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Synthesis and UV-Shielding Characterization of Plate-Like Titanate/Calcia-Doped Ceria Composite

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Abstract. In order to obtain further performance improvement concerning UV-shielding materials with good comfort and safety, a ball-milling assisted three-step coating method was carried out. First, the calcia-doped ceria (CDC) nanoparticles were prepared using co-precipitation method at pH12.0. Secondly, the as-prepared CDC powder was dispersed by ball-milling to break the big agglomerations of CDC. Thirdly, the colloid of ball-milled CDC particles was used to coat the CDC on plate-like titanate (PLT) substrate at a low pH of 6.5 to obtain the PLT/CDC composite. The effect of ball milling on the dispersion of CDC nanoparticles was checked by a laser diffraction particles size analyzer (SALD-7000, SHIMADZU). The morphology of PLT/CDC composites were evaluated by a field-emission scanning electron microscope. The oxidation catalytic activities, the UV-shielding ability and the dynamic friction coefficient of the obtained PLT/CDC composites were characterized. PLT/CDC composite with good comfort and low oxidation catalytic activity was successfully synthesized by the combination of PLT and CDC dispersed by ball-milling.

1. Introduction
The damages caused by UV rays have been paid much attention and various kinds of UV-shielding materials have been designed in response. Generally, high efficiency of UV-shielding ability, comfort and safety are three of the most important points for sunscreen. The materials should be transparent to visible light, but have excellent ultraviolet absorption ability, and appears natural on the skin without imparting an excessive pale white look. Fine powders of ZnO and TiO₂ which have highly effective UV-shielding abilities are widely used as the UV-shielding materials in personal products, but their high refractive indices can make the face look unnaturally white, and their photo catalytic activities which can facilitate the generation of reactive oxygen species cause the safety worry [1]. Here, the calcia-doped ceria (Ce₁₋ₓCaₓO₂₋ₓ) (donated as: CDC) nanoparticles were used as the UV-shielding coating material since the value of the refractive index of ceria (n = 2.05) is lower than that of rutile (n = 2.72), anatase (n = 2.5), and zinc oxide (n = 2.2) and the oxidation catalytic activity of it can be decreased by the doping of calcia [2-6]. So that the CDC has not only lower photo and oxidation catalytic activities, lower refractive index, but also broad-spectrum UV-shielding abilities. Unfortunately, the comfort and covering capability on skin of inorganic nanoparticles are generally modest due to the agglomeration. In contrast, the plate-like particles show excellent comfort when applied on skin and are often used to improve the comfort and covering ability of nanoparticles. Here,
the plate-like potassium lithium titanate (donated as: PLT)/CDC nanoparticles possessing UV-shielding ability were used as a substrate to improve the comfort and covering capability of CDC nanoparticles used as the UV-absorbent. In our previous works [7-10], the PLT/CDC composites were prepared using co-precipitation method at both high pH (12.0) and low pH (6.5) solutions. But the fabrication at low pH resulted to increase the oxidation catalytic activity of as-prepared CDC nanoparticles due to the dissolution of Ca^{2+}. On the other hand, the fabrication at high pH resulted in inhomogeneous coating of CDC particles on PLT due to the electrostatic repulsive force between PLT and CDC particles. Here, in order to resolve these problems the synthesis of PLT/CD composites was divided into three steps. First, the CDC nanoparticles were prepared using co-precipitation method at pH 12.0. Secondly, the as-prepared CDC powder was dispersed by ball-milling to break the big agglomerations of CDC. Thirdly, the colloid of ball-milled CDC particles was used to coat CDC on the PLT substrate at a low pH of 6.5.

2. Experimental

2.1. The synthesis of CDC nanoparticles
Nanoparticles of calcia-doped ceria (Ce_{0.8}Ca_{0.2}O_{1.8}) were prepared via soft solution chemical routes at 40°C as follows. First, 0.08 M CeCl₃ and 0.02 M CaCl₂ mixed aqueous solution and 0.6 M NaOH aqueous solution were simultaneously dropped into distilled water at 40°C with stirring to precipitate Ca^{2+}-doped Ce(OH)₃ at pH 12. Then, the H₂O₂ (0.2 M) aqueous solution was added to oxidize it to form Ce_{0.8}Ca_{0.2}O_{1.8}. The solution pH was adjusted to and kept at pH 12.0 with 1 M NaOH and/or 1 M HCl through a pH controller. The chemical reactions can be expressed as follows:

\[
0.8\text{CeCl}_3 + 0.2\text{CaCl}_2 + 2.8\text{NaOH} \rightarrow \text{Ce}_{0.8}\text{Ca}_{0.2}(\text{OH})_{2.8} + 2.8\text{NaCl}
\]

\[
\text{Ce}_{0.8}\text{Ca}_{0.2}(\text{OH})_{2.8} + 0.4\text{H}_2\text{O}_2 \rightarrow \text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{1.8} + 1.8\text{H}_2\text{O}
\]

Finally, the precipitate was washed with water and methanol and vacuum dried at 60°C overnight.

