

## Preparation and Characterization of Gallium Doped ZnO/Epoxy Composite as Thermal-Insulating Coating

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In this article, transparent gallium doped zinc oxide (GZO)/epoxy composites, as glass thermal insulation coating, were prepared by incorporating gallium doped zinc oxide nanoparticles into a transparent epoxy matrix. The effects of gallium doped zinc oxide content on the optical and thermal insulation property of gallium doped zinc oxide/epoxy coating were studied. The results reveal that the gallium doped zinc oxide/epoxy composite coating with 0.5 wt % gallium doped zinc oxide possesses excellent optical properties, *i.e.*, visible light transmittance above 45 % and shading coefficient of 0.43 are simultaneously achieved. In addition, the large stable temperature difference between chamber with gallium doped zinc oxide/epoxy coated glasses and common glass indicates that the prepared gallium doped zinc oxide/epoxy coating has excellent thermal insulation property.

**Key Words:** Gallium doped zinc oxide, Epoxy, Nanocomposites, Thermal insulation.

### INTRODUCTION

In recent decades, the large windows and glass curtain walls have been widely used in buildings, which have caused increasing energy consumption in buildings. This leads to increasing the usage of air-condition in summer and heater in winter. To reduce the energy consumption, solar filters have been used as coatings for architectural or vehicle glasses *etc.* Generally, such filters should have high shielding efficiency for near-infrared (NIR) and high transmittance for visible light (VIS). These properties would contribute low heat gain and undiminished luminosity inside the buildings. Unfortunately, most commercially available architectural glasses do not perform optimally. Most of them transmit 80 % of solar irradiance while others use highly reflective coatings that diminish luminosity inside the buildings<sup>1</sup>.

Zinc oxide is a well-known n-type semiconductor with a wide band gap of 3.4 eV. It has been extensively studied for a long time because of its wide applications ranging from optoelectronics, acoustic devices, transistor, UV-absorber to light-emitting diodes<sup>2-6</sup>. Doping of ZnO can be achieved by replacing Zn<sup>2+</sup> atoms with the elements of higher valency such as Ga, Al and In, *etc.* This substitution usually induces dramatic changes in its electrical and optical properties<sup>7-10</sup>. More importantly, Ga, Al and In doped ZnO has shown good visible light transmittance and excellent infrared radiation shielding efficiency<sup>7-9</sup>, which makes them good candidates as solar filters. Among

the metal dopants, gallium seems to be the best for ZnO due to fact that atomic radius of Ga<sup>3+</sup> is similar to Zn<sup>2+</sup> and its lower reactivity to oxygen<sup>9</sup>.

In our previous work, gallium doped zinc oxide nanoparticles have been prepared with a facile polymer-pyrolysis method<sup>11</sup>. In this paper, transparent gallium doped zinc oxide/epoxy composites, as transparent glass thermal insulation coatings, were prepared by incorporating gallium doped zinc oxide nanoparticles into a transparent epoxy matrix. The effects of gallium doped zinc oxide content on the optical and thermal insulation property of gallium doped zinc oxide/epoxy coating were studied. The prepared transparent gallium doped zinc oxide/epoxy coating showed excellent thermal insulation properties and exhibited a great potential as building energy saving material.

### EXPERIMENTAL

**Preparation of gallium doped zinc oxide/epoxy thermal insulation coating:** gallium doped zinc oxide nanoparticles doped with 4 mol % Ga were prepared by the polymer pyrolysis methods as reported<sup>11</sup>. Room temperature curing transparent epoxy (two components: A and B) was used as matrix of thermal insulating coating. As-prepared gallium doped zinc oxide nanoparticles were dispersed in an iso-propanol solution with the aid of ultrasonication and then pretreated with 3 wt % coupling agent 3-glycidoxypropyltri-methoxysilane at room temperature for 24 h. The resulted mixture was then mixed

with epoxy A and curing agent B. The weight ratio of A and B is 2:1. The epoxy and curing agent were stirred until a homogeneous mixture was obtained. The mixture was coated onto glass sheet using a glass bar. After curing at room temperature for 24 h, the gallium doped zinc oxide/epoxy coated thermal insulation glass sheet was obtained.

