Immobilization of Nanoscale Sunscreening Agents onto Natural Halloysite Micropowder

Yong Jae Suh1,2 and Kuk Cho3,*

1Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, 124 Gwahang-no, Yuseong-gu, Daejeon 305-350, Republic of Korea
2Nanomaterials Science and Engineering, Korea University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 305-350, Republic of Korea
3Department of Environmental Engineering, Pusan National University, 2 Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 609-735, Republic of Korea

Titanium dioxide (TiO2) nanoparticles contained in sunscreen products are typically smaller than 30 nm in order to enhance the efficacy of the sun protection. TiO2 nanoparticles of this size range raise toxicity concerns because of the generation of reactive oxygen species (ROS) and the ability to penetrate into the skin tissue. To solve these problems, we immobilized the nanoparticles on a natural tubular powder, halloysite. The nanoparticle-halloysite hybrid powders are prepared by two synthetic methods: an ex situ immobilization of TiO2 nanoparticles (after separate synthesis of a nanoparticle batch), and an in situ generation of TiO2 nanoparticles inside halloysite. Notably, TiO2 nanoparticles of pure rutile phase are synthesized so that the ROS generation is suppressed before immobilization. The ultraviolet-visible (UV-vis) light extinction results show that the sunscreening efficacy of the hybrid powder produced via the ex situ route appears to be 22% higher than that of the hybrid powder fabricated by the in situ method. An increase in the hybrid powder concentration results in a sunscreening efficacy equivalent to that of the bare TiO2 nanoparticles. Our results can be used to produce nanoparticle-halloysite hybrid powders suitable for UV light screening while reducing the potential toxicity concerns. [doi:10.2320/matertrans.M2015086]

(Received March 2, 2015; Accepted April 3, 2015; Published May 15, 2015)

Keywords: colloid, nanomaterials, penetration, absorption, scattering, functional cosmetics

1. Introduction

The use of inorganic ultraviolet (UV) filters, such as TiO2 and ZnO nanoparticles, has been increasing significantly, especially in sunscreen products for children and people with sensitive skin.1) The inorganic UV-screening ingredients are contained in commercially available skin care creams and lotions, makeup foundations, eye shadows, and even in lip balms. Among the inorganic ingredients, titanium dioxide (TiO2) nanoparticles are typically adopted as the main UV-screening agent.

The sunscreen is required to block the UV solar radiation over the whole UVB (290–320 nm) and UVA (320–400 nm) ranges, while being transparent to visible light for cosmetic aesthetics. To satisfy the cosmetic efficacy, TiO2 nanoparticles in the range of 20–50 nm have been considered as an optimal material.2–4) On the other hand, TiO2 nanoparticles of this size range have also been used as catalysts because of their high photoactive efficiency; in particular, TiO2 particles with a size of approximately 33 nm show the highest activity.5–7) The photoactive surfaces of the TiO2 nanoparticles produce reactive oxygen species (ROS), such as ‘OH, O2•−, and H2O2,8–10) which are known to be cytotoxic. For example, hydroxyl radicals (‘OH) generated from photocative TiO2 nanoparticles cause damage to DNA plasmids in vitro and to the whole human skin cells in cultures.11,9) Accordingly, the generation of ROS has been suppressed by modifying the TiO2 nanoparticles surface with other materials, e.g., Al2O3, SiO2, and ZrO2, which form hydrated oxides that capture the hydroxyl radicals and thus reduce the photoactivity.11) For the same reason, the rutile phase is more advantageous than the anatase phase, as the latter shows the highest activity among the TiO2 polymorphs.12) The most effective phase at generating ROS is likely to exhibit the highest cytotoxicity.12)

Moreover, as the dermal exposure to TiO2 nanoparticles occurs regularly during the use of sunscreen products, nanoparticles penetration through the skin has become a growing concern.13–22) For example, the normal flexing movement of the skin facilitates the penetration of 0.5 and 1.0 µm particles into the dermis.22) Besides, when a sunscreen lotion containing TiO2 nanoparticles is rubbed on a skin area burned by the sun or damaged by acne, the TiO2 nanoparticles may enter the human body through the skin and have harmful effects.

The toxicity of the sunscreen nanoparticles can be prevented by encapsulating them in a micro-container, reducing the chance of direct exposure of the skin to the nanoparticles themselves. As a result, the ROS generated by the UV light remain in the proximity of the nanoparticles inside the container without entering in contact with the skin. In addition, the nanoparticles are located inside the container and cannot infiltrate through the container walls, excluding the possibility of their penetration. Even the nanoparticles strongly adsorbed onto the outer surface of the container cannot penetrate through the damaged skin. A good candidate for the fabrication of such containers is a naturally occurring mineral: halloysite.

