Preparation and Characterization of Thermal Insulating Coating for Buildings

Bo Yang, Yang Yang, Shuanghong Zhang, Wei Zhai, Maodong Li and Lin Yang

ABSTRACT

ATO@SiO2@ATO, the nano-power with new core-shell structure was prepared, with nano-ATO grain further coated with silicon dioxide and ATO on the surface. According to the test result of XRD, SEM, laser grain size analysis, heat insulation performance analysis, it showed that ATO@SiO2@ATO powder was the grain of which grainsize was nanometer level and uniform with spherical structure. After testing the thermal insulation coatings made of nano-ATO powder, ATO@SiO2 powder and ATO@SiO2@ATO powder, the result showed that the insulation performance of ATO@SiO2@ATO-10% powder was better than ATO.

INTRODUCTION

Antimony-doped Tin Dioxide (nano-ATO), owning the advantage of ATO material and nano material at the same time, has the unique photoelectric property, resistance to ionizing radiation, good antireflection, infrared absorption, thermal stability and high ion selective exchange capacity for some elements, which can be used for preparing thermal insulation coatings, low-eglass for buildings, infrared absorption and insulation materials, antistatic plastic, radiation protection and antistatic coating material, fiber, electrode material, gas sensors and so on, so the preparation and application is attached more and more importance to [1-3]. Abroad, especially in Japan and America, the research of preparation and application of nano

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ATO material has been in the stage of mass production. But the research in China started late, so it has to rely on imports to get related products. A amount of economic and social benefits have been involved in the process. The thermal insulation principle of nano-ATO grain is the absorption of infrared rather than reflection. The infrared absorbed can heat the substrate (such as glass) and dissipate heat at the same time to prevent infrared heat from penetrating the substrate directly, so the result of “reflecting” infrared can be got. Because of the special optical property, nano-ATO material has been used the most widely in the research of transparent thermal insulation coating in recent years[4]. Nano-heat-insulating materials a new energy-saving material, which many scholars at home and abroad have done a detailed study of it[5].

TEST

Experiment Material and Equipment

The main reagents used in this experiment as follows: stannic chloride pentahydrate, antimony trichloride, ammonia, pure alcohol, acetylacetone, hydrochloric acid, nitric acid, tetraethyl orthosilicate, distilled water and so on.

The reagent for experiment was weighed accurately by the electronic balance CP114 made from OHAUS Instrument co. LTD, the experiment product was dried by the electricity heat drum wind drying oven DHG-9070A, and pH of the solution during the preparation of nano-ATO powder was controlled with digital pH-meter pH-25 made from Shanghai instrument scientific instrument co., LTD.

The characterization of the target product was tested as follows. It was scanning electron microscope Hitachi SU1510 of Japan's Hitachi LTD that tested the micro morphology of nano ATO powder, SiO2@ATO, ATO@SiO2 powder, ATO@SiO2@ATO powder and its substrate. It was the laser grain analyzer MICROTRAC S3500 of The United States muncie co. LTD that analyzed grain size of ATO, ATO@SiO2, SiO2@ATO, ATO@SiO2@ATO powder. It was XRD diffractometer TD-3500 that analyzed and researched the phase and grain size of the sample.

In this experiment, waterborne nanothermal insulation coating was prepared with waterborne acrylic resin as film forming material, nano ATO and other compound powder as the filler and the coordination of additives, which was brushed on the surface of the aluminum sheet to form the layer of thermal insulation film. The experiment coating obtained by stirring 0.2g sample and 1.8g aqueous acrylic of which the mass fraction was 10% was brushed uniformly on the aluminum plate with uniform size to endure the single variable and the same thickness of the coating film. The plate was used for contrast test after natural drying.

The experiment environment was as follows. The room temperature was 29℃ by indoor test. Dried aluminum plates and foam boxes were kept in the same ambient temperature for 2 hours to balance equipment temperature and the ambient
temperature. Besides, during the test doors and windows should be closed to keep the experimental environment wind speed 0m/s for reducing experimental error. Schematic diagram of the thermal insulation device was shown in Figure 1.