Transmission electron microscopy (TEM) of gallium doped zinc oxide samples was performed with a Hitachi JEM-2100 type TEM and the particle sizes from TEM were estimated with the software of Photoshop 7.0. To reveal the crystalline structure of gallium doped zinc oxide powders, X-ray diffraction (XRD) was carried out on a X-Ray diffractometer (Bruker D8 ADVANCE) at a voltage of 40 kV with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  ranging from  $10\text{-}75^\circ$ .

The optical properties of the gallium doped zinc oxide/epoxy coating were studied by using a UV-VIS-NIR spectrophotometer (Varian, Cary 5000). The transmittance spectra were scanned in the range of 250-2500 nm with a 1 nm interval. The thermal insulation properties of the prepared gallium doped zinc oxide/epoxy coating were investigated by the in-house made environmental simulating apparatus, as shown in Fig. 1. It consists of a halogen lamp, a thermal insulating chamber with open window fixed with changeable glass and a temperature recording system.

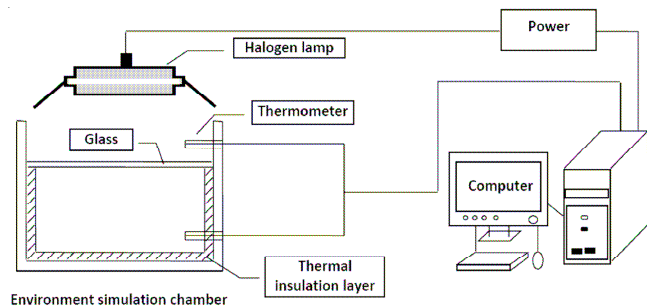
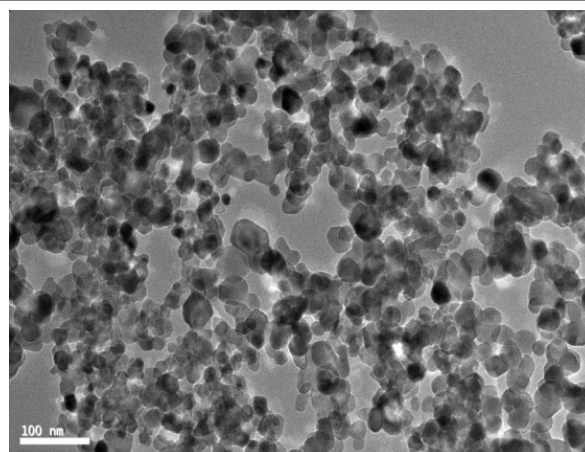


