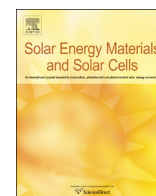




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## Porous carbon–titania nanocomposite films for spectrally solar selective absorbers

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## ABSTRACT

Selective solar absorbers based on composition of porous titania and carbon with a well-defined interconnected macropores structure have been fabricated by a photopolymerization-induced phase-separation method in the framework of a sol–gel technique. Scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, thermogravimetric and differential thermal analysis, Fourier transform infrared spectroscopy, and spectroscopic ellipsometry were used to characterize the C–TiO<sub>2</sub> films. The results showed that the macroporous structures of the films could be tuned by changing the reaction parameters. The reduction of the HNO<sub>3</sub> concentration in the solution effectively decreases the mean size of pores, carbon content, and the thickness of the nanocomposite films, leading to an optimization of the spectral selective absorption performance. The solar absorptance ( $\alpha$ ) and thermal emittance ( $\epsilon$ ) of the optimized single layer film with a thickness of about 300 nm were about 0.95 and 0.12, respectively. The films also show good stability under the high temperature ( $\sim 500$  °C). Based on these results, porous carbon–titania composite films proved to be a good candidate as solar selective absorbers.

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## 1. Introduction

With the development of economy, energy issues have become increasingly prominent. Among the available energy resource, solar energy is considered to be infinite, easily-handled, and available anywhere on the earth. The search for the efficient and low-cost spectrally selective solar absorber materials which play the key role in the solar photo-thermal devices continues to be unabated [1–5]. Such materials are required to have high absorption in the solar wavelength range (0.3–2.5  $\mu\text{m}$ ) and a low thermal emittance in the infrared wavelength range (greater than 2.5  $\mu\text{m}$ ). At the same time, these solar absorbers should have to be stable against the heat and water, exposed to the heat-transfer solvents, and corrosive environments. More important, to realize industrialization, the components of these materials have to be nontoxic, sufficiently cheap, and must be easy to produce.

One of the designs to achieve such requirements is the metal-nanoparticle-embedded oxide films deposited on the metal substrate [6–8], namely, the metal–dielectric composites, such as

nickel-pigmented Al<sub>2</sub>O<sub>3</sub>, which have been widely investigated by theoretical and experimental studies [9,10]. However, such metal–dielectric absorbers suffered from the degradation over a long period for the oxidation of the metal nanoparticles, especially in high temperature and high humidity environments.

In 2002, Mastai et al. described a new design for solar selective absorbers which are carbon nanoparticles dispersed in porous silica matrix [11]. The nanocomposites films were prepared by a sol–gel spin-coating method from tetramethylorthosilane (TMOS) based coating solution containing  $\beta$ -methylated cyclodextrin ( $\beta$ -MCD) as a carbon precursor. The best single layer C–SiO<sub>2</sub> film reported has high absorbance with a value of 0.94 and low emissivity with a value of 0.15, and shows good stability under the humidity and high temperatures (250–300 °C) [12]. More recently, by using a sol–gel technique, Katumba et al. [13,14] compared the optical properties and the stabilities of carbon dispersed in three different oxides matrix (C/SiO<sub>2</sub>, C/ZnO, and C/NiO) on an aluminum substrate. The sucrose was used as the carbon precursor with polyethylene glycol (PEG) as structural directing template to manipulate the microstructure. The results show that C–NiO absorbers exhibit better optical properties and structural stability than both C–SiO<sub>2</sub> and C–ZnO, indicating that the matrix is very important for the composites performance. They

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also found disk-like pores with diameter of about 200 nm in the coatings, which are possibly caused by the evaporations of the PEG during the annealing. This feature might be used to adjust the refractive index of the film to improve the solar absorption by reducing the reflectivity and enhancing the scattering. According to the authors' knowledge, however, no further research has been reported.

Here, we provide a selective solar absorber based on porous carbon–titania composites prepared by a sol–gel method. A photopolymerization-induced phase-separation method (PIPS) was introduced to mold the pores in the composites without any template. The PIPS method was widely used for the fabrication of the microstructures since the phase separation temperature and the rate of polymerization can be chosen independently [15–18]. Three-dimension porous titania network structures are used as the skeleton, whereas the carbon nanoparticles remained in the gap are employed as the light-absorbing component. Both materials are easily-available, non-toxic and stable against the most external conditions. The thermo analysis, Fourier transform infrared spectroscopy, spectroscopic ellipsometry, and X-ray diffraction were conducted to see if these materials are suitable for selective solar absorbers.