![Figure 1. Schematic diagram of the device to test thermal insulation effect.](image)

(1. the tungsten lamp; 2. the sample of aluminum plates; 3. thermometer; 4. the foam box)

**Preparation Methods of Experimental Samples**

Adopting the chemical coprecipitation method, weigh SnCl$_4$-5H$_2$O and SbCl$_3$ with 3% antimony doping concentration and dissolve it in 2 mol/L HCl. Then compound the mixed solution with ammonia according to a certain proportion; heat it for 30min in the water with 60°C, the constant temperature; Afterwards the deep blue powder, that is nano-ATO, could be got through filtration, abstersion, drying and calcination.

It was Sol-gel method that was adopted to prepare SiO$_2$ gel beads: the mixed solution compounded ethanol and ammoniain certain proportion was stirred and TEOS was added to. Then it took 4 hours for reaction. Afterwards, the ultra-light white nanoSiO$_2$ powder should be got through filtration, abstersion, drying and calcination.

SnCl$_4$-5H$_2$O and SbCl$_3$ was weighed of which the mixture contained 3% antimony and dissolved in 2 mol/L HCl. Then compound the mixed solution with ammonia was compounded according to a certain proportion and heated for 30min in the water with 60°C. Through suction filtration and abstersion some solid was got. The mixed solution of ethanol where the solid was disperse and ammonia was stirred for 30min in 3 file and then added with TEOS during stirred in 4 file. The total length of reaction was 3.5 hours. Afterwards, yellow precipitate could be got through filtration and abstersion and pearl blue ATO@SiO$_2$ powder could be obtained through drying and calcination.
30g SnCl₄·5H₂O was added with different quality of SbCl₃ according to different doping amount of Sb (5%, 7%, 10%, 15%) and dissolved into the ethanol containing acetylacetone. Then after ultrasonic dispersion of 15 min and magnetic stirring of 30 min the mixed solution was transformed into transparent light yellow clear solution. Added with a little distilled water the solution was stirred for 1 hour and dominated by aging for 24 hours. Afterwards nano-ATO sol was obtained.

1.0 g SiO₂ powder was put into a 100 mL beaker, and added with 50 mL nano-ATO sol with different doping concentration of Sb. Then after ultrasonic dispersion of 15 min and placed indoor for 24 hours the mixture produced some solid. Afterwards through suction filtration, abstersion by ethanol, 80°C drying, 650°C calcination for 2 hours, nano- SiO₂@ATO powder was obtained.

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RESULT AND DISCUSSION

Composition and Grain Structure Analysis of ATO, ATO@SiO₂, SiO₂@ATO and ATO@SiO₂@ATO Powder

ATO, ATO@SiO₂, SiO₂@ATO and ATO@SiO₂@ATO powder prepared was tested by XRD respectively. Figure 2 was XRD spectra of ATO, ATO@SiO₂ powder, and Figure 3 was XRD spectra of SiO₂@ATO and ATO@SiO₂@ATO powder with different doping concentration of Sb.

![Figure 2. The XRD spectra of ATO and ATO@SiO₂ powder.](image)

As seen in Fig4, each diffraction peak data of ATO sample was the same as the diffraction peak of SnO₂ tetragonal cassiterite structure(JCPDS card number:
The absence of the peak of antimony oxide indicated that all Sb ion entered into the SnO2 lattice to replace part of the Sn ion. Comparing the diffraction intensity curves of two sample, it can be found that the diffraction peak of ATO@SiO2 powder was wider than that of ATO powder, and the intensity of diffraction peak decreased, which indicated that the grain size of ATO@SiO2 powder was smaller. In the figure, there was not obvious characteristic peaks of SiO2, which showed that the coated SiO2 was amorphous and the coating thickness was thin. Taking the strongest peak of ATO@SiO2 and ATO to calculate the grain size, it was calculated according to Scherrer formula that the average grain size of ATO@SiO2 powder d=2.049nm and the average grain size of ATO powder was d=3.919nm. The color of ATO powder coated with SiO2 became shallow and the grain size became smaller.

