



# Solar spectral optical properties of rutile TiO<sub>2</sub> coated mica–titania pigments



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## ABSTRACT

Different shaped rutile TiO<sub>2</sub> coated mica–titania pigments were prepared by hydrolysis of TiCl<sub>4</sub> ethanolic solution at 70 °C. SnO<sub>2</sub> as a rutile promoting additive was deposited onto mica prior to TiO<sub>2</sub>. The use of TiCl<sub>4</sub> played a crucial role in controlling the morphology of rutile TiO<sub>2</sub> coatings. Monodisperse nano-needles were assembled into nanoflowers with an increasing particle size as the TiO<sub>2</sub> loading increased. A possible crystal growth mechanism of rutile TiO<sub>2</sub> with rich nanostructures was proposed. The obtained rutile samples showed stronger ultraviolet shielding ability and higher near-infrared reflectance property than that of anatase sample. What's more, the rutile TiO<sub>2</sub> coating with smaller particle size possessed higher reflectance in the region of 1300–2500 nm in accordance with the Kubelka–Munk theory. The near-infrared solar reflectance of the rutile TiO<sub>2</sub> coated mica–titania pigment was as high as 97%, making them good candidates for solar reflective pigments.

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## 1. Introduction

Utilization of solar reflective coatings has shown great potential to reduce solar heat gain and cooling loads of urban buildings while improving indoor thermal conditions [1]. Solar reflective coatings are characterized by high solar reflectance and infrared emittance values [2]. This technique is low cost, energy efficient and may be widely applied to roofs, walls and pavements.

It is well-known that visible light (Vis, 400–700 nm) accounts for only 43% of the energy in the air-mass1.5 global solar irradiance spectrum (300–2500 nm) typical of North-American insolation; the remainder arrives as near-infrared radiation (NIR, 700–2500 nm, 52%) or ultraviolet radiation (UV, 300–400 nm, 5%) [3]. Therefore, a solar reflective coating should be highly reflective in the visible light and near-infrared parts of the electromagnetic spectrum in order to maintain a high solar reflectance. The optical properties of the coatings are primary influenced by pigments [2]. Thus there is a strong incentive to develop novel solar reflecting inorganic pigment.

Mica–titania pigments are based on TiO<sub>2</sub> precipitated onto platelets of mica, exhibiting outstanding qualities of luster, brilliance and iridescent color effects [4,5]. These pigments are widely applied in optical filters, cosmetics, plastics, printed products, ceramic, industrial coatings, and car paints [6,7]. Several studies have reported the luster and color properties of mica–titania pigments [8,9]. To our knowledge, few researches have reported solar spectral optical properties of rutile TiO<sub>2</sub> coated mica–titania pigments, although these pigments may have high reflectance and photostability [10].

In this paper, we demonstrated a simple and facile solution process for depositing rutile TiO<sub>2</sub> onto mica substrates at 70 °C. The effect of phase composition, morphology and particle size on the solar spectral optical properties of mica–titania pigments was investigated.

## 2. Experimental

### 2.1. Materials

The mica used as the substrate in this study was synthetic mica. Analytical grade titanium tetrachloride (TiCl<sub>4</sub>), tin tetrachloride (SnCl<sub>4</sub>), absolute ethanol (C<sub>2</sub>H<sub>5</sub>OH), sodium hydroxide (NaOH), hydrochloric acid (HCl) and distilled water were used in the experiments.

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## 2.2. Preparation method

The synthesis of anatase TiO<sub>2</sub> coated mica–titania pigments was carried out in the following way [11]. Mica particles with a diameter of 10–100 μm and a thickness of less than 1 μm were used as raw materials and were dispersed in distilled water. The batch was then heated to 70 °C and the pH value was adjusted to 1.0 with dilute hydrochloric acid. Then TiCl<sub>4</sub> ethanolic solution (120 mL) was introduced into the agitated slurry within 4 h. The pH value of the slurry was kept constant by simultaneous addition of NaOH solution. After the addition was completed, the slurry was aged for 1 h and then allowed to settle and cool to room temperature. Finally, the particles were separated, washed with distilled water and dried at 70 °C for 24 h. This sample was labeled as mica-A-TiO<sub>2</sub>.