## 2. Experimental details

### 2.1. Sample preparation

The carbon-porous titania thin films were prepared by using the sol–gel spin-coating method on quartz and copper substrates (4 cm × 4 cm). The preparation of the titania sol was detailed in Ref. [17]. Briefly, the mixtures with the  $C_{16}H_{36}O_4Ti$  (TTB, Sino-pharm): $C_2H_5OH:H_2O:HNO_3:DMF(GR)$  composition of 1:10:3: $x$ :4 (molar ratio) were used as the precursor solution, where  $x$  was varied from 0.7 to 0.4 to investigate the effect of the  $HNO_3$  concentration on the microstructure and optical properties. It is worthy to note that in such solution the reduction of  $HNO_3$  strongly enhances the hydrolysis and polymerization rate of TTB [16,17], resulting in that the solidification rate of the solution was too faster to prepare the film by the spin-coating method when the  $HNO_3$  molar ratio was less than 0.4. 0.01 M of pentaerythritol tetraacrylate (PETA, Aldrich) was used as the photomonomer, 0.035 g of 2, 2'-Azo bisobutyronitrile (AIBN, AR) as the radical initiator, and 1.5 g of polyvinylpyrrolidone k30 (PVP, Sigma) were dissolved in the solution. The configuration process of sol was under the ice-cooled condition for 30 min with vigorous stirring. Using the above sol, the films were fabricated by spin coating at 2000 rpm for 20 s on the cleaned substrates, and the resultant films were irradiated by UV light ( $\lambda=365$  nm, 7 mW/cm<sup>2</sup>) for 10 min and then directly subjected into an inert atmosphere for carbonization. These films were pre-heated at 200 °C for 10 min and 600 °C for 60 min (with 10 °C/min heating rate).

### 2.2. Characterization method

The structures of the as-prepared films were investigated by using an X-ray diffractometer (XRD, Rigaku D/max 2550pe) with the Cu K $\alpha$  radiation operated at 4 kV and 300 mA. The surface morphology, thickness, and energy dispersive spectroscopy (EDS) were measured by using a scanning electron microscope (SEM, Hitachi S-4800) with an accelerating voltage of 15 kV. The thermogravimetric and differential thermal analysis (TG–DTA) was performed by using a Thermo plus TG 8210 (Rigaku) at a heating rate of 10 °C/min from 30 °C to 800 °C. The powder for the TG–DTA measurements was made from the gel that was irradiated by the UV light for 10 min and dried at 70 °C for 48 h. The diffusive

reflection spectroscopy measurements in the UV/vis/Near-IR range were carried out at room temperature by a Shimadzu UV-3600 spectrophotometer equipped with a large-sample compartment MPC-3100 which has a built-in integrating sphere. A BaSO<sub>4</sub> tablet was used as the reference and the integrating sphere was coated with BaSO<sub>4</sub> for accurate reflection measurement in the wavelength range of 0.3–2.5  $\mu$ m. The IR measurements were conducted by a Fourier transform infrared spectroscopy (FTIR, Tensor27, Bruker) with a gold mirror reference. The optical parameters were measured with a spectroscopic ellipsometry (SE, GES 5E, Semilab). A CCD detector was used in spectroscopic ellipsometry measurement, resulting to a nonnegligible noise in the long wave range beyond 1.1  $\mu$ m; therefore, only the fitting result in the range of 310–900 nm was shown in the present work. The regression work was carried out on a software package *WinElli II* from Semilab, obtaining the specific structural and optical parameters until the evaluation based on the mean square error converges to the minimum.

## 3. Results and discussion

### 3.1. Morphology of the prepared films

Although all samples present interconnected macropores in the matrix with diameter of about hundreds of nanometers, different surface characteristics are obtained depending on the  $HNO_3$  concentration as depicted by SEM in Fig. 1. For the sample of the  $HNO_3$  concentration  $x=0.7$  (Fig. 1A), a flat surface consisting of shallow plate-like pits can be seen above the interconnected macropores. When the  $HNO_3$  concentration decreases to  $x=0.6$ , the interconnected macropores are still covered by the relative flat surface, but the diameter of the plate-like pits decreases to about 1  $\mu$ m leading to a little roughness (Fig. 1B). When the  $HNO_3$  concentration keeps decreasing, the plate-like pits disappear and the interconnected macropores are exposed leading to a rougher surface consisting of the open pores (Fig. 1C and D). And the mean pore size decreases from 400 nm to 200 nm with the decrease of the  $HNO_3$  concentration from  $x=0.5$  to  $x=0.4$ . To further investigate the porous microstructure of the C–TiO<sub>2</sub> composites, the samples annealed in air conditions were examined by SEM as shown in Fig. 2. The interconnected macropores could be found in the films, but presenting a collapse-like morphology. This can be explained by the fact that low concentration of  $HNO_3$  suppresses the photopolymerization reaction leading to the smaller polymer domain and then the smaller pore size left after the evaporations of poly-PETA during the annealing [15–17]. Meanwhile, the long annealing time in air (60 min) results in the collapse of the pore structure, while the film prepared by reducing the annealing time to 10 min has a good three-dimensional pore structure as presented in Fig. 3. When annealed in the inert atmosphere, the carbonization of the emerging polymer remained in the films could form the carbon and titania cross-linked composites, enhancing the structure stability that maintain the well-defined pores structure even after the 60 min annealing process (Fig. 1).

### 3.2. XRD results

As shown in Fig. 4, four XRD patterns of the as-prepared-in-air TiO<sub>2</sub> films show six peaks at  $2\theta$  of 27.5°, 36.1°, 41.2°, 44.1°, 54.3° and 56.6°, which were attributed to the rutile phase (JCPDS, No. 21-1276), and simultaneously, a peak at  $2\theta$  of 25.3° attributed to the anatase phase (JCPDS, No. 21-1272) was observed for the sample prepared with  $HNO_3$  concentration  $x=0.4$ . When more  $HNO_3$  was added into the solution, the peak at  $2\theta$  of 25.3° disappeared. This is because increasing of  $HNO_3$  concentration enhances the polymerization of

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