Fig. 1. Schematic image of thermal insulation property test setup

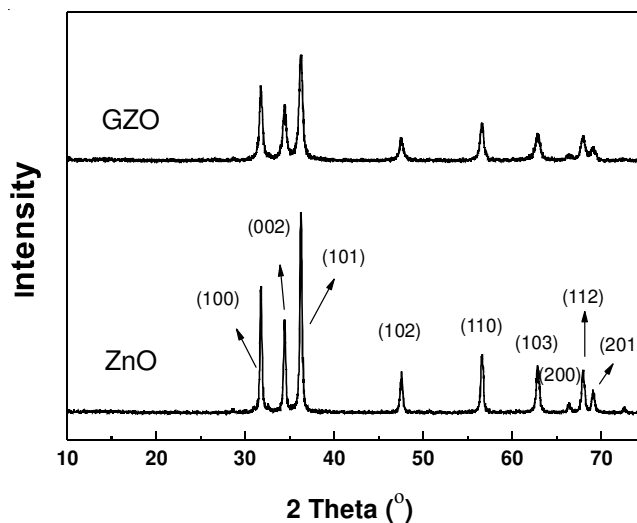
## RESULTS AND DISCUSSION

Gallium doped zinc oxide nanoparticles have been prepared *via* polymer-pyrolysis method, this method is simple to operate and suitable for industrial production of gallium doped zinc oxide nanoparticles. The detailed microstructures of the prepared products were observed by TEM and shown in Fig. 2(a). It can be seen that gallium doped zinc oxide particles are spherical in shape with mean particle size of about 26 nm and the obtained gallium doped zinc oxide particles are well dispersed. Fig. 2(b) shows XRD patterns of gallium doped zinc oxide and pure ZnO nanoparticles that also were prepared by the polymer-pyrolysis method. It can be seen that all the peak positions of gallium doped zinc oxide agree well with the reflections of bulk wurtzite ZnO. No characteristic diffraction peak corresponding to Ga or Ga compound impurity phase is observed, indicating that all gallium ions come into the crystal lattice of bulk ZnO to substitute for zinc ions.

Since gallium doped zinc oxide is an N-type semiconductor, as the classical Drude theory indicate that gallium doped zinc oxide nanoparticles with the best electrical conductivity possess the best IR shielding properties<sup>9,12</sup>. According to previous investigation, gallium doped zinc oxide nanoparticles doped



(a)



(b)

Fig. 2. (a) TEM image of gallium doped zinc oxide nanoparticles and (b) XRD patterns of ZnO and gallium doped zinc oxide nanoparticle

with 4 mol % Ga have the best electrical conductivity. Thus, transparent gallium doped zinc oxide/epoxy coatings were prepared by incorporation of gallium doped zinc oxide nanoparticles doped with 4 mol % Ga into transparent epoxy matrix. The UV-VIS-NIR transmittance spectra of glass and gallium doped zinc oxide/epoxy coated glasses are shown in Fig. 3. Compared with common glass sheet, the light transmittance of gallium doped zinc oxide/epoxy coated glasses in the whole UV-VIS-NIR range is decreased. With the increase of gallium doped zinc oxide content, the light shielding efficiency is increased. For gallium doped zinc oxide/epoxy coating with 0.5 wt % gallium doped zinc oxide, the visible light transmittance is above 45 %, which can meet the need of luminosity inside the building. More importantly, the light transmittance in near infrared range is lower than in visible light and more than 70 % of near infrared light is shielded.

The ability for a window to transmit solar heat relative to that for 3 mm (1/8-inch) clear, double-strength, single glass can be determined with the shading coefficient. It is usually a value ranging from 1 to 0 and lower values indicate better performance in reducing summer heat gain and therefore air-conditioning loads. The shading coefficient ( $S_c$ ) is calculated with the following equation<sup>13</sup>:

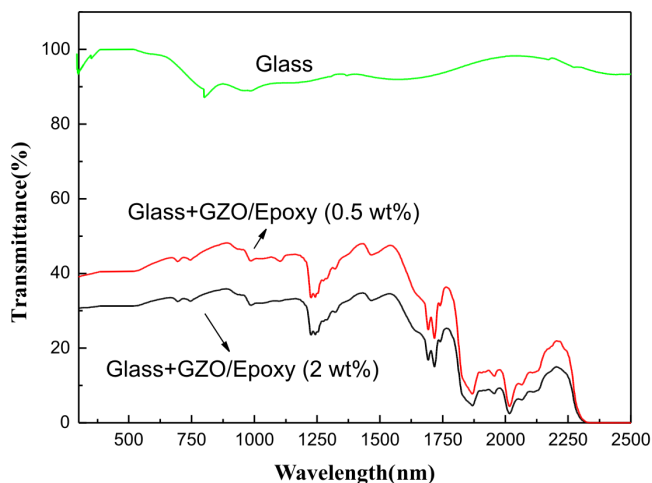


Fig. 3. UV-VIS-NIR spectra of blank glass, pure epoxy and gallium doped zinc oxide/epoxy coated glasses

