MORPHOLOGY CONTROL OF CERIUM PHOSPHATES FOR UV-SHIELDING APPLICATION

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Abstract: Plate-like semiconductor particles possessing bandgap energy of ca. 3 eV have attracted attention because of their UV-shielding ability and excellent comfort when applied on the skin. Hydrated cerium phosphate, Ce₂(PO₄)₂HPO₄·H₂O, possessing two dimensional layer structure tends to grow as plate-like microparticles under solvothermal reaction conditions, and are easily converted to other cerium phosphates such as CeP₂O₇ and CePO₄ with retaining plate-like morphology by the calcinations under mild conditions less than 700°C. These plate-like cerium phosphates may be candidate materials for cosmetic grade UV-shielding application because of the unique UV-shielding ability, low catalytic activity and excellent comfort.

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INTRODUCTION

It is well known that sunlight on the earth contain about 5% of UV-ray which causes several problems such as photodegradation of organic materials, discoloration of painting, damages to human health such as sunburn, suntun, acceleration of aging, causing cancer, etc¹-³). Therefore, damaging effects of UV rays have attracted attention nowadays and various UV-shielding materials have been developed in response. Generally, organic UV-absorbents show excellent UV-absorption ability, however, they are suspected to be absorbed in the body through the skin, raising safety concern when used at high concentration. Accordingly, attention has been focused on the stable and safe inorganic UV-absorbents.

DESIGN OF INORGANIC UV-SHIELDING MATERIALS

In order to cut off UV-ray less than 400 nm in wavelength by inorganic materials, the electric transition of semiconductors possessing bandgap energy about 3 eV are used. In addition, UV shielding materials are also expected to be transparent in the visible light range. The light scattering can be depressed by decreasing particle size as shown in FIGURE 1², and the particles became quite transparent when the particle size becomes less than 20 nm, since the Rayleigh scattering (s) is in proportion to the particle size to the sixth power as shown by eq. (1).

\[ s = Kd^6/\lambda^4 \]  

K: constant, d: grain size, \( \lambda \): light wavelength

Now, nanoparticles of titania, zinc oxide and ceria have been commercially used as inorganic sunscreens in personal care products, since they can effectively cut off UV-ray of the wavelength less than 400 nm as shown in FIGURE 2. It is well known that the high refractive indice of titania can make the skin look unnaturally white. In addition, TiO₂ and ZnO possess high photocatalytic activity and generate reactive oxygen species which are suspected to cause damages to DNA in the body. In contrast, calcia-doped ceria possessing band gap energy of about 3 eV corresponding to the electric transition from oxygen 2p to cerium 4f state and a lower refractive index is quite transparent in visible light so...
that looks natural on the skin⁴. In addition, calcia-doped ceria shows quite low photocatalytic activity. Therefore, calcia-doped ceria nanoparticles have recently commercially used as a new inorganic UV-blocking materials⁴).

In addition, inorganic UV-shielding materials are demanded to show excellent comfort when applied on the skin. FIGURE 3 illustrates the relation between the particle size, transparency and comfort when applied on the skin⁵. Generally, the transparency of particles can be improved with decreasing particle size, but the comfort of nanoparticles is not good because of the agglomeration. In contrast, the micrometer sized plate-like particles such as mica, talc, etc. provide good comfort and are used as extender pigments for cosmetics. These plate-like particles are often used to improve the comfort of inorganic UV shielding materials. However, the combination of UV-shielding inorganic nanoparticles with conventional extender pigments results in a decrease in the UV-shielding performance since these materials do not possess UV-absorption ability.

**PANOSCOPIC ASSEMBLING**

In order to improve the feeling of wearing nanoparticles of inorganic UV-shielding materials without loss of UV-shielding performance, the panoscopic assembling of nanoparticles with plate-like semiconductor particles possessing UV-shielding ability as shown in FIGURE 4 is conducted³,⁶.

![FIGURE 4 Schematic illustration of the panoscopic assembling of plate-like semiconductor/UV-absorbent nanoparticles.](image)

As-expected, by coating calcia-doped ceria, Ce₀.₈Ca₀.₂O₁.₈, nanoparticles of 15-20 nm in diameter on plate-like microparticles of lepidocrocite type potassium lithium titanate, K₀.₈Li₀.₂₆Ti₁.₇₃O₄, of 10-20 µm in diameter and possessing the band gap energy of ca. 3.5 eV (FIGURE 5), the kinetic friction coefficient of Ce₀.₈Ca₀.₂O₁.₈ could be decreased, i.e., the comfort of wearing Ce₀.₈Ca₀.₂O₁.₈ nanoparticles can be improved as shown in FIGURES 6.⁶

