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# Development of an Antimony Doped Tin Oxide/TiO<sub>2</sub> Double-Layers Coated HGM: A High Reflectivity and Low Transmittance Building Thermal Conservation Material

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# Abstract

A novel antimony doped tin oxide (ATO) and  $TiO_2$  double-layers coated HGM was developed in this project. The ATO, which has excellent IR-insulation property, was coated on the HGM as the first layer and the  $TiO_2$ , which has high reflectivity, was the outmost layer. Therefore, when the modified HGM is coated on the outside of the building walls, the incident light is firstly reflected by the  $TiO_2$  layer then insulated by the ATO layer. Most of the radiative thermal transfer was blocked by this double-layers coating. The building envelope can be thus protected by the HGM for less heat gains. Compared with original HGMs, the reflectivity increased by 19.6% and the transmittance decreased by 85.7%. In addition, this coating barely changed the thermal conductivity, which only increased by about 8%. By this method, most of the thermal transfer are blocked. The energy consumption and carbon emission of a building can be reduced.

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Keywords: ATO, TiO<sub>2</sub>, HGM, double-layers coating, low transmittance, high reflectivity.

# 1. Introduction

In the total energy consumption, the air condition in a modern building weights a high percentage. Aiming to reducing the energy consumption and carbon emission, the heat-insulating materials with high performance is studied. Among them HGM (hollow glass microspheres) is attracting more and more attentions.

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HGM is a promising inorganic material since its special structure. Its size ranges from  $10~100 \mu m$  and the shape is nearly the perfect spherical. <sup>[1-3]</sup> The most obvious feature is the hollow structure, which provides the light density and perfect thermal conservation property. Therefore, it is widely applied in hydrogen storage <sup>[4]</sup>, nuclear fusion <sup>[5]</sup>, emulsion explosive <sup>[6]</sup>, deep-sea detecting <sup>[7]</sup>, aerospace <sup>[8]</sup>, thermal conservation <sup>[9]</sup> etc. However, HGM is only able to prevent the heat conduction. Since the chemical nature of HGM is glass, most of the light is still able to transmit and heat the inner body directly via the thermal radiation. Thus, a special material which reduces the radiative heat transfer should be combined with HGM. There are few researches focused on this area. The most-often applied material was TiO<sub>2</sub> since its relatively high reflectivity. Jing Yuan <sup>[10]</sup> et al. reported a method of coating anatase TiO<sub>2</sub> on HGM surface aiming to enhance the reflectivity. In the fact, only the reflecting effect cannot effectively block most of the radiative heat transfer. Therefore, antimony doped tin oxide (ATO) was associated with TiO<sub>2</sub>. ATO is reported as a material with excellent IR insulation property and conductivity. <sup>[11]</sup>

In this work, a novel  $TiO_2/ATO$  double-layers coated HGM was synthesized. First of all, ATO nano particles must be fine-dispersed in aqueous phase before the coating. Then,  $TiO_2$  was deposited on the ATO coated HGM as the second layer via hydrothermal method. In this way, the  $TiO_2$  firstly reflected part of the incident light, then the ATO layer block the rest incident light. Therefore, most of the radiative heat transfer can be blocked by the two layers coating. With this feature, the overall heat insulation property of the coated HGM can be enhanced.

Nomenclature	
HGM	Hollow glass microsphere
ATO	Antimony doped tin oxide
PFOTES	1H,1H,2H,2H-perfluorooctyltriethoxysilane
TBOT	Tetrabutyl titanate
SEM	Scanning Electron Microscope

# 2. Experiments

#### 2.1. Materials

In this work, all of the HGM was provided by the Technical Institute of Physics and Chemistry, Chinese Academy of Sciences. The HGM particle density was 0.3753g/cm<sup>3</sup> and the tapped density was 0.2g/cm<sup>3</sup>. The HGM wall-thickness ranged between 3% and 8% of its diameter. <sup>[12]</sup> TBOT and SnCl<sub>4</sub> were all purchased from Sigma-Aldrich. The ATO particles were bought from National Engineering Research Centre for Nanotechnology.

