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Highly Solar Radiation Reflective Cr_2O_3−$3TiO_2$ Orange Nanopigment Prepared by a Polymer-Pyrolysis Method

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ABSTRACT: The present study reports the preparation and characterization of an orange nanopigment with high solar radiation reflective properties. Complex Cr_2O_3−$3TiO_2$ nanoparticles were prepared by the pyrolysis of Cr−Ti precursors at high temperature, and the effects of the calcination temperature on the structure of Cr_2O_3−$3TiO_2$ nanopigment were investigated by thermal analysis, X-ray diffraction, and transmission electron microscopy. The results reveal that the Cr_2O−-$3TiO_2$ pigments having rutile structure can be prepared by the calcination of the precursor at above 600 °C. All Cr_2O_3−$3TiO_2$ pigments are granular in nature and present a homogeneous particle size of around 20 nm. The ultraviolet−visible near infrared (UV−vis-NIR) reflection spectra show that the Cr_2O_3−$3TiO_2$ nanopigments have a reflection peak at around 600 nm, which reflects the orange color of these pigments. The average reflectance of Cr_2O_3−$3TiO_2$ in the NIR range is around 53%, respectively, which is much higher than that of the visible light range. The prepared orange Cr_2O_3−$3TiO_2$ nanopigments have a great potential in applications such as cool materials used for buildings with energy saving performance.

KEYWORDS: *Orange pigment, Reflective, Solar, Polymer-pyrolysis*

INTRODUCTION

The incidence of the urban heat island (UHI), a phenomenon caused mainly by the removal of natural vegetation and its replacement with buildings and paved surfaces, is increasing in large metropolitan centers and produces temperatures exceeding 10 °C above those in surrounding areas.[1] The UHI has the effect of increasing energy consumption, particularly by the air conditioners that are widely used in large buildings in hot seasons. The use of highly reflective "cool" materials helps in maintaining lower exterior surface temperatures of buildings and consequently contributes toward increasing indoor thermal comfort levels, resulting in reduction of energy need for cooling.[1−3]

The reflective cool materials, usually bright white, can remain approximately up to 30 °C cooler than traditional materials during peak summer conditions. Such as TiO_2, a white pigment with a high solar reflectance of about 87%, is currently regarded as the best pigment for cool materials.[4] However, cool colored materials are often preferred for the cases where the use of light colors creates glare problems or when the aesthetics of darker colors is preferred.[3,5,6] Complex inorganic color pigments, which reflect near-infrared (NIR) radiation irrespective of the selective visible light reflection/adsorption and thus may be in any color, have well-known applications in masking products, interior car paint, materials for spectator areas of stadiums, and parking areas to fire-resistant paints,[4,7,8] and moreover, they are also used specifically in cool materials for exterior surface of buildings. Chromium oxide (Cr_2O_3), green pigment with a medium high NIR reflectance in the range of 50−57%, is a good candidate to make nonwhite cool materials.[9,10] On the basis of Cr_2O_3, different complex color pigment systems with excellent reflectance have been developed, such as green, gray, and black.[9−13] However, very few studies report orange pigments based on Cr_2O_3.

In recent years, the polymer pyrolysis method has been developed by our group for preparation of semiconductor and pigment nanoparticles.[14−16] When compared with solid state reaction methods, the conventional method of synthesis of ceramic pigments, the polymer pyrolysis method has some advantages: (a) easy to get nanoscale particles, which possess better solar reflectance than traditional microscale pigments, (b) easy to operate, no need of milling or sieving to adjust particle size, and (c) easy to scale-up in batch form.[7,17,18] In this paper, the preparation of Cr_2O_3−$3TiO_2$ nanopigments by pyrolyzing Cr−Ti precursor is reported. The Cr_2O_3−$3TiO_2$ pigments prepared show brilliant orange color with particle size of around 20 nm and high NIR reflectance above 50%. The orange Cr_2O_3−$3TiO_2$ nanopigment prepared has great potentials in applications for energy saving buildings as cool materials.

