD, SEM, TEM and XPS, respectively. The electrical conductivity was evaluated through measuring the antistatic property of polyester fiber treated by the as-synthesized products. The results show that a mild combustion phenomena without release of smoke can be taken on and perfect azury rutile ATO crystal with complete substitution can be formed rapidly under the appropriate synthetic conditions. The antistatic property of the polyester fiber treated by the as-synthesized ATO products is enhanced remarkably. The triboelectricity voltage below 1.0 kV, half life below 1.0 s and surface resistance below $1.0\times10^6\ \Omega$ can be attained.
Key words: antimony-doped tin dioxide; combustion; self-assembly; antistatic

1 Introduction

Recently, much attention has been focused on the modification of metal oxide by doping or substituting with special atoms[1−4]. Among these doping systems, antimony-doped tin dioxide(ATO) has attracted considerable attention owing to its potential applications as gas sensor, solar battery, transparent electrode, electricity-conducting coatings and so on[5−6]. Therefore, different methods including solid blend, chemistry co-deposition, sol-gel, metal alkoxide hydrolyzation and hydrothermal technologies have been proposed to prepare ATO[7−12]. Although conventional chemistry co-deposition method is the common method because of its economy and controllability, it is difficult to prepare excellent ATO powder and the technology is very unfriendly to the environment. Other methods cannot be applied widely because they are usually time-consuming, expensive and special equipment is needed usually. For example, high-pressure reactor and long time high-temperature treatment are essential in hydrothermal technology. The major challenges in preparing nano-ATO are the control of the hydrolyzation process and the genuine substitution of Sb^{5+} for Sn^{4+} in tin dioxide. It is quite difficult to render substitution reaction at low temperature in short time. While the conventional substituting process at high temperature in long time results in the rapid growth and agglomeration of particles inevitably, which has important negative effects on the characteristics of ATO. Although the hydrothermal technology is reported to prepare perfect and monodisperse ATO nanoparticles, long time heat-treatment (about 12 h) is essential and washing process repeatedly with deionized water is still inevitable[13], which make the technology limited in practical application.

Combustion method is well known as an effective technology for producing a mass of simple and complex inorganic materials having high chemical purity and excellent physical and mechanical properties[14−17]. The reaction based on molecule level assures the complete crystallographic rearrangement, and the ultrashort reaction time (20−30 s) controls the growth of particles. However, there are limited reports about the preparation of substituting system via combustion method and there exist many intricate problems on combustion theory and technology. Furthermore, the poor quality, low product yield and safety in conventional combustion reaction also restrict the practical

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application of the technology.

ZHANG and GAO[18] reported a kind of combustion method called Pechini to prepare nano-ATO. However, the sol-gel process and heat-treating at high temperature (600 ℃) for long time (2 h) are still inevitable.

In present work, we report the synthesis of rutile nanometer ATO by a rapid and safe method called self-assembly combustion technique(SAC). The key idea is that, the fuel components are chosen carefully and assembled in an appropriate molar ratio (hereafter termed as ψ), which ensures the stability of the reaction course and thereby enhances the characteristics and product yield. More importantly, the reaction course is mild and safe without a release of smoke. The corresponding technique has been reported in our patent[19]. This paper focused on the microcosmic and antistatic property of ATO synthesized by SAC technique.

2 Experimental

All reagents were commercially available and used without further purification. In a typical experiment, firstly, $SnCl_4$ was dissolved in distilled water to attain 0.5−2.0 mol/L solutions, and citric acid was added dropwise to the $SnCl_4$ solution until a pH value of 3−4 was reached. The chosen fuels, including ammonium perchorate (AP), ammonium nitride (AN), urea (U) and salvolatile (S), were assembled in an appropriate ψ, to form self-assembly fuel compounds. Then, a suitable amount of $SbCl_3$ modificated and self-assembly fuel compounds were mixed well with the above $SnCl_4$ solution by stirring to attain a ropy paste (hereafter termed as precursor). This precursor was put into a resistance furnace pre-heated to the given temperature. After going through boiling, evaporating and concentrating, the precursor suddenly foamed up and deflagrated, leaving a very finely azury flocculent powder like sponge.

The crystalline phase was determined by X-ray diffraction (XRD-6000, model D/Max-ⅢB, Shimadzu) instrument with Cu K_α radiation (λ=0.15418 nm). The scanning rate of 0.05(°)/s was applied to record the pattern in the 2θ range of 20°−80°. The crystal size was calculated with Scherrer's equation.

The morphological feature of the products was investigated by scanning electron microscope(SEM) (Japan S−570) and transmission electron microscope (TEM) (JEMβ200 CX).

The analysis of element content was done with Thermo ESCALAB 250 XPS instrument (America) using Al K_α radiation ($h\nu$=1 486.6 eV).

The antistatic property of the as-synthesized sample was estimated according to the following approach. ATO aqueous dispersion was prepared by adding 0.2−1.0 g of the as-synthesized sample and 0.2 g of polymer surfactant polyvinylpyrrolidone(PVP) into 100 mL of distilled water with pH value adjusted to 8.5, then keeping stirred at 60 ℃ for 30 min. 5.0 g of polyester fiber was washed before use for several times in acetone for 20 min using an ultrasonic bath to remove surface impurities. After being dried, it was impregnated for 30 min in a treatment solution containing the ATO aqueous dispersion, 0.5 g binder agent and 1.0 g silicone softener, then was padded twice (take-up 70%) on a laboratory padding mangle. After they were padded, the polyester fiber was immediately dried at 100 ℃ for 2.0 min and cured at 160 ℃ for 1.0 min. The triboelectricity voltage, half life and surface resistance of the treated polyester were measured by Static Honestmeter S−5109 (environment pressure 5 kV) and Surface Resistance Instrument SIMCO.

3 Results and discussion

3.1 Effect of fuel

ATO powder can be synthesized by combustion reaction using single fuel and fuel compounds. However, it is noted that the nature of combustion and the appearance of the as-synthesized samples are completely different with the different fuels. Using single fuel, such as ammonium perchorate(AP), ammonium nitride(AN) and urea(U), results in rough powder including yellow and navy blue sheet substances, companied with dazzling firelight and amounts of light-brown smoke during the initial period of combustion reaction. Whereas using fuel compounds assembled according to appropriate molar ratio as fuel, perfect azury ATO powder like flocculent can be attained and controllable combustion reaction course is presented, going through a series of phenomena such as boiling, evaporating and concentrating, foaming up and deflagrating. Fig.1 demonstrates two typical appearances of the as-synthesized samples using ammonium perchorate and fuel compounds (ψ value 4/2/3/1) as fuels respectively at igniting temperature of 500 ℃, which were screened by digital camera.

3.2 Effect of mass ratio of fuel compounds to tin tetrachlorine

The mass ratio of fuel compounds to tin tetrachlorine plays an important role in controlling the morphology and particle size of the as-synthesized powder. Fig.2 displays the typical XRD patterns of the as-synthesized samples under different mass ratio of fuel compounds to tin tetrachlorine.

In Fig.2(a), the diffraction peaks are very weak and wide, which indicates that the sample synthesized under