#### 2.2. Experimental procedures

5g of ATO and 5ml DI water were firstly mixed with 1g SnCl<sub>4</sub> in a ball-miller jar. Then the zirconium beads ( $\varphi$ 2mm) were added until the mixture turned to mortar. After that, it was ball-milled in 3000 r/min for 12h. The dispersed sample was collected by water extraction. Following that, 5g of HGM was mixed with 30 ml DI water. It was stirred in the speed of 400 r/min. The as-prepared ATO dispersion liquid (10% wt.) was added in the system (1 drop/7 second). Two hours later, the ATO coated HGM was obtained after

the filtering and drying. Then, it was mixed with 47.5 ml ethanol and 2.5ml DI water in a three-necked flask with pre-mixing for 20 min by the stirrer in 400r/min. Next, 15g TBOT and 30 ml ethanol were mixed and then dropped into the flask by the speed of 1 drop per 7 seconds. After 3 hours, they were all transferred into a hydrothermal reactor. The reaction lasted for 6 hours in 180 °C. Subsequently, the samples suspended on the liquid were collected. The final products were obtained after dried in 80 °C for 4 hours. Then, it was coated on glass substrate for latter characterizations. The coating thickness was 0.2mm.

## 3. Results

#### 3.1. The SEM characterizations

The SEM image of as-prepared ATO/TiO<sub>2</sub> double-layers coated HGM was shown in Figure 1a. Figure 1b was the magnified image of the black circled area in Figure 1a. Then point EDS was conducted in three red pointed areas in Figure 1b. The results were shown in Figure 1c, d and e respectively. As shown in Figure 1c, the corresponded point was the point 1 in Figure 1b, which was the shell of HGM surface. Therefore, the weight percentage of Si (the main element of HGM) was 23.07% and Ti, Sn were relatively low, which were only 2.52% and 5.01% respectively. For the point 2 in Figure 1b, the EDS result was shown in Figure 1d. As shown in this figure, the Sn weight percentage was increased to 32.54%, but the Si and Ti were only 12.11% and 9.18% respectively. This represented ATO particles was coated on the HGM surface as the first layer. Then, the EDS result of outmost coating (point 3) was shown in Figure 1e. From this figure, Ti weight percentage increased to 26.62% and the Si and Sn were decreased to 7.02% and 11.21% respectively. It referred that the outmost coating was mainly composed of TiO<sub>2</sub>. Therefore, the double-layers coating was demonstrated successfully prepared.

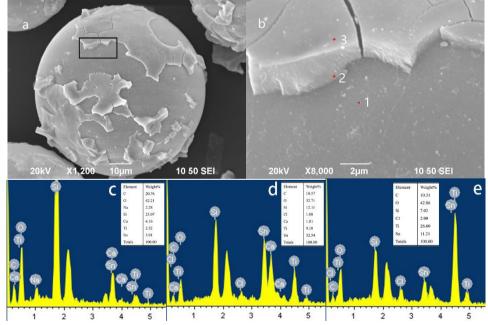


Figure 1 a: The ATO/TiO<sub>2</sub> double-layers coated HGM; b: The magnified image of the black circled area in a; c, d, e represented the point EDS results of the 1, 2, 3 point in b respectively

#### 3.2. The thermal conductivity characterizations

The thermal conductivity of original HGM and ATO/TiO<sub>2</sub> double-layers coated HGM was shown in Figure 2. The value of original HGM was 0.0475 W/(m•K) and that of ATO/TiO<sub>2</sub> double-layers coated HGM was 0.0514 W/(m•K). It only decreased by 8%. Therefore, the coating slightly influenced the thermal conductivity.

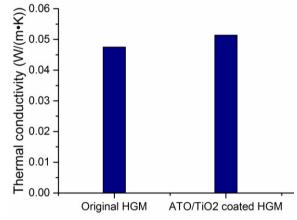


Figure 2 The thermal conductivity of original HGM and ATO/TiO<sub>2</sub> coated HGM

### 3.3. The Vis-NIR reflectivity and transmittance characterizations

After the as-prepared ATO/TiO<sub>2</sub> double-layers coated HGM was stuck on glass substrate, the Vis-NIR reflectivity and transmittance characterizations were conducted. For comparison, the original HGM was also investigated. The results were shown in Figure 3. As shown in Figure 3a, the double-layers coated HGM showed better reflectivity at all band especial the band above 1500nm. The reflectivity also increased from about 30~35% to 35~45%. Since the reflectivity cannot be compared directly, their curve integral areas were used to reflect the reflectivity. The increasing of curve integral area was 19.6%. Therefore, it was demonstrated that the IR reflectivity had relatively enhancement.