![FIGURE 5 Scanning electron micrographs of the samples of (a) plate-like K₀.₈₁Li₀.₂₇Ti₁.₇₃O₄, (b) Ce₀.₈Ca₀.₂O₁.₈ nanoparticles and (c) K₀.₈₁Li₀.₂₇Ti₁.₇₃O₄/50 mass % Ce₀.₈Ca₀.₂O₁.₈ nanocomposites.](image)

It is notable that UV-shielding ability of Ce₀.₈Ca₀.₂O₁.₈ nanoparticles is decreased by coupling with mica, but increased by coupling with plate-like K₀.₈₁Li₀.₂₇Ti₁.₇₃O₄, although the UV-shielding ability of K₀.₈₁Li₀.₂₇Ti₁.₇₃O₄ is lower than that of Ce₀.₈Ca₀.₂O₁.₈ (FIGURE 7). This may be due to the improvement of covering ability of Ce₀.₈Ca₀.₂O₁.₈.
nanoparticles by the depression of the agglomeration with plate-like microparticles of \(K_{0.81}Li_{0.27}Ti_{1.73}O_4\) as shown in FIGURE 8.

**FIGURE 6** Kinetic friction coefficient of various samples. \(\mu_o\): Artificial leather, \(\mu\): Artificial leather applied the sample powder on. A: \(\text{TiO}_2\) (Ishihara Sangyo Co., TTO-55A), B: Talc coated with 50 mass\% \(\text{TiO}_2\) (Catalysts & Chemicals Ind. Co, Coverleaf PC-2055T), C: \(\text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{1.8}\), D: \(K_{0.81}Li_{0.27}Ti_{1.73}O_4\) coated with 50 wt\% \(\text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{1.8}\), E: \(K_{0.81}Li_{0.27}Ti_{1.73}O_4\), F: \(\text{BN}\) (Mizushima Ferroally Co., SHP-4).

**FIGURE 7** UV-Vis transmittance spectra of thin films of (a) \(K_{0.81}Li_{0.27}Ti_{1.73}O_4\) coated with 70 mass\% \(\text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{1.8}\), (b) \(\text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{1.8}\), and (c) \(K_{0.81}Li_{0.27}Ti_{1.73}O_4\).

Therefore, it is clear that coupling semiconductor nanoparticles with plate-like semiconductor possessing UV-absorption ability results in two advantages such as better comfort upon application and improved coverage ability of semiconductor nanoparticles on the skin. These factors may enhance the UV-shielding ability of calcia-doped ceria nanoparticles.

**FIGURE 8** Schematic illustration of the assembling of calcia-doped ceria nanoparticles combined with plate-like titanate particles.

**PLATE-LIKE CERIUM PHOSPHATE PARTICLES**

In order to further improve the UV-shielding performance of ceria nanoparticles, the plate-like semiconductor particle used are expected to show excellent absorption ability of UV-A (\(\lambda = 320-400\) nm), excellent affinity with ceria, low photocatalytic activity and low reflective index. Plate-like microparticles of hydrated cerium phosphate, \(\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4\text{H}_2\text{O}\), which possesses two dimensional layered structure (FIGURE 9)\(^7,8\) and smaller band gap energy than layered titanate showing better absorption ability of UV-A (FIGURE 10)\(^9,10\) can be easily prepared by the hydrothermal reactions of \(\text{Ce}(\text{SO}_4)_2\) in \(\text{H}_3\text{PO}_4\) aqueous solutions (FIGURE 11)\(^9,10\). It is also expected that \(\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4\text{H}_2\text{O}\) show better affinity to ceria since \(\text{PO}_4^{3-}\) ion in hydrated cerium phosphate may be strongly adsorbed at \(\text{Ce}^{4+}\) site in ceria according to the Fajan-Paneth rule\(^11,12\).

**FIGURE 9** Perspective views of the crystal structures of \(\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4\text{H}_2\text{O}\).
FIGURE 10 Transmittance spectra of the thin film of Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O synthesized at 200°C for 3 h in 2.5 M H$_3$PO$_4$ with P/Ce atomic ratio of (a) 2.5 by the normal hydrothermal reaction and (b) 5.0 by microwave assisted solvothermal reaction together with those of (c) plate-like K$_{0.8}$Li$_{0.27}$Ti$_{1.73}$O$_4$ and (d) CeO$_2$ nanoparticle.

Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O showed stepwise thermal decomposition as follows.$^{7,8}$

\[
\begin{align*}
\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4\cdot\text{H}_2\text{O} & \xrightarrow{\text{- 600°C}} 0.5\text{Ce}_2(\text{PO}_4)_2\text{P}_2\text{O}_7 + 1.5 \text{H}_2\text{O} \\
& \downarrow \quad \text{- 650°C} \\
\text{CePO}_4 + \text{CeP}_2\text{O}_7 + 0.25\text{O}_2 & \downarrow \quad \text{- 800°C}
\end{align*}
\]

1.5CePO$_4$ + 0.5CeP$_2$O$_7$ + 0.25O$_2$

\[
\downarrow \quad > 800°C
\]

2CePO$_4$ + 0.5P$_2$O$_5$

It is well known that the morphology of solid material can sometimes be retained even after chemical reaction if the reaction topotactically proceeds. Actually, such topotactic reactions are used to prepare needle-like γ-Fe$_2$O$_3$ and plate-like BaTiO$_3$ by using needle-like α-FeOOH and plate-like K$_{1.07}$Ti$_{1.73}$Li$_{0.27}$O$_2$ precursors, respectively.$^{13,14}$ The preparation of plate-like cerium phosphates by the morphology transcription of plate-like Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O was also succeeded as shown in FIGURE 12 by calcinations at 700°C as follows.$^{15,16}$

Without additive (FIGURE 12 (b)):

\[
\begin{align*}
\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4\cdot\text{H}_2\text{O} & = \text{CePO}_4 + \text{CeP}_2\text{O}_7 + 3/2 \text{H}_2\text{O} \\
& \quad (2)
\end{align*}
\]

With cerium hydroxide (FIGURE 12 (c)):

\[
\begin{align*}
\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4\cdot\text{H}_2\text{O} + \text{Ce(OH)}_3 & = 3\text{CePO}_4 + 3 \text{H}_2\text{O} + 1/2\text{O}_2 \\
& \quad (3)
\end{align*}
\]

With NH$_4$H$_2$PO$_4$ (FIGURE 12 (d)):

\[
\begin{align*}
\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4\cdot\text{H}_2\text{O} + \text{NH}_4\text{H}_2\text{PO}_4 & = 2\text{CeP}_2\text{O}_7 + \text{NH}_3 + 3 \text{H}_2\text{O} \\
& \quad (4)
\end{align*}
\]

CHARACTERISTICS OF PLATE-LIKE CERIUM PHOSPHATES

Transmittance spectra of the thin film of Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O (a), CePO$_4$–CeP$_2$O$_7$ mixture (b), CePO$_4$ (c) and CeP$_2$O$_7$ (d) are shown in FIGURE 13$^9$ together with those of calcia-doped ceria, Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$, nanoparticles (e) and plate-like
particles of potassium lithium titanate, $\text{K}_0.8\text{Li}_{0.266}\text{Ti}_{1.734}\text{O}_4$. Transparency of visible light region of plate-like cerium phosphates ((a)-(d)) and $\text{K}_0.8\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$ (f) are almost identical and lower than that of $\text{Ce}_{1.8}\text{Ca}_{0.2}\text{O}_{1.8}$ nanoparticles, probably due to the scattering of light by large particles. The onset of absorption of $\text{K}_0.8\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$ is around 350 nm. In contrast those of $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$, $\text{CeP}_2\text{O}_7$ and $\text{CePO}_4$ are around 420, 400 and 380 nm, respectively, which is close to that of $\text{Ce}_{1.8}\text{Ca}_{0.2}\text{O}_{1.8}$, 400 nm, indicating that the absorption abilities of UV-A of cerium phosphates are higher than that of $\text{K}_0.8\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$. It is also seen that the absorption ability of UV-light around 300 nm was in the order $\text{Ce}_{1.8}\text{Ca}_{0.2}\text{O}_{1.8} > \text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O} > \text{CeP}_2\text{O}_7 > \text{CePO}_4 > \text{CeP}_2\text{O}_7-\text{CePO}_4$ mixture $> \text{CePO}_4 > \text{K}_0.8\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$, indicating that UV-absorption ability of trivalent cerium phosphate, $\text{CePO}_4$, is lower than that of tetravalent cerium phosphates, $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$ and $\text{CeP}_2\text{O}_7$, but still higher than that of $\text{K}_0.8\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$. 15,16)

![FIGURE 13](image-url) Transmittance spectra of thin films of (a) $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$ as-prepared, (b) $\text{CeP}_2\text{O}_7-\text{CePO}_4$ mixture, (c) $\text{CePO}_4$ and $\text{CeP}_2\text{O}_7$ prepared by calcination at 700°C for 5 h, (e) $\text{Ce}_{1.8}\text{Ca}_{0.2}\text{O}_{1.8}$ nanoparticles and (f) plate-like $\text{K}_0.8\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$.

