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A novel transparent thermal insulation bilayer coating based on ATO/Black TiO2

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Abstract

Significant progress has been made in transparent thermal insulation coating by various effective materials in recent years. More recently, Low-E coating, as a high reflection coating, has been applied in many buildings, but the coating would cause light pollution due to visible light reflection, resulting in prohibiting use in many countries. Hence, a novel transparent thermal insulation coating based on ATO/Black TiO2 is proposed in this paper. The bilayer coating exhibited a high near infrared light blocking rate of 86%, and the visible light transmittance was about 62%. Meanwhile, the structural thin films had excellent photocatalytic property, which could degrade approximately by 45% of methylene blue in 3 hours under fluorescent lamp. The double layered coating had shown a water contact angle of lower than 5° after activating. Overall, these structural films show a great potential for applications in energy conservation windows.

Keywords: ATO; Black TiO2; thermal insulation; window; photocatalytic property

1. Introduction

In Hong Kong, more than 40% of the energy is consumed by large-scale usage of air conditioning systems for buildings because of hot weather [1]. A lot of heat gains is through building windows (the transparent component of buildings). Transparent thermal insulation coatings, which can strongly shield

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the near infrared (NIR) light and UV light, have been widely explored and used in energy conservation of buildings. More recently, Low-E coating, which has high reflection, has been applied in much more buildings. However, the Low-E coating tends to cause light pollution because of visible light reflection, which has been prohibited in many countries. Hence, to develop an absorption thermal insulation layer was necessary [2].

Transparent conductive oxide (TCO) such as doped indium, doped tin, zinc oxide, because of their unique high electrical conductivity and visible light transmittance, which are widely used in solar cells and flat panel display device such as a thin layer of transparent electrodes, smart Windows and chemical sensors, etc. In recent years, more scientists have shifted their eyes from thin films to nano-TCO crystals. ATO (Antimony-doped tin oxide) has an optical band gap of more than 3.6eV, which exhibits a high transmittance in the visible light range and high blocking rate in near infrared (NIR) light range [3]. Therefore, the ATO, as Low-E beneficial alternatives, has broad potential of research and application [4].

Anatase TiO2, a traditional semiconductor, shows a high visible light transmittance due to the large band gap of 3.2eV, which can be used in photocatalyst. However, the narrow of the absorption spectrum limited its application. Therefore, most research was focus on doping other element into the TiO2 crystal to change the band gap and local surface plasma resonance [5]. In this paper, a self-doped black TiO2 layer was obtained by electrochemistry and combined with ATO film to enhance the blocking rate of NIR light. Meanwhile, this bilayer coating exhibited an excellent self-cleaning property.

2. Experiment

All of the chemical reagents used in this experiment were of analytical grade and purchased from Aladdin Chemical Co. Ltd. The hydrothermal reactor and mechanical agitation was from Shanghai Jingke Co. Ltd. The direct-current electrical source was purchased in Han's Laser Technology Co. Ltd. The automatic spraying equipment was from Dongguan Dongyangguang Technology Co. Ltd.

In a typical synthesis of ATO layer, 2g of Sn powder and 1g of Sn2O3 were dissolved into 20ml concentrated sulfuric acid, and then the matrix was mixed with 10ml H2O2 (35vol.%). The mixture solution was put in stainless steel hydrothermal reactor and heated with stage elevation: 180℃ for 1h, 200℃ for 2h, and 230℃ for 5h. The Vapor pressure was up to 4MPa eventually. The resulting product was collected and washed with water, and finally dried at 100℃. The final solid powder was dispersed in waster by ball-milling with adding dispersing agent of SN5040. After ball-milling in 4 hours, an aqueous dispersion would be obtained. Then, waterborne polyurethane was added into the aqueous dispersion, and after string with mechanical agitation in a speed of 5000rmp in 2 hours. Finally, the aqueous coating could be obtained and the ATO layer could be fabricated by automatic spraying equipment.