Halloysite is an aluminosilicate clay belonging to the kaolin group and with a composition of Al2Si2O5(OH)4·2H2O; the ratio of aluminum to silicon is 1:1.23) Halloysite is mostly found in the form of a tubular structure with a 15–125 nm internal lumen, a 30–250 nm outer diameter, and a length of less than a few microns (Fig. 1(a)). The outer surface of the halloysite comprises a silicate SiO2− layer, whereas the inner surface comprises an alumina Al2O3+ .
powder produced by the extinction than that fabricated by the in situ method shows higher UV-vis extinction efficiency with that of the bare TiO\textsubscript{2} nanoparticles at the same concentration. The hybrid powder produced by the ex situ method shows higher UV-vis extinction than that fabricated by the in situ method. An increase in hybrid powder concentration makes the extinction efficiency equivalent to that of the bare TiO\textsubscript{2} nanoparticles. Our study enables the synthesis of nanoparticle-halloysite hybrids suitable for use as UV-screening agents while mitigating the toxicity concerns.

2. Experimental Procedure

A sample of halloysite was donated by Atlas Mining Company, USA. Titanium tetraisopropoxide (TTIP, Aldrich, 97%), HCl (Junsei, GR, 35.0–37.0%), NaOH (Kanto, Cica reagent, min. 97%), anhydrous ethanol (Sigma-Aldrich, >99.5%), and T805 TiO\textsubscript{2} nanoparticles (AEROXIDE\textsuperscript{TM} TiO\textsubscript{2} T 805, Evonik, Germany) were used as received. All the chemical solutions not specifically mentioned were prepared with ultra-high-purity deionized water.

The hybrid powder of TiO\textsubscript{2} nanoparticles and halloysite was prepared by either of the following two methods. The first method is an ex situ TiO\textsubscript{2} colloidal method based on the direct loading of TiO\textsubscript{2} nanoparticles into halloysite. The second entails the in situ TTIP-HCl solution method that generates TiO\textsubscript{2} nanoparticles inside halloysite by vacuum-pulling the nanoparticle precursor into the halloysite lumen.

The TiO\textsubscript{2} colloidal method is used to immobilize the TiO\textsubscript{2} nanoparticles, which are prepared separately, directly into halloysite. The synthetic process for the rutile phase TiO\textsubscript{2} nanoparticles is developed based on the study conducted by Han’s group.\textsuperscript{30} In detail, a 1 M HCl (80 mL) solution is placed in a 250 mL beaker and stirred using a magnetic bar; TTIP (20 mL) is then slowly added and stirred at 60°C for 3 h. When the TiO\textsubscript{2} nanoparticles are produced, the solution is left to cool to room temperature, and the TiO\textsubscript{2} nanoparticles are collected by centrifugation at 10000 rpm (= 15260 \times g) for 3 min. The collected TiO\textsubscript{2} nanoparticles are added to distilled water (20 mL) and dispersed with ultrasonic waves for 30 min to prepare a colloidal solution. Then, halloysite powder (3 g) is added to the colloidal solution and the resulting mixture is vacuum pulled. Subsequently, the hybrid powder is collected by centrifugation, washed with a pH 1 solution twice, with distilled water once, and then dried at 60°C.

The in situ TTIP-HCl solution method is used to load the TiO\textsubscript{2} nanoparticles into halloysite by adding halloysite in the early formation stages of the TiO\textsubscript{2} nanoparticles. In detail, a TTIP solution (20 mL) is added to a 1 M HCl solution (80 mL) and stirred at 60°C for 30 min. Next, the halloysite powder (3 g) is added to the resulting solution and then vacuum pulled. Subsequently, the powder is collected by centrifugation and washed with anhydrous ethanol once. Then, the collected powder is dispersed in a 1 M HCl solution (80 mL), and the resulting mixture is stirred at 60°C for 3 h. After cooling the resulting solution to room temperature, the hybrid powder is collected by centrifugation and washed with a solution with pH 1 once, with distilled water once, and then dried at 60°C.