To obtain the rutile phase of TiO<sub>2</sub> onto mica substrate, the introduction of SnO<sub>2</sub> was done using SnCl<sub>4</sub> solution. First, mica (10 g) was suspended in distilled water (1 L) and heated to 70 °C, and the pH value of the slurry was adjusted to 2.0 using HCl. Then, SnCl<sub>4</sub> aqueous solution (15 g/L, 11.1 mL) was added dropwise while the pH value was held constant by simultaneous addition of NaOH solution for 1 h. The weight ratio of SnO<sub>2</sub> to mica was 0.96%. Then, the pH value was adjusted to 1.0, and the TiO<sub>2</sub> coating was deposited on mica by addition of TiCl<sub>4</sub> ethanolic solution in the same way as described above. The amount of TiCl<sub>4</sub> ethanolic solution was 20 mL, 40 mL, 80 mL, and 120 mL, respectively and gave samples labeled as mica-R20-TiO<sub>2</sub>, mica-R40-TiO<sub>2</sub>, mica-R80-TiO<sub>2</sub>, and mica-R120-TiO<sub>2</sub>, respectively.

## 2.3. Characterization

Raman spectroscopy was done on a LabRAM Aramis (HORIBA Jobin Yvon) with spectral resolution of 1 cm<sup>-1</sup>. The laser line of the exciting source was at 532 nm. Scanning electron microscopy (SEM) images were recorded on a Nova NanoSEM 430. The operation voltage was 10 kV. The weight ratio of TiO<sub>2</sub> in pigments was determined by X-ray fluorescence spectrometry using a model PANalytical Axios. UV–Vis–NIR diffuse reflectance spectra were collected using a UV–Vis near-infrared spectrometer (Lambda950, PerkinElmer, United States). Optical measurements were performed in the 200–2500 nm range. The solar reflectance in the wavelength range from λ<sub>1</sub> to λ<sub>2</sub> can be determined by applying the following formula:

$$R = \frac{\int_{\lambda_1}^{\lambda_2} r(\lambda)i(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} i(\lambda)d\lambda} \quad (1)$$

where  $r(\lambda)$  is the spectral reflectance (W m<sup>-2</sup>) obtained from the experiment and  $i(\lambda)$  is the solar spectral irradiance (W m<sup>-2</sup> nm<sup>-1</sup>) obtained from ASTM standard G173.

To investigate the colorimetric values of the pigments, the pigment powders were pressed into a wafer with a diameter of 2.5 cm. Then, the CIE *Lab* of the pigment samples under 10° were measured by the X-Rite Inc model spectrophotometer (D65 illuminant).

To investigate the photostability of the pigments, rutile TiO<sub>2</sub> coated mica particles (mica-R80-TiO<sub>2</sub>) or commercial rutile TiO<sub>2</sub> pigment were dispersed in an acrylic resin emulsion and then the coating was coated to calcium silicate board. The mass ratio of pigments to acrylic resin emulsion was 1:20. Finally, the coatings were dried at room temperature for 24 h. The films composed of mica-R80-TiO<sub>2</sub> or commercial rutile TiO<sub>2</sub> pigment were labeled as F1, F2, respectively. The paint films were weathered for 168 h using

a QUV weatherometer (Dongguan Zhenglan Precision Instrument CO., LTD, light intensity – 924 mW/cm<sup>2</sup>). The durability of the films was measured by X-Rite Inc model spectrophotometer. Color changes ( $\Delta E$ ) during the UV weathering of films can be determined by applying the following formula:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (2)$$

where  $\Delta E$  is the color change,  $\Delta L$  is the decline of  $L$  (lightness) after UV weathering,  $\Delta a$  is the decline of  $a$  (red-green index) after UV weathering, and  $\Delta b$  is the decline of  $b$  (yellow-blue index) after UV weathering.