EXPERIMENTAL SECTION

Preparation of Cr_2O_3−$3TiO_2$ Nanopigments. The chemical reagents tetra-*n*-butyl titanate ($Ti(C_4H_9O)_4$), chromium(III) acetate ($Cr(CH_3COO)_3$) 50% solution, ammonium persulfate ($(NH_4)_2S_2O_8$), and acrylic acid (CH_3COOH) are analytical grade and used without

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further purification processes. In a typical experiment, $Cr(CH_3COO)_3$ (0.002 mol) and $Ti(C_4H_9O)_4$ (0.003 mol) were added into 20 g of CH_3COOH aqueous solution ($CH_3COOH:H_2O$ = 70:30 wt %) under magnetic stirring. Afterward, a small amount (1 g) of 5 wt % $(NH_4)_2S_2O_8$ aqueous solution as initiator was added to the mixed CH_3COOH solution to promote the polymerization. Under heating at 90 °C, the mixed solution was stirred for 20 min to form the well-distributed polyacrylate precursor. The obtained precursor was dried at 200 °C for 2 h and, then, calcined at 600 and 800 °C for 2 h, respectively. Finally, the obtained orange Cr_2O_3−$3TiO_2$ nanopigments were denoted as Cr_2O_3−$3TiO_2$-600 and Cr_2O_3−$3TiO_2$-800, respectively.

Characterization. Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis was performed using a NETZSCH STA 409PC instrument under air in the temperature range of 30−800 °C at a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer at a voltage of 40 kV with Cu Kα radiation (λ = 1.5406 Å) in the 2θ ranging from 15° to 75°.

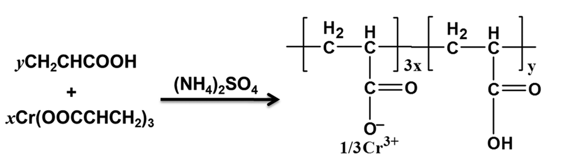
Transmission electron microscopy (TEM) of Cr_2O_3−$3TiO_2$ samples was performed on a transmission electron microscope (Model JEM-2100, Hitachi) and the particle sizes from TEM were estimated with a software (Photoshop 7.0). The optical properties of the Cr_2O_3−$3TiO_2$ nanoparticles were studied using an ultraviolet−visible-near-infrared (UV−vis-NIR) spectrophotometer (Varian, Cary 5000) with integrating sphere. The reflection spectra were scanned in the range of 250−2500 nm with a 1-nm interval.

RESULTS AND DISCUSSION

Cr_2O_3−$3TiO_2$ nanopigments were prepared by a polymer-pyrolysis method. The polymeric precursors were made by in situ polymerization of the mixed aqueous solution of acrylic acid in the presence of metal salt with $(NH_4)_2S_2O_8$ as the initiator. This affords a composition which has the predetermined ratio of Cr to Ti (2:3) to be compatible with the final product (Cr_2O_3−$3TiO_2$) according to the following reactive formula.

$$Ti(OCH_2CH_2CH_2CH_3)_4 + 4H_2O \longrightarrow Ti(OH)_4 + 4CH_3CH_2CH_2CH_2OH \quad (1)$$

$$Cr(OOCCH_3)_3 + 3CH_2CHCOOH \longrightarrow Cr(OOCCHCH_2)_3 + 3CH_3COOH \quad (2)$$



(3)

In the above formula, x and y represent the molar ratio of $Cr(CH_3COO)_3$ and CH_3COOH, respectively. When the value of x is close to y, the polymerization reaction is difficult to initiate, and lead to ill-defined products. Thus, it is necessary to choose starting materials with $x \ll y$.[15,16,19] With the existence of a large amount of H_2O, $Ti(C_4H_9O)_4$ mainly hydrolyze with the water in situ and lead to an immediate nucleation of $Ti(OH)_4$, which is distributed randomly within the polymer precursor, as shown in Figure 1. The Cr (III) ions are bound by the ionic bonds between the metallic ions and carboxylate ions in a polymeric chain or between the polymeric chains. This uniform distribution of Cr (III) ions and $Ti(OH)_4$ in the precursor is key to the formation of Cr_2O_3−$3TiO_2$ complex pigment in the following pyrolysis process.