2.2. Deaggregation of CDC nanoparticles by ball-milling
The as-prepared CDC nanoparticles were ball-milled before being coated on PLT substrate. The as prepared CDC nanoparticles (2.0 g) were poured into plastic bottle with an inner diameter of 50 mm and a capacity of 100 ml. Zirconia balls with a diameter of 1.0 mm were used as the milling media, and the charged volume of ball media was about 20% of the vessel capacity. After adding 30 ml acetone the bottle was sealed and rotated at 80 rpm for a given time. After ball-milling, the CDC particles were separated by filtration, washed with deionized water and acetone, and vacuum dried at 60°C overnight. In order to investigate the ball-milling effect on the particle size distribution the particles size of CDC was analyzed in different time and the zeta potential of the CDC particles was measured before and after ball milling.

2.3. The synthesis of PLT/CDC micro/nano composite
In a typical process, first appropriate PLT (0.5 g) and CDC (0.5 g) were dispersed into 100 ml deionized water by strong ultrasonic treatment, respectively. Then the slurry of CDC was added dropwise to the PLT dispersion under violent stirring at 40°C. During the experiment the pH value of the mixture of PLT and CDC was kept at 6.5 using the solution of NaOH (0.1 M) or HCl (0.1 M) by pH controller. After addition of CDC slurry, the mixture was kept stirring for given time. The precipitate was washed by deionized water and ethanol in turn for three times and vacuum dried at 60 °C overnight.

2.4. Characterizations
The particle size distributions of CDC and PLT/CDC composite were measured by using a laser diffraction particles size analyzer (SHIMADZU, SALD-7000). The zeta-potential of the PLT and CDC were measured by using a multi-purpose titrator system (Malvern Instruments Ltd, Zeta Sizer Nano-ZS) at 25°C. The morphology of PLT/CDC composites were evaluated by a field - emission
scanning electron microscope (Hitachi, FE-SEM S-4800). The catalytic ability for oxidation of organic material was determined by a conductometric determination method (Rancimat method) [3] using cosmetic grade castor oil as an oxidized material. The sample powder (0.5 g) was mixed with the castor oil (10 g) and set at 120°C with bubbling 10 L h⁻¹ of air, where the air was introduced into 100 ml deionized water. The catalytic ability of sample was determined by measuring the increase in the electric conductivity of deionized water by dissolving the volatile molecules coming from the oxidation of castor oil on heating. The UV-shielding ability of the prepared samples were evaluated by measuring the transmittance spectra of thin films uniformly dispersed the sample powders with an UV-Vis spectrophotometer (SHIMADZU, UV-2450), where 0.5 g of the sample, 1 g of nitrocellulose of industrial grade, 2.5 g of ethyl acetate and 2.25 g of butyl acetate were mixed uniformly using the paint shaker and 10 g of zirconia ball with 1.0 mm in diameter for 40 h. Then, the dispersion mixture was applied onto a quartz glass plate with an applicator. The feeling of wearing the composite powder on skin was evaluated by measuring the dynamic friction coefficient using a friction tester (Katotech KES-SE) which employs a piano wire as a friction sensor and the artificial leather as the substrate where the sample uniformly applied on using a make-up brush.

3. Results and discussion

3.1. The effect of ball milling on the preparation of PLT/CDC composite material

The particle size distribution of as-prepared CDC nanoparticles before ball milling is shown in figure 1a. The size of CDC nanoparticle was widely distributed from 60 nm to 40 µm with a average about 3.35 µm. (i.e., the agglomeration of CDC nanoparticles was formed during the preparation and drying of them). The agglomeration of CDC nanoparticles is adverse of the coating on PLT. In order to reduce the agglomeration of CDC ball milling was carried out. First, in order to check the effect of solvent on the size distribution of CDC nanoparticles different solvents, including deionized water, ethanol, acetone and ether, were used as the ball-milling medium. As a result, with the increase of polarity of solvents the size distribution of CDC became a little worse with the same treatment time. The solvent with lower polarity is better to obtain the sharp particle size distribution of CDC. Secondly, the effect of processing time was also checked. For the same medium the samples were treated for 1, 3, 7, 12 and 24 h, respectively. And it was found that 24 h was necessary for a good size distribution of CDC nanoparticles. The result after 24 h ball milling using ether as the medium is shown in figure 1b. After ball milling although there was still a spot of large agglomeration, the size of CDC particles was mainly distributed from 20 nm to 200 nm.

![Figure 1](image_url)

**Figure 1.** The particle size distribution patterns of CDC nanoparticles (a) before and (b) after ball milling treatment.

3.2. Preparation and characterization of PLT/CDC composite
In order to utilize the electrostatic attraction between the CDC and PLT particles, the zeta-potential of them were measured at 25 °C as a function of pH. As shown in figure 2, the isoelectric points (IEP) of CDC and PLT were determined as 7.5 and 2.5, respectively. Based on these data, the electrostatic attraction between negatively charged PLT substrate and positively charged CDC nanoparticles can be expected at pH between 2.5 and 7.5.