In a typical synthesis of black-TiO2. Firstly, the self-dispersing TiO2 coating was obtained by controllable hydrothermal reaction [6]. And TiO2 layer on the surface of the glass could be fabricated by automatic spraying equipment. Then, the Black TiO2 thin film was developed by an in-house made reactor, as shown in figure 1, where every film was placed on the surface of conductive glass and soaked inside a glass container containing the NH4Cl, deionized water, and ethylene glycol. This device was equipped with direct-current electrical source (DCES), which control the electric current of 2A and voltage of 5V.

For the film process, firstly, the black TiO2 film was coated on the side of the glass sheet, and then the thermal insulation coating based on nano ATO was sprayed on the surface of another side by automatic spraying equipment. The details of the film process are shown in figure 2. And the diagram of the final structural black TiO2/ATO thermal insulation coating was shown in figure 3.

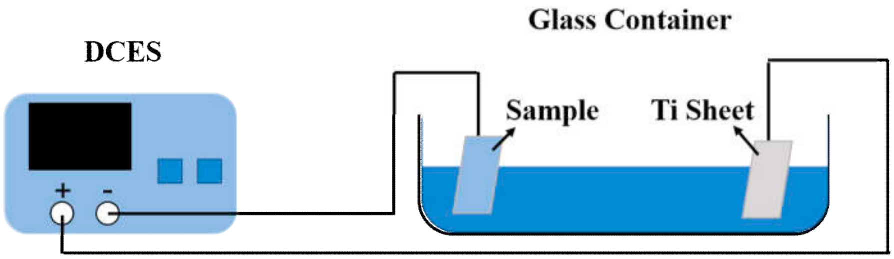

Figure 1 Electric reduction equipment

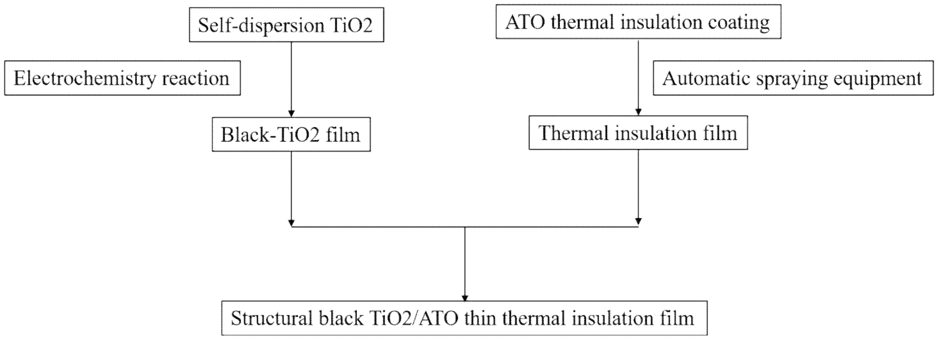

Figure 2 The flow chart of the structural black TiO2/ATO thermal insulation coating

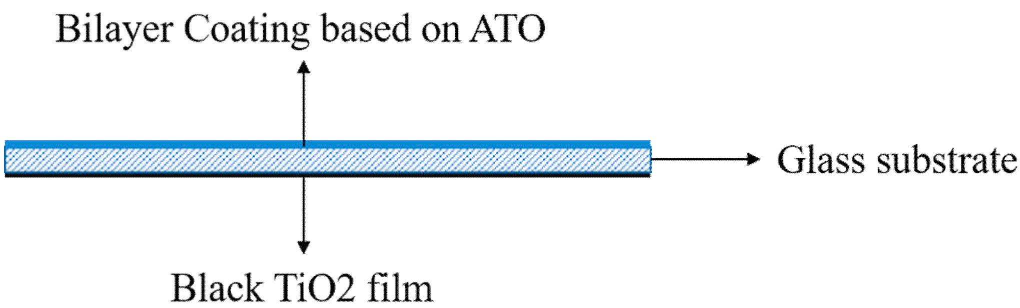

Figure 3 The diagram of the structural black TiO2/ATO thermal insulation coating filmed on the glass substrate