As shown in Figure 2, the compositional and structural changes of copolymeric precursors associated with a thermal pyrolysis process are characterized using TG-DSC. The TG curve reveals that the weight loss proceeds in three different

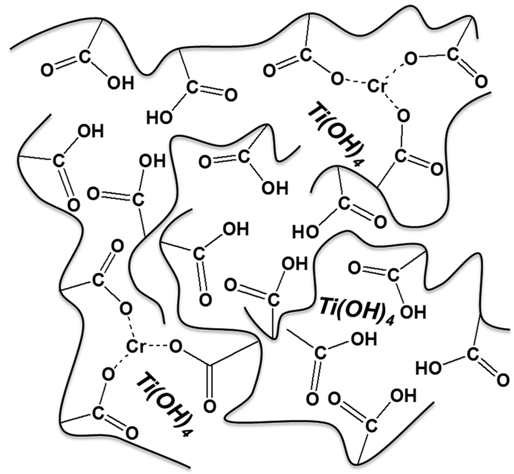


Figure 1. Schematic representation of polymeric precursor.

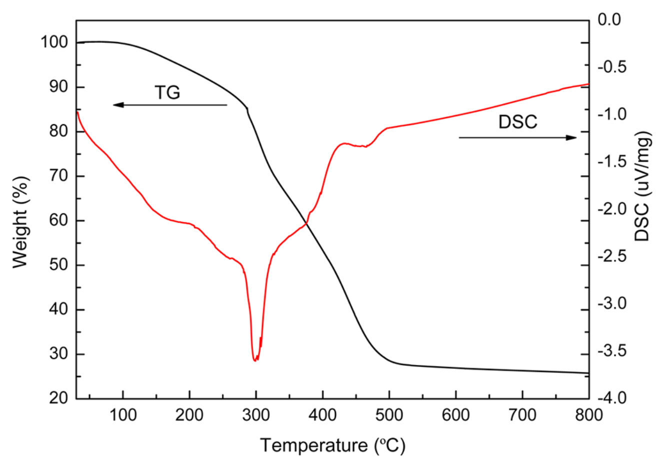


Figure 2. TG-DSC curves of Cr_2O_3−$3TiO_2$ precursor.

stages with increasing temperature and that the total weight loss is about 74%. From the room temperature to around 300 °C, the mass of polymer precursor decreases gradually with about 15% loss, which is associated with the removal of the residual water, acetate and unpolymerized acrylic acid molecular in the precursor. Most significant weight loss occurs in the temperature range of 300 to 500 °C, and more than 55% of the mass is lost at this stage, which is associated the pyrolysis of precursor into Cr_2O_3−$3TiO_2$ complex pigment. It is also observed that a high exothermic peak occurs at around 300 °C, indicating the transformation of the precursor to Cr_2O_3−$3TiO_2$. It should be noted that the weight is almost unchanged above 600 °C, indicating the formation of Cr_2O_3−$3TiO_2$ nanoparticles. Hence, 600 and 800 °C was optimized as the calcination temperature in preparation of Cr_2O_3−$3TiO_2$ pigments, respectively.

Figure 3 displays XRD patterns of Cr_2O_3−$3TiO_2$ pigments calcined in air at different temperature. It is clear that the main diffraction peak positions of pigments calcined at 600 and 800 °C both present a pure rutile phase. In the traditional solid-state method, obtaining a pure rutile phase is difficult in this temperature range. Generally, anatase-to-rutile transformation occurred at 900 °C for the traditional method, and pure rutile was detected at 1000 °C.[20] Although with a high Cr content (40 mol %), no Cr_2O_3 related phases are seen in any of the samples, indicating that Cr ions diffused completely into the