![Figure 2](image)

**Figure 2.** The zeta-potential curves of CDC nanoparticles prepared at pH 12 and PLT.

Typical scanning electron microscope (SEM) images of PLT before coating and PLT/CDC composite are shown in figure 3. The surface of PLT was smooth before coating (figures 3a and 3b). The typical SEM images of as-prepared PLT/CDC composite materials with a 30 mass% CDC content are shown in figure 3c and 3d. It is obvious that after coating there are still some big particles on the surface of PLT substrate, which should come from the agglomerates of CDC nanoparticles. In order to remove the redundant CDC nanoparticles and the agglomerates of CDC, the as-prepared PLT/CDC composite was dispersed into water using ultrasonic irradiation and decanted. After decantation most irregularly shaped agglomerates could be removed as shown in figure 3e. The coating layer of CDC is uniform and compact. The size of primary CDC nanoparticles is about 5~10 nm and the secondary CDC nanoparticles is about 20~100 nm (figure 3f), which is in good agreement with above particle size distribution profile.
The results of Rancimat test to evaluate the oxidation catalytic activity of PLT/CDC composites prepared with co-precipitation method and ball milling assisted three-step method are shown in figure 4A and 4B, respectively. For each method the oxidation catalytic activities of PLT/CDC composites with different CDC concentrations are listed. Because of the dissolution of Ca2+ in CDC nanoparticles caused during co-precipitation at low pH of 6.5, the oxidation catalytic activity of PLT/CDC prepared by co-precipitation method (figure 4A) is a little higher than that by the three-step method (figure 4B), which is adverse in the application of cosmetic products. For example, the oxidation stability time of PLT/CDC (70 mass %) prepared by co-precipitation (ca. 700 min; line g in figure 4A), which is much shorter than that of PLT/CDC (70 mass %) prepared by three-step method (1200 min; line g in figure 4B). Other PLT/CDC composites with various CDC concentrations for both preparation methods have the same tendencies.

The UV-shielding properties of as-prepared PLT/CDC composites were evaluated by measuring the transmittance spectra of the thin films consisting of uniformly dispersed sample powder. As shown in figure 5, the onsets of absorption of PLT (line a in Figure 5A) and CDC (line g in Figure 5A) were ca. 330 and 400 nm, respectively. The transmittance tendency with the increase of CDC concentration around 300 nm, 400 nm and 700 nm in UV-Vis transmittance spectra is shown in Figure 5B. The transparency in the visible light region of PLT/CDC slightly decreased with the increase of CDC content in PLT/CDC. This should be attributed to the thickness and size increase of PLT/CDC with the increase of CDC quantity. The larger particles possess higher scattering coefficient for visible light. This phenomenon also proved that the CDC was effectively covered on the surface of PLT. The absorption of UV-light of PLT/CDC composites increase with the increase of CDC concentration. When the concentration of CDC was 70 mass%, the UV-shielding ability of PLT/CDC composite was almost the same as that of CDC nanoparticles.
Figure 5. UV-Vis transmittance spectra of thin films of (a) PLT before coating, PLT/CDC composite with (b) 10 mass %, (c) 30 mass %, (d) 40 mass %, (e) 50 mass %, (f) 70 mass % and (g) CDC nanoparticles.

In order to evaluate the comfort of PLT/CDC when applied on skin, the dynamic friction coefficients of artificial leather before and after being applied various sample powders on were measured by using a friction tester. The results are shown in figure 6, where the TiO2 (P25) nanopowder was used as the reference. As expected the dynamic friction coefficient of nanoparticles of P25 and CDC were high and that of PLT was lower than that of CDC nanoparticles and the dynamic friction coefficient of CDC decreased by coupling with PLT. At relatively lower concentrations (10~50 mass %) the dynamic friction coefficient of PLT/CDC were quite small. The dynamic friction coefficients of PLT/CDC increased with the increase of CDC concentrations and the feeling of PLT/CDC got worse when the concentration of CDC exceeded 70 mass %. It may be attributed to the redundant CDC particles that were not coated on PLT surface in the sample.

Figure 6. Dynamic friction coefficients of various samples. (µ0: Artificial leather without sample; µ: Artificial leather applied the sample powder on). A: P25 (TiO₂); B: CDC particles; C: PLT before coating; D: PLT/CDC 10 mass%; E: PLT/CDC 20 mass%; F: PLT/CDC 30 mass%; G: PLT/CDC 40 mass%; H: PLT/CDC 50 mass%; I: PLT/CDC 70 mass %.

4. Conclusions
From the experimental results, following conclusions may be drawn. First, the agglomerates of CDC nanoparticles could greatly eliminated by the ball-milling. The oxidation catalytic activities of PLT/CDC composites were obviously decreased by using three-step coating method. That means three-step method can increase the concentration of Ca²⁺ doped in the CDC nanoparticles. The UV-shielding ability of PLT/CDC composites increased with the increase of CDC concentration. The
dynamic friction coefficients of PLT/CDC composites can be greatly improved in a wide range of CDC concentration from 10 mass % to 50 mass %.

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