The photocatalysis of the coating was investigated by performing photocatalytic activity experiments to evaluate degradation of the aqueous methylene blue (MB) solution by placing the thin films under illumination of fluorescent lamp light source (12w, 150mm long, broad emission peak range is 365nm-750nm, and the centre peak is 550nm). The experiment was placed at room temperature where each sample was soaked in a glass container containing the MB solution and the glass containers were placed in a photocatalyzed reactor which was pained in black. The distance between the fluorescent lamp and the sample is 10cm. After 3h of irradiation time, the absorbance of the MB solution would be measured by UV-Vis-NIR spectrophotometer for wavelength range of 580nm-700nm and the scanning rate of 100nm/min. Finally, the degradation efficiency of the MB solution was calculated by using the equation (1)

$$D = \frac{Ab_0 - Ab_i}{Ab_0} \times 100\% \tag{1}$$

where Ab0 is the absorption of the light irradiated aqueous MB solution and Abi is the absorption of the MB solution after degradation by samples.

3. Results and discussion

The crystal structure of the nanoparticles was recorded by XRD and are shown in Figure 4A. It can be fund that the peak positions of sample in red line is well agree with the reflections of bulk cassiterite SnO2 in black line. And no other impurities peaks in samples can be recorded, which is indicating that all antimony ions are uniformly replaced the tin ions in SnO2 crystal structure.

The morphology of ATO nanoparticles were observed by TEM and are shown in figure 4B. The particle size of ATO is homogeneous and the size distribution is around 5-10nm. The SAED pattern taken form a part of the ATO nanoparticles in figure 4B are shown in figure 4C, which can be fund that the nanoparticles possess interplanar spacings of 3.3470, 2.6427, 2.3487, 2.2694, 1.7641, and 1.4155Å corresponding to the (110), (101), (200), (111), (211), and (301) planes, respectively. Figure 4D shows the HRTEM image of the ATO nanoparticles. In this image, the lattice plane of ATO nanoparticles was (111) with a lattice space of 2.2694Å. Figure 4F shows the EDX of the ATO samples which can be fund that the major elemental composition are Sn, Sb and O. The characteristic peak of Sn element is at 3.1, 3.5, 3.9, 4.2 and 4.3KeV, and the characteristic peak of Sb element appeared at 3.3, 3.4, 4.0, and 4.6KeV. In addition, the peak of O element at 0.5KeV can be observed in this figure. Besides, the Cu and C elements in the EDX pattern are from the TEM copper grid. Hence, it can be deduced from the results that the sample can be regarded as the well-organized ATO structures.

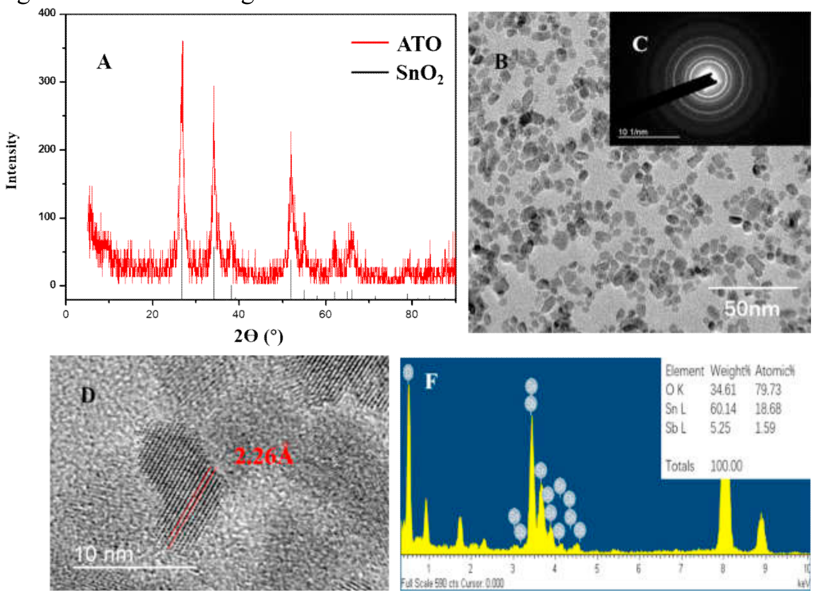

Figure 4 The Characterization of ATO nanoparticles
A: XRD pattern for ATO; B: TEM image for ATO nanoparticles; C: SAED image for ATO nanoparticles; D: HRTEM image for ATO nanoparticles; F: EDX pattern for ATO nanoparticles