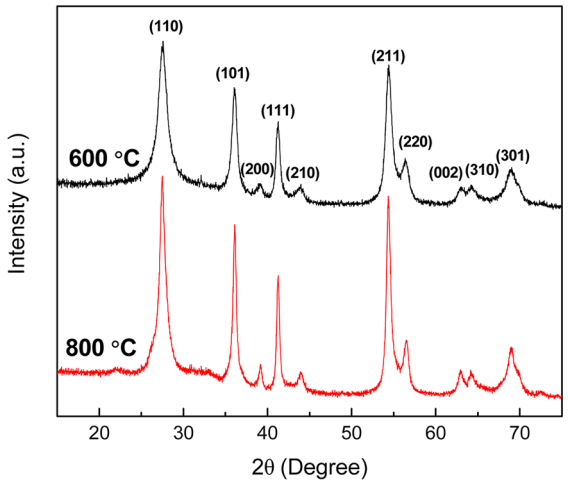
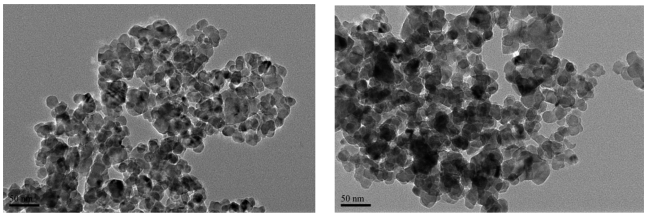


Figure 3. XRD patterns of Cr_2O_3−$3TiO_2$ nanoparticles with different calcinations temperature.

rutile lattice. Previous results also reveal that phase separation between TiO_2 and Cr_2O_3 can be observed only when Cr content is higher than 50 mol %.[21] In addition, all diffraction peaks are broadened, indicating the size of obtained samples in nanoscale. The peaks became sharper and more intense as the calcination temperature increased, indicating improved crystallization and increased crystallite size. For Cr_2O_3−$3TiO_2$-600 and Cr_2O_3−$3TiO_2$-800, the average particle sizes calculated from the Scherrer equation are 14.1 and 20.3 nm, respectively.[22]

The morphology and particle sizes of Cr_2O_3−$3TiO_2$ pigments prepared can be observed by TEM. As shown in Figure 4, all Cr_2O_3−$3TiO_2$ samples are granular in nature and



(a) (b)

Figure 4. TEM images of Cr_2O_3−$3TiO_2$ nanoparticles with different calcinations temperature: (a) 600 and (b) 800 °C.

present a homogeneous nanoscale particle size. Excellent dispersion is observed in all samples with a narrow grain sizes with the distribution in the range of 10−100 nm. In addition, the grain size slightly increases with an increase of calcination temperatures. For Cr_2O_3−$3TiO_2$-600 and Cr_2O_3−$3TiO_2$-800, the average particle sizes are 16.7 and 24.7 nm, respectively. These results are in a good agreement with the crystallite sizes calculated by the XRD technique, the particle size of Cr_2O_3−$3TiO_2$ increases with increasing calcination temperature. Thus, the particle sizes of Cr_2O_3−$3TiO_2$ nanoparticles are adjustable by controlling the calcination temperature. In the traditional solid-state reaction method, the calcined products must be milled and sieved to adjust the grain size of the ceramic pigments, and only microscale pigment particles can be obtained.[20] In the present work, nanoscale pigment can be prepared directly by the high temperature pyrolysis polymer precursor, without requiring milling or sieving.

For the Cr_2O_3−$3TiO_2$ complex pigment, Cr is inserted into the TiO_2 (rutile) lattice, the electronic transitions of Cr ions result in substantial absorption in the visible region. The UV−vis-NIR reflection spectra of Cr_2O_3−$3TiO_2$ prepared are shown in Figure 5, and both samples show three distinct absorption

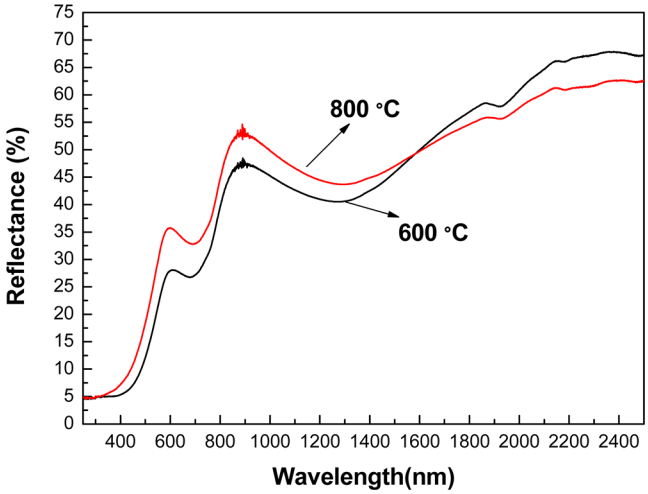


Figure 5. UV−vis-NIR spectra of Cr_2O_3−$3TiO_2$ pigments.