## 3. Results and discussion

### 3.1. Synthesis of rutile TiO<sub>2</sub> coated mica–titania pigments

Raman spectra are effective to identify the phase structures, especially for distinguishing the anatase TiO<sub>2</sub> from rutile TiO<sub>2</sub>. According to the group theory, rutile has four Raman active modes: A<sub>1g</sub> + B<sub>1g</sub> + B<sub>2g</sub> + E<sub>g</sub>. The allowed modes reported were at 143 cm<sup>-1</sup> (B<sub>1g</sub>), 235 cm<sup>-1</sup> (two-photo scattering), 447 cm<sup>-1</sup> (E<sub>g</sub>), 612 cm<sup>-1</sup> (A<sub>1g</sub>), and 826 cm<sup>-1</sup> (B<sub>2g</sub>) [12,13]. As for anatase, only six bands were reported in the same wave number range corresponding to the six Raman active vibration modes: 144 cm<sup>-1</sup> (E<sub>g</sub> (1)), 197 cm<sup>-1</sup> (E<sub>g</sub> (2)), 399 cm<sup>-1</sup> (B<sub>1g</sub> (1)), 513 cm<sup>-1</sup> (A<sub>1g</sub>), 519 cm<sup>-1</sup> (B<sub>1g</sub> (2)) and 639 cm<sup>-1</sup> (E<sub>g</sub> (3)) [14]. Fig. 1 shows the Raman spectra of the TiO<sub>2</sub> samples. As we can see from Fig. 1(b), the peaks appearing at 150, 512, 632 cm<sup>-1</sup> are typical anatase bands. The TiO<sub>2</sub> sample (mica-R120-TiO<sub>2</sub>) with a prior deposition of SnO<sub>2</sub> as a seed layer reveals spectral features basically corresponding to the rutile phase (234, 443, 612 cm<sup>-1</sup>). Other weak peaks appearing at 102, 325 and 682 cm<sup>-1</sup> can be ascribed to B<sub>g</sub> and A<sub>g</sub> modes of mica. So the Raman spectra confirm that the prior deposition of SnO<sub>2</sub> leads to the formation of pure rutile TiO<sub>2</sub> coating. The rutile promoting effects of SnO<sub>2</sub> could be ascribed to the structural similarity of rutile and cassiterite [15].

Fig. 2 shows the Raman spectra of TiO<sub>2</sub> thin layers deposited on mica with different TiO<sub>2</sub> loadings. The peaks appearing at 325, 443, 612 cm<sup>-1</sup> are typical rutile bands, and the other peaks could be ascribed to mica. So the Raman spectra confirm that TiO<sub>2</sub> loadings have little influence on the phase composition of the TiO<sub>2</sub> coatings. With the increase of TiO<sub>2</sub> loading, the intensity of these rutile peaks

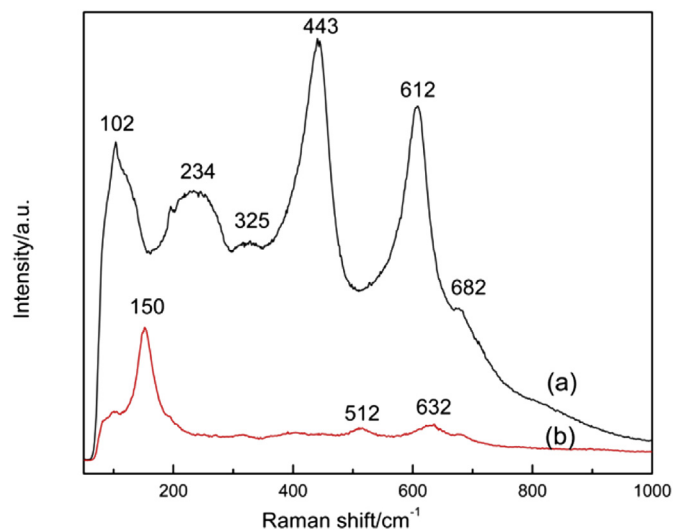


Fig. 1. Raman spectra of (a) mica-R120-TiO<sub>2</sub> and (b) mica-A-TiO<sub>2</sub>.

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