![Figure 3. The XRD spectra of SiO2@ATO and ATO@SiO2@ATO powders.](image)

The diffraction peak of ATO@SiO2 powder of the composite ATO was almost unchanged, and the crystal was still ATO with rutile structure, and the peak position was migrated a bit. The diffraction peak of ATO@SiO2@ATO powder was wider than that of ATO@SiO2 powder, and the intensity of diffraction peak decreased slightly. The result showed that the grain size of ATO@SiO2@ATO powder was smaller. The grain size obtaining the strongest one of each peak of ATO@SiO2@ATO, according to Scherrer formula, it was calculated to obtain that, the average grain size of ATO@SiO2@ATO-5% powder was d=1.726 nm, the average grain size of ATO@SiO2@ATO-7% powder was d=1.741 nm, the average grain size of ATO@SiO2@ATO-10% powder was d=2.115nm, the average grain size of ATO@SiO2@ATO-15% powder was d=1.856 nm. The result showed that the grain size of ATO@SiO2@ATO powder increased at first and then decreased with the increase of Sb doping amount.
Grain Size Analysis of ATO, ATO@SiO\textsubscript{2}, SiO\textsubscript{2}@ATO, ATO@SiO\textsubscript{2}@ATO Powder

The result of laser grain size analysis of ATO, ATO@SiO\textsubscript{2}, SiO\textsubscript{2}@ATO, ATO@SiO\textsubscript{2}@ATO powder was shown in Figure 4, figure 5, Figure 6 and Figure 7 as follows.

![Figure 4. The test result of ATO grain size.](image)

![Figure 5. The test result of ATO@SiO\textsubscript{2} grain size.](image)

The test results showed that of grain size distribution of ATO powder was mainly in the range of 0.4 ~ 2.5um, that of ATO@SiO\textsubscript{2} powder was concentrated in 0.3 ~ 0.7 um, accounting for 68.3% of the proportion, and that of part of the powder was concentrated in 1.2-5.0 um, accounting for 31.7%. There were two distribution peaks, which was caused by particle agglomeration. Particle agglomeration can be reduced by ultrasonic dispersion. But after ultrasonic dispersion, grains may be agglomerated again; it was possible to suck up the upper clear liquid with the lower
particle that leaded to grain aggregation to decrease the accuracy of laser grain size analysis result.

![Figure 6. The test result of SiO$_2$@ATO grain size.](image)

![Figure 7. The test result of ATO@SiO$_2$@ATO grain size.](image)

According to Fig.3, the of the sample was calculated from the strongest diffraction peak of sample XRD. The data showed that the grain size of the sample increased with the increase of Sb doping amount of ATO sol. Selecting SiO$_2$@ATO-15% powder, ATO@SiO$_2$@ATO-15% powder, the result of the laser grain size analysis and comparison showed that the grain size of SiO$_2$@ATO-15% powder ranged between 0.3 ~ 10 nm, of which the total proportion accounted for 90.4% and that of ATO@SiO$_2$@, ATO-15% powder ranged from 0.4 to 60 nm, of which the curve had two distribution peak, caused by the grain agglomeration.
Micro Morphology Analysis of ATO, ATO@SiO$_2$ Powder

ATO powder and ATO@SiO$_2$ powder, ATO@SiO$_2$@ATO-15% powder, SiO$_2$@ATO-15% powder was tested by SEM to directly observe morphology and grain size of the powder. As shown in Figure 8, the picture was taken in the magnification of 10 K on the upper right of which the picture was taken in the magnification of 15 K.

![Figure 8. The SEM diagram of ATO and ATO@SiO$_2$ powder.](image)

The scanning electron microscopy, that is Fig8, showed that the morphology of nano-ATO powder compounded by chemical coprecipitation synthesis method was uneven block, the average grain size of which was about 0.5 um. In comparison, the grain size of ATO coated with SiO$_2$ was smaller and more evenly distributed, the particle morphology was spherical, and the average grain size was less 0.3 um than nano-ATO powder. The comparison showed that the grain size of the samples obtained by SEM analysis was much bigger than that calculated by XRD (DXRD), of which the reason was that DSEM was size of grains composed of a plurality of grain agglomeration and DXRD was single grain size. Therefore, only when the
powder was single crystal, the measured value of SEM could be close to the value of XRD calculation. ATO@SiO$_2$@ATO powder was spherical like ATO@SiO$_2$, distributed evenly, and coated thickly, which showed that the aggregation growth of grain size of ATO was related to coating time and sol solubility. The distribution of nano-SiO$_2$@ATO powder was uniform and the morphology was spherical. The spherical structure of the SiO$_2$@ATO-15% powder coated can be clearly observed.