bands between 250 and 1600 nm. The absorption band less than 600 nm is attributed to the charge transfer band of Cr(III) → Ti(IV) and parity-forbidden transitions of Cr(III) in octahedral coordination. The presence of the Cr^{3+} ions caused significant shifts of absorption bands into the visible region compared to the absorption threshold of pure TiO_2 near 400 nm.[23] The two weak absorption peaks located around 680 and 1300 nm are due to Cr (III) spin forbidden transitions.[20] In addition, it can be observed that the Cr_2O_3−$3TiO_2$ pigments have a reflection peak in ∼600 nm, which reflects the color of these pigments. As shown in Figure 6, the Cr_2O_3−$3TiO_2$

Figure 6. Images of TiO_2 and Cr_2O_3−$3TiO_2$-600 nanopigments.

pigments prepared show a deep and brilliant orange color when compared with the white TiO_2, which has great potential application when the aesthetics of darker colors is preferred.

The sunlight, although it is more intense in the visible range, also emits a substantial amount of energy in the invisible UV and NIR range. In fact, about half of all solar power arrives as invisible NIR radiation, which results in the heat built-up on the surface of buildings.[5,24] As shown in Figure 5, a reflection peak in ∼890 nm and a broad reflection band above 1400 nm are seen in the NIR range (800−2500 nm), it is obvious that the reflectance of Cr_2O_3−$3TiO_2$ in the NIR range is much higher than that of the visible light range (400−800 nm). The average reflectance of Cr_2O_3−$3TiO_2$ in NIR range and visible light range is around 53% and 25%, respectively. Furthermore, in the

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visible light range, the reflectance of Cr_2O_3−$3TiO_2$-800 °C is higher than Cr_2O_3−$3TiO_2$-600 °C due to the particle size effect. However, in the NIR range (above 1600 nm), the trend is reversed. The reflectance of Cr_2O_3−$3TiO_2$-800 is higher than that of Cr_2O_3−$3TiO_2$-600. A similar phenomenon has been also reported in of $NiTiO_3$ pigments.[14] Although the NIR reflectance of Cr_2O_3−$3TiO_2$ is lower than white TiO_2 (87%), it is comparable with green Cr_2O_3 pigment (50−57%). The replacement of conventional orange pigments in commercial paint formulations with cool Cr_2O_3−$3TiO_2$ pigments that absorb less NIR radiations allows the development of products with similar in color but high solar reflectance. Consequently, cool coatings absorb less solar energy, which keeps the building surface at a lower temperature and decreases energy transfer by radiation.

CONCLUSIONS

In this paper, orange nanopigments Cr_2O_3−$3TiO_2$ having a high NIR solar reflectance for building surface materials have been developed. Pigment nanoparticles were prepared by pyrolysis of Cr−Ti polymeric precursors via in situ polymerization. Thermal analysis and XRD measurements reveal that the Cr_2O_3−$3TiO_2$ pigments with rutile structure can be prepared by calcination of the precursor at above 600 °C. All Cr_2O_3−$3TiO_2$ samples are granular in nature and present a homogeneous particle size of around 20 nm. The UV−vis-NIR reflection spectra show that the Cr_2O_3−$3TiO_2$ pigments have a reflection peak in ∼600 nm, which reflects the orange color of these pigments. The average reflectance of Cr_2O_3−$3TiO_2$ in the NIR range is around 53%, which is much higher than that of the visible light range. The prepared orange Cr_2O_3−$3TiO_2$ nanopigments are promising materials for preparing building coatings with energy saving performance.

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Notes

The authors declare no competing financial interest.

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