$$S_c = \frac{\sigma_s}{\sigma_e} \quad (1)$$

$\sigma_s$  is the total solar heat transmittance of 3 mm glass,  $\sigma_e$  is the total solar heat transmittance of gallium doped zinc oxide/epoxy coated glass. The calculated shading efficient for gallium doped zinc oxide/epoxy with 0.5, 1.0 and 2.0 wt % gallium doped zinc oxide is 0.43, 0.34 and 0.22, respectively. These results indicate that the prepared gallium doped zinc oxide/epoxy composite coating has good thermal insulating properties.

Furthermore, the thermal insulating properties of gallium doped zinc oxide/epoxy coated glasses were investigated. As shown in Fig. 4, under the luminous halogen light, the chamber temperature gradually increases with the lapse of time and reaches stable after 1 h. For the chamber with gallium doped zinc oxide/epoxy coated glasses, the chamber temperature increased more slowly than with common glass sheet. In addition, the temperature under stable condition of the chamber with gallium doped zinc oxide/epoxy coated glasses is lower than with common glass sheet. The highest temperature difference between chambers with gallium doped zinc oxide/epoxy

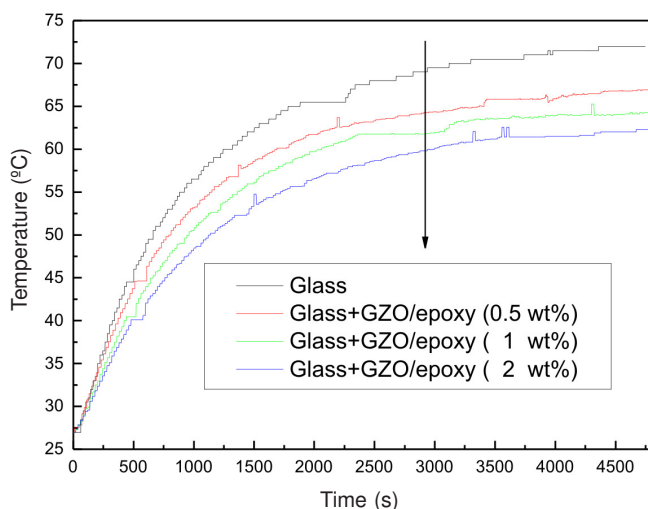


Fig. 4. Effect of gallium doped zinc oxide/epoxy coating on the chamber temperature under simulated environment

(0.5 wt % gallium doped zinc oxide) coated glass and common glass is about 5 °C. For the gallium doped zinc oxide/epoxy with 2 wt % gallium doped zinc oxide, the temperature difference is increased to about 10 °C. Moreover, the cooling process was also investigated, the temperature of the chamber with gallium doped zinc oxide/epoxy coated glass decreased more slowly than with common glass sheet. The above results reveal that gallium doped zinc oxide/epoxy composite coating has good thermal insulating properties, indicating that the gallium doped zinc oxide/epoxy composite coating is promising for application in building window and other thermal management fields.

## Conclusion

In summary, the transparent gallium doped zinc oxide/epoxy coating was successfully prepared by incorporation of the as-obtained gallium doped zinc oxide nanoparticles into a transparent epoxy matrix. The results show that the gallium doped zinc oxide/epoxy coating with 0.5 wt % gallium doped zinc oxide has optimal optical properties, *i.e.*, the visible light transmittance above 45 % and shading coefficient of 0.43 are simultaneously achieved. In addition, the large temperature difference under stable condition between chambers with gallium doped zinc oxide/epoxy coated glasses and chamber with common glass indicates that the prepared gallium doped zinc oxide/epoxy coating has excellent thermal insulation property. The as-prepared transparent gallium doped zinc oxide/epoxy thermal insulation coating has great potential for uses in building window and other thermal management fields.

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