The morphology of self-dispersion TiO2 nanoparticles were observed by TEM and are shown in figure 5A. The particle size of TiO2 is homogeneous and the size distribution is around 5nm. The SAED pattern taken form a part of the self-dispersion TiO2 nanoparticles in figure 5a are shown in figure 5b, which could be fund that the nanoparticles possess interplanar spacings of 3.5213, 2.4320, 2.3787, 2.3322, 1.8926, and 1.7000 Å corresponding to the (101), (103), (004), (112), (200), and (105) planes, respectively. Figure 5c shows the HRTEM image of the self-dispersion TiO2 nanoparticles. In this image, the lattice plane of TiO2 nanoparticles was (101) with a lattice of 3.5Å.

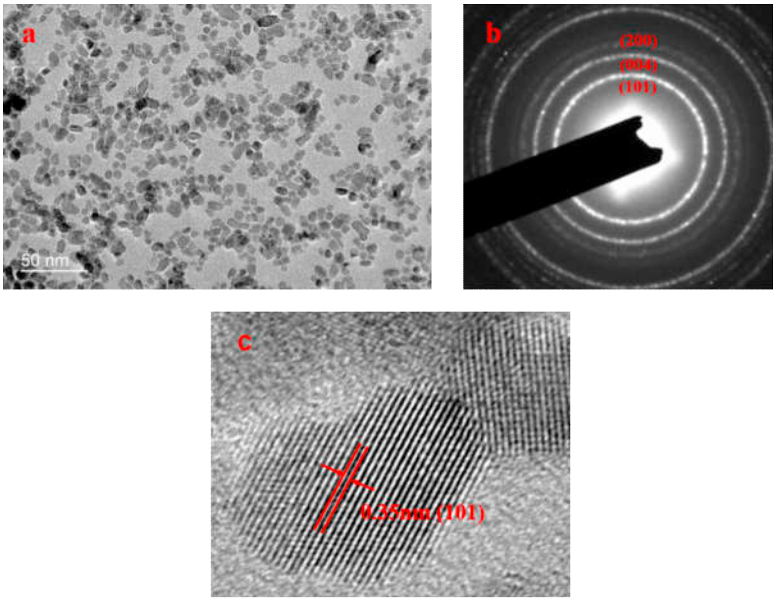

Figure 5 The TEM image of the TiO2(a), SAED pattern of the TiO2 (b) and the HRTEM image of the TiO2 (c)

The morphology of the black TiO2 film was observed by SEM and was shown in figure 5A. It could be fund that a uniform coating was on the surface of substrate glass. The crystal structure of black TiO2 was measured by XRD and is shown in figure 3B. It could be found that the peak positions of sample are well agree with the reflections of anatase TiO2.

Reaction time is very important in the electrochemistry reaction, because on the doped degree of the black TiO2 film. In this paper, the effect of the reaction time would be investigated. The electricity and the voltage in the reaction were maintained in 2A and 5V, respectively. The mass concentration of the NH4Cl and mass ratio between deionized water and ethylene glycol were 15wt% and 1:1, respectively. The reaction time was adjusted in 3, 5, 10 and 15 minutes.

Figure 6 shows the photos of the samples under different reaction time. It could be found that the colour would be getting darker with the reaction time extend, due to the long reaction time can increase the doped degree of the black TiO2 films. Thus, the voltage in electrochemistry reaction is very important.