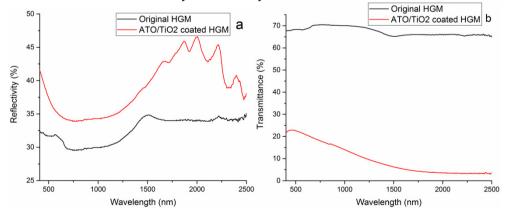


Figure 3 a: The reflectivity of original HGM and ATO/TiO<sub>2</sub> coated HGM; b: the transmittance of original HGM and ATO/TiO<sub>2</sub> coated HGM

As for Figure 3b, the transmittance data of original HGM and double-layers coated HGM were compared. The transmittance of ATO coated HGM was quite lower than that of original HGM. Especially when the band was above 1500 nm, the transmittance was only about 5%. The decreasing of curve integral area was 85.7%. The main IR insulation effect of ATO was absorption. Even though part of the absorbed IR turned to heat, the HGM had quite low thermal conductivity therefore most of the thermal conduction was blocked by the hollow structure of HGM.

## 4. Conclusions

In this work, the novel ATO/TiO<sub>2</sub> double-layers coated HGM was developed. HGM had excellent low thermal conductivity. ATO was coated on HGM as the first layer and the TiO<sub>2</sub> was selected as the second layer. After it was coated on building walls, the incident light on building envelopes was firstly reflected by the TiO<sub>2</sub> layer and then insulated by the ATO layer. Therefore, the radiative thermal transfer can be maximally reduced. Compared with original HGM, the reflectivity increased by 19.6% and the transmittance decreased by 85.7%. However, the thermal conductivity barely changed, which only increased by about 8% due to the increase of the wall thickness.

In the future work, the influence of modified HGM on the reducing of energy consumption will be detailed investigated by simulation.



#### **Biography**

Mr. Hu Yan, PhD candidate in The Department of Building Services Engineering, The Hong Kong Polytechnic University.

#### References

[1] Yung KC, Zhu BL, Yue TM, Xie CS. Preparation and properties of hollow glass microsphere-filled epoxy-matrix composites[J]. Compos Sci Technol 2009; 69 (2): 260-264.

[2] Xu N, Dai JH, Zhu ZB, Huang X, Wu PW. Synthesis and characterization of hollow glass-ceramics microspheres[J]. Compos Sci Technol 2012; 72 (4): 528-532.

[3] Li B, Yuan J, An ZG, Zhang JJ. Effect of microstructure and physical parameters of hollow glass microsphere on insulation performance[J]. Mater Lett 2011; 65 (12): 1992-1994.

[4] Schmitt, M., Shelby, J., and Hall, M., Preparation of hollow glass microspheres from sol-gel derived glass for application in hydrogen gas storage[J]. Journal of Non-Crystalline Solids, 2006. 352(6-7): p. 626-631.

[5] QIU L, FU Y, WEI Y, et al. Mathematical simulation of the physical process to fabricate hollow glass microspheres by liquid droplet method [J]. High Power Laser & Particle Beams, 2002, 3: 020.

[6] SONG J, WANG X, YU Y, et al. Detonation Velocity Characteristics of Emulsion Explosives Sensitized by Glass Micro-balloons [J]. Journal of University of Science and Technology Beijing, 2000, 6.

[7] SUN C, XING Y, WANG Q C. High-strength deep-sea buoyancy material made of polymer filled with hollow glass micro-beads [J]. Journal of University of Science and Technology Beijing, 2006, 6.

[8] Geleil, A., Hall, M., and Shelby, J., Hollow glass microspheres for use in radiation shielding[J]. Journal of Non-Crystalline Solids, 2006. 352(6): p. 620-625.

[9] Liang J Z, Li F H. Measurement of thermal conductivity of hollow glass-bead-filled polypropylene composites[J]. Polymer Testing, 2006, 25(4): 527-531.

[10] Yuan J, An Z, Li B, et al. Facile aqueous synthesis and thermal insulating properties of low-density glass/TiO 2 core/shell composite hollow spheres[J]. Particuology, 2012, 10(4): 475-479.

[11] Lin Y J, Wu C J. The properties of antimony-doped tin oxide thin films from the sol-gel process[J]. Surface and Coatings Technology, 1997, 88(1): 239-247.

[12] PAN S, ZHANG J, SONG G. Research progress of hollow glass microsphere and solid buoyant material for deep-sea application[J]. Journal of Tropical Oceanography, 2009, 4: 004.