The size and shape of the nanoparticles and hybrid powders were characterized by transmission electron microscopy (TEM, Philips, CM12, Netherlands) and field emission scanning electron microscopy (FE-SEM, FEI, Quanta650F, Netherlands). The crystalline structure of the nanoparticles was characterized by X-ray diffractometry (XRD, Rigaku Denki Co. Ltd., RU-200B, Japan). The UV-screening efficiencies of the TiO\textsubscript{2} nanoparticles, halloysite, and hybrid powders are measured as follows. T805 and synthesized TiO\textsubscript{2} nanoparticles are dispersed in anhydrous ethanol, whereas raw halloysite and the hybrid powders are

Fig. 1 Transmission electron microscopy (TEM) micrographs of (a) raw halloysite, (b) TiO\textsubscript{2} nanoparticles synthesized at 60°C for 3 h in this study, and (c) T805 TiO\textsubscript{2} nanoparticles manufactured by Degussa.
dispersed in a pH 10 aqueous solution. All the samples with a concentration of 0.0025 mass% are sonicated for 10 min to disperse uniformly the particles. The measurement sample is injected into a 1 cm path length quartz cuvette and mounted in a UV-vis spectrophotometer (Scinco, S3100, Korea). Then, the light transmittance of the sample is measured in the wavelength (λ) range of 250–500 nm.

3. Results and Discussion

To obtain the rutile phase TiO2 nanoparticles, we modified the synthetic process reported by Han’s group.30) The reaction time was shortened from 48 to 3 h, the reaction temperature was raised from room temperature to 60°C, and no stabilizing agents were utilized. On the other hand, hydrochloric acid was used to control the hydrolysis and condensation of the TTIP precursor. The use of stabilizing agents, such as the Pluronic P-123 polymer, should be avoided, as their bulky structure prevents the movement of the TiO2 nanoparticles into the lumen of halloysite; besides, they may be unsuitable for cosmetics. As a result, oblong TiO2 nanoparticles with an average size of 15 nm × 70 nm were fabricated (Fig. 1(b)). This size appears to be similar to that of T805, which exhibits an average size of 21 nm (Fig. 1(c)). T805 is a fumed TiO2 nanoparticles treated with octylsilane to form a hydrophobic surface and widely used as a physical UV-filter in sunscreen and daily care products.

The crystalline structures of the synthesized TiO2 nanoparticles were confirmed by the XRD patterns (Fig. 2). The synthesized particles show sharp peaks at the characteristic angles of rutile phase and no peaks at those of anatase phase, confirming the formation of a pure rutile phase. On the other hand, T805 shows a mixed pattern revealing the presence of both the rutile and anatase phases, and exhibiting sharper peaks at the characteristic angles of the anatase phase.

The UV-vis extinction of the nanoparticle suspensions can be determined by measuring the transmittance of the radiation between 250 and 500 nm.31) The absorbance, \( A = \log(I/I_0) \), is calculated from the Beer–Lambert law:32)

\[
A = \varepsilon cl
\]

where \( I/I_0 \), \( I_0 \), \( e \), \( c \), and \( l \) represent the transmittance, intensity of the light transmitted through the sample, intensity of the incident light, extinction coefficient, concentration of the nanoparticles, and path length of the light passing through the sample, respectively.

First, the UV extinctions of the raw materials before hybridization were examined (Fig. 3). All the TiO2 nanoparticles show a strong extinction tendency across most of the UVB and UVA spectra, whereas halloysite is nearly transparent. This result indicates the dependence of the light scattering efficiency on the material optical properties, such as the refractive index.32) The broad-spectrum protection shown by the TiO2 nanoparticles can impart high values of sun protection factor (SPF) at relatively low concentrations.33) The highest absorbance of T805 may be attributed to the large presence of the anatase crystalline phase, as anatase phase is more photoactive than rutile phase.5,10,11,13,14) The TiO2 nanoparticles synthesized in this study show a dependence of the absorbance on the reaction time. This variation is due to their size difference, as the particle size is the key parameter that determines the light scattering characteristics.32) By prolonging the particle growth time, the average size of rutile nanoparticles increased from 12 nm × 50 nm (data not shown) to 15 nm × 70 nm (Fig. 1(b)) as the reaction time increased from 2 to 3 h.

Next, the UV extinctions of the hybrid powders were examined and compared with that of halloysite and bare TiO2 nanoparticles synthesized in this study (Fig. 4). The hybrid powders show an intermediate absorbance between halloysite and bare TiO2 nanoparticles, indicating the extent of the TiO2 nanoparticle immobilization on halloysite, as the contribution of halloysite is very low. Between the two hybrid powders, that prepared by following the TiO2 colloidal method exhibits a higher UV extinction efficiency. The amounts of TiO2 nanoparticles immobilized on halloysite in the hybrid powders can be qualitatively estimated by inspecting the SEM micrographs (Fig. 5). The outer surface of halloysite in the hybrid powder prepared by the in situ TTIP-HCl solution method is covered by a small number of nanoparticles (Fig. 5(b)). Conversely, the surface of halloysite in the hybrid
powder prepared by the ex situ TiO₂ colloidal method is covered by a large number of nanoparticles (Fig. 5(c)). Considering a rather narrow halloysite inner lumen and the oblong TiO₂ particle shape, a higher amount of TiO₂ nanoparticles can be immobilized in the case of the TiO₂ colloidal method. Despite the lower sunscreening efficiency, however, the TTIP-HCl solution method would be considered more advantageous if the contact between the photocatalytic particles and the skin has to be avoided.