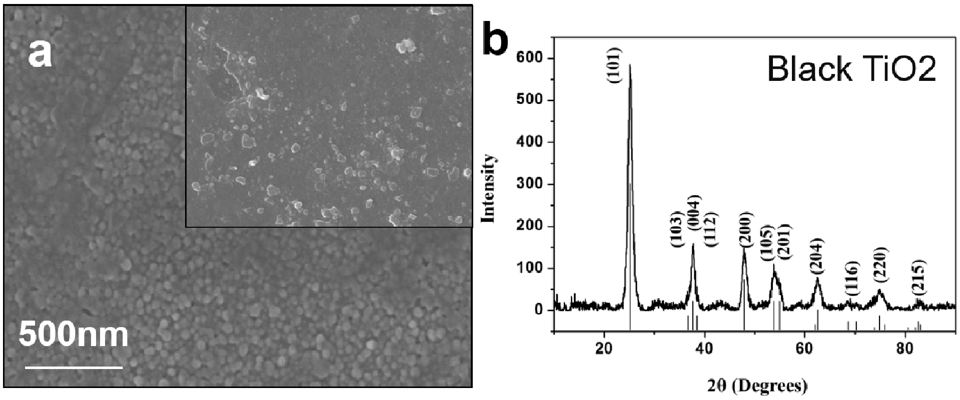

Figure 5 The Characterization of Black TiO2 film
A: SEM image of the Black TiO2 film; B: XRD of the TiO2 film

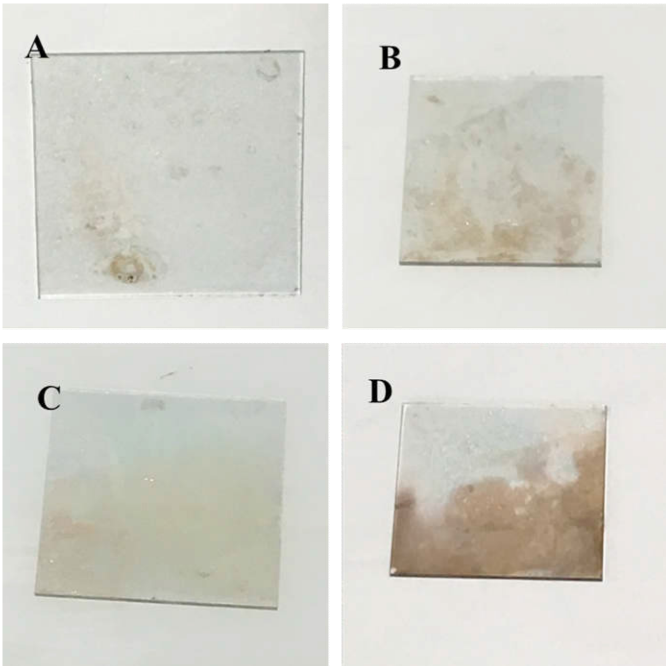

Figure 6 The photos of the samples under different reaction time
A: 3min; B: 5min; C: 10min; D: 15min

The figure 7 shows the UV-Vis-NIR transmittance of the samples under different reaction time. It could be fund that all the samples exhibited a high transmittance in the visible light range of 380~780nm, and a high blocking rate in the NIR light range of 780-2500nm, especially in the range of 1500-2500nm. With reaction time extension, the NIR transmittance would decrease. After the reaction time higher than 10min, the light transmittance exhibited a slight change.

Owing to the above investigation, the optimum reaction time in the electrochemistry reaction was 10 minutes.

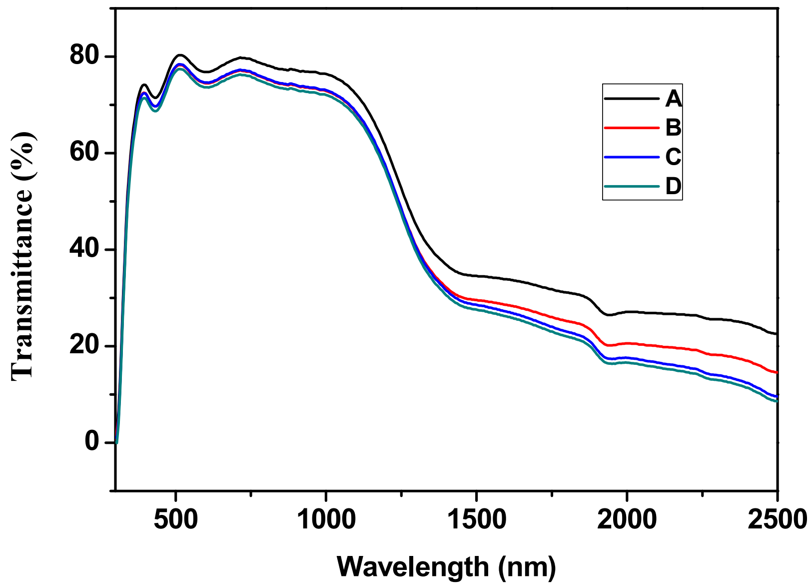

Figure 7 The UV-Vis-NIR transmittance of the samples under different reaction time (A: 3min; B: 5min; C: 10min; D: 15min)