**Thermal Insulation Performance Analysis**

The aluminum plate coated with thermal insulation coating was put above the hole on the foam box with the $34 \times 25 \times 10$cm specification, and it should been sured that the foam hole was filled without gap. The 500W tungsten lamp with the spectrum similar to solar of thermal insulation effect testing device washed above 30cm of the box. Time was recorded when the lamp opened and air temperature in the box was recorded every 2 min. When the temperature change did not exceed 0.5 degrees (as to the equilibrium temperature), recording data was stopped. Compared with the air temperature in the ATO box, the air temperature difference between experiment box with the box coated with commercially available ATO reflected the thermal insulation effect of the coatings.

After the test of the samples, according to the experimental data obtained, compared with the insulation effect of the commercial goods ATO, the result was shown in Fig 9 and Fig 10 as follows.

![Figure 9. The contrast diagram of the thermal insulation effect between ATO, ATO@SiO$_2$ and commercial ATO.](image-url)
Fig 9, Fig 10 and Fig 11 showed that in incandescent light irradiation, with the extension of time temperature in the test device box rose. The rise range was large in the beginning and gradually leveled off. After 20 minutes of irradiation, the air temperature in the box gradually balanced. According to the analysis of graphs, the thermal insulation effect of 5 sample was better than commercial ATO, that is precipitation ATO, ATO@SiO$_2$, ATO@SiO$_2$@ATO-5%, ATO@SiO$_2$@ATO-10%, SiO$_2$@ATO-15%, SiO$_2$.

Figure 10. The contrast diagram of the thermal insulation effect between composite sample.

Figure 11. The contrast diagram of the thermal insulation effect between SiO$_2$, ATO@SiO$_2$, SiO$_2$@ATO-15% and commercial ATO.
Fig 9 showed that the thermal insulation effect of ATO coated with SiO\textsubscript{2} was better than precipitation ATO. Fig 10 showed that among 4 kinds of ATO@SiO\textsubscript{2}@ATO sample with core-shell structure, in addition that the thermal insulation effect of ATO@SiO\textsubscript{2}@ATO-10% powder was better than ATO ATO@SiO\textsubscript{2} powder without coated ATO. The heat insulation effect of the rest was worse than ATO@SiO\textsubscript{2} powder. The thermal insulation effect of ATO@SiO\textsubscript{2}@ATO-7% powder and ATO@SiO\textsubscript{2}@ATO-15% powder was as good as ATO good. Figure 11 showed that the thermal insulation effect SiO\textsubscript{2}@ATO-15% powder was better than SiO\textsubscript{2}. In addition, the coating order of ATO and SiO\textsubscript{2} has obvious influence on the thermal insulation effect. The thermal insulation effect of SiO\textsubscript{2}@ATO-15% powder was better than ATO@SiO\textsubscript{2} powder as so as better than commercial goods ATO.

CONCLUSION

(1) After coating with different amount of Sb doped ATO sol, the XRD test result showed that the grain size of 4 groups of powder are small enough and reached the nanometer level. The single grain size of sample calculated by Scherrer formula increases first and began to decrease when the doping amount of Sb was 10%, while the color of powder became from light slate gray to celandine green.

(2) The ATO@SiO\textsubscript{2}@ATO@15% grains were coated completely and the outer sol coating thickness was larger, which was the reason of grain agglomeration.

(3) The thermal insulation effect of ATO@SiO\textsubscript{2}@ATO-10% powder was the best which was obtained after ultrasonic dispersion, suction filtration, 80°C drying and 650°C calcination for 2 hours for the mixture of ATO@SiO\textsubscript{2} and ATO sol with 10% doping amount of Sb.

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REFERENCES