FIGURE 14 shows the results of the oxidation catalytic activity evaluation by the Rancimat method7,17 for $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$ and $\text{CeO}_2$ nanoparticles using a cosmetic grade Castor oil as an oxidation substrate. It can be seen that the onset of electric conductivity increase of distilled water according to the absorption of the oxidation product in the presence of $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$ is around 20 h and those of $\text{CeP}_2\text{O}_7-\text{CePO}_4$ mixture, $\text{CePO}_4$ and $\text{CeP}_2\text{O}_7$ are more than 30 h. These values are much longer than that of $\text{Ce}_2\text{O}_3$ nanoparticles, i.e., 3 h, indicating that the oxidation catalytic activities of these cerium phosphates are much lower than that of $\text{Ce}_{1.8}\text{Ca}_{0.2}\text{O}_{1.8}$. 15,16) It is a great advantage when they are used for cosmetics material.

The kinetic friction coefficients ($\mu$) of the artificial leather before and after applying plate-like cerium phosphate powders on are shown in TABLE 1, where the relationship among the friction force ($f$), kinetic friction coefficient ($\mu$) and applied force ($N$) to the material after moving can be written by eq. (5).

$$f = \mu N$$

(5)

As expected, plate-like particles of $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$, $\text{CeP}_2\text{O}_7-\text{CePO}_4$ mixture and $\text{CePO}_4$ show much lower kinetic friction coefficient than titania nanoparticles (Degussa P25) which is used as a reference material. 15,16) $\text{CeP}_2\text{O}_7$ particles shows a little higher kinetic friction coefficient, probably due to the partial collapse of plate-like morphology (see FIGURE 12(d)), but the value is still much lower than that of titania nanoparticles. Therefore, it may be expected that all of plate-like cerium phosphate, $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$, $\text{CeP}_2\text{O}_7-\text{CePO}_4$ mixture, $\text{CePO}_4$ and $\text{CeP}_2\text{O}_7$ are useful as a means to improve the comfort of applying $\text{Ce}_{1.8}\text{Ca}_{0.2}\text{O}_{1.8}$ nanoparticles on skin. 15,16)

![FIGURE 14](image-url) Results of by a Ranshimat test for the valuation of oxidation catalytic activity of (a) $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$ as-prepared, (b) $\text{CeP}_2\text{O}_7-\text{CePO}_4$ mixture, (c) $\text{CePO}_4$ and $\text{CeP}_2\text{O}_7$ prepared by calcination at 700°C for 5 h.

TABLE 1 Kinetic friction coefficient ($\mu$) of the various samples.

<table>
<thead>
<tr>
<th>Sample powder</th>
<th>$\mu/\mu_0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$</td>
<td>35.2</td>
</tr>
<tr>
<td>$\text{CeP}_2\text{O}_7-\text{CePO}_4$ mixture</td>
<td>29.0</td>
</tr>
<tr>
<td>$\text{CePO}_4$</td>
<td>33.2</td>
</tr>
<tr>
<td>$\text{CeP}_2\text{O}_7$</td>
<td>46.4</td>
</tr>
<tr>
<td>$\text{TiO}_2$ (Degussa P25)</td>
<td>84.0</td>
</tr>
</tbody>
</table>

$\mu_0$: Artificial leather without sample, $\mu$: Artificial leather applied the sample powder on.

CONCLUSIONS

1) Plate-like particles of $\text{Ce}_2(\text{PO}_4)_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$ can be prepared by the hydrothermal reaction of $\text{Ce(SO}_4)_2$ and $\text{H}_2\text{PO}_4$ at 200°C for 3 h.
2) Plate-like particles of CeP$_2$O$_7$–CePO$_4$ mixture, CePO$_4$ and CeP$_2$O$_7$ can be prepared by the heat treatment of the plate-like particles of Ce$_2$(PO$_4$)$_2$HPO$_4$H$_2$O without additive and with cerium hydroxide and NH$_4$H$_2$PO$_4$, respectively.

3) Plate-like cerium phosphates show low oxidation catalytic activity, excellent comfort and superior UV-shielding ability than plate-like titanate, K$_{0.81}$Li$_{0.27}$Ti$_{1.73}$O$_4$.

4) All of plate-like particles of Ce$_2$(PO$_4$)$_2$HPO$_4$H$_2$O, CeP$_2$O$_7$–CePO$_4$ mixture, CeP$_2$O$_7$ and CePO$_4$ may be useful to improve the comfort of Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$ nanoparticles without loss of UV-shielding ability instead of K$_{0.81}$Li$_{0.27}$Ti$_{1.73}$O$_4$ particles.

REFERENCES