The water contact angle (WCA) of black TiO2 film in different electronchemisty reaction time is show in figure 4A. It could be fund that the WCA was decreased with the reaction time extended. It is because that the doping degree was improved after extending the reaction time. When the time was tended to 100 minutes, the WCA of the film was lower than 5°

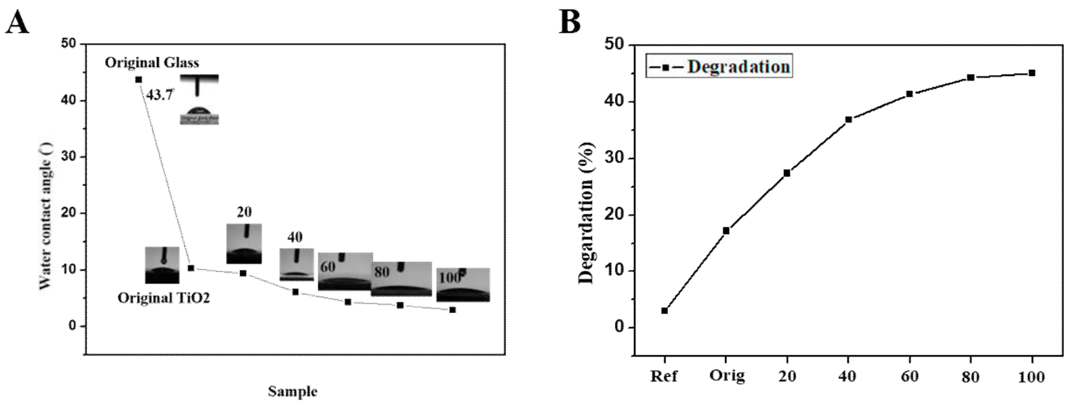

Figure 4 WCA (A) and the degardation (B) of the film in different reaction time

The figure 5 shows the optical properties of different samples. It could be found that the thermal insulation coating shown a high NIR light blocking rate of 87.4%, and the visible light transmittance was approximately 62%.

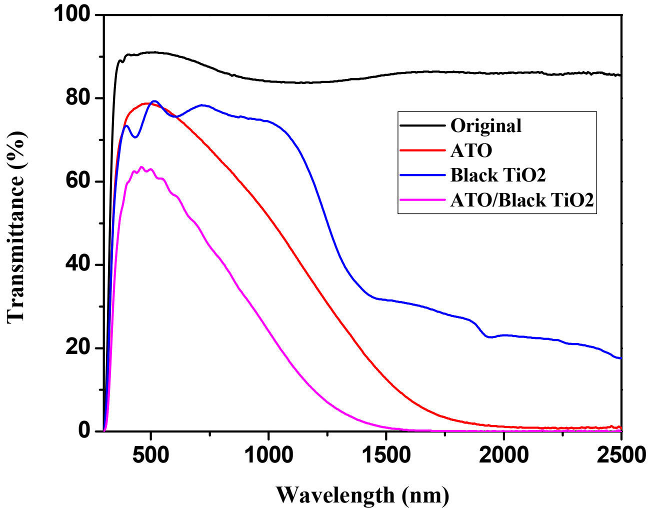

Figure 5 The Optical properties of different samples

4. Conclusion

A novel transparent thermal insulation coating based on ATO/Black TiO2 was obtained. The bilayer coating exhibited a high near infrared light blocking rate of 86%, and the visible light transmittance was about 62%. Meanwhile, the structural thin films had excellent photocatalytic property, which could degrade approximately 45% of methylene blue in 3 hours under fluorescent lamp, and the double layered coating shown a water contact angle of lower than 5° after activating. Owing to the above investigation this structural film shows a great potential in energy conservation window

5. Copyright

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