It is noted that raw halloysite is a natural clay mineral exhibiting a broad spectrum of size distributions. Although the SEM micrograph of Fig. 5(a) shows many smaller particles, not shown in the TEM micrograph of Fig. 1(a), all the particles are natural. In the cosmetic applications, if needed, these small particles can be easily removed by a simple separation technique such as centrifugation.

To compare the overall sun-screening performance, we defined a representative UV light extinction efficiency by integrating the UV light absorbance with respect to wavelength over the UVB (290–320 nm) and UVA (320–400 nm) ranges. The order of the representative extinction performance is TiO₂ nanoparticles > hybrid powder produced by the TiO₂ colloidal method > hybrid powder produced by the TTIP-HCl solution method (Fig. 6). This order is the same for both the UVB and UVA wavelength ranges. The representative extinctions of the hybrid powders produced by the colloidal method and solution method are 31.3% and 25.6% of that of the bare TiO₂ nanoparticles, respectively.

According to the Beer–Lambert law, the light extinction is proportional to the concentration, and thus it is expected that a four times higher concentration of the hybrid powders will exhibit a greater extinction performance than the bare TiO₂ nanoparticles. To demonstrate this assumption, the dependence of the UV extinction efficiency on the particle concentration was investigated using the hybrid powders produced by the TiO₂ colloidal method. In this experiment, to optimize the synthetic process, the hybrid powder was prepared in different conditions from the previous experiment. The volume ratio between TTIP and 1 M HCl, i.e., TTIP:HCl was reduced to 1 : 10 from 1 : 4 and the reaction was conducted at 80°C for 30 min. Therefore a lower amount of TTIP was used and the reaction time was shortened. The shape and crystalline structure were examined by TEM (Energy Filtering TEM, Carl Zeiss, 200 kV, Germany). TiO₂ nanoparticles located in the halloysite can be hardly seen; most TiO₂ nanoparticles appear to cover the outer surface of halloysite (Fig. 7). This implies that the majority of the TiO₂ nanoparticles lie on the outer surface of halloysite when synthesized by the colloidal method. The selected area diffraction (SAD) pattern clearly shows a highly crystallized rutile phase TiO₂ (Inset of Fig. 7). At 0.0025 mass%, the absorbance of the hybrid powder synthesized at a lower TTIP concentration (Fig. 8) is lower than that of the previous sample powder (Fig. 4). This decrease in the absorbance is attributed to a lower TiO₂ nanoparticle proportion in the same total solid concentration of 0.0025 mass%. Nevertheless, the hybrid powder at 0.01 mass% shows higher absorbance in the UVB wavelength range than the bare TiO₂ nanoparticles at 0.0025 mass%. The hybrid powder at 0.02 mass% shows a significantly higher absorbance over the whole UV light wavelength range. Notably, the increase of the hybrid powder concentration may not cause any problems in the cosmetic
The former TiO$_2$ is located inside the halloysite lumen. The latter TiO$_2$ nanoparticles on halloysite, a naturally occurring clay mineral. The former TiO$_2$ nanoparticles of pure rutile phase were synthesized to prevent the ROS generation. The nanoparticles were synthesized in the absence of any surfactants, eliminating any possibility of inclusion of harmful ingredients in the final sunscreen products. An increase in the hybrid powder concentration led to a sunscreening efficiency equivalent to that of the bare TiO$_2$ nanoparticles. Although this increase in the total solid concentration can limit the usability, the adoption of a natural clay mineral in cosmetics is preferable for some applications. We conclude that this study provides two methods for producing nanoparticle-halloysite hybrid powders that are suitable for UV light screening while reducing the potential toxicity concerns.

**Acknowledgments**

This work was supported in part by the Brain Korea 21 PLUS project in the Division of Creative Low Impact Development and Management for Ocean Port City Infrastructures, the PM2.5 research center supported by Ministry of Science, ICT, and Future Planning (MSIP) and National Research Foundation (NRF) of Korea (NRF-2014M3C8A5030890), and the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources.

**REFERENCES**