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OMC Nano-emulsion을 포집하고 있는 Nano-TiO_2-paste의 합성과 화장품의 응용

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Inorganic-organic nano-hybrid; Preparation of Nano-sized TiO_2 Paste Trapped OMC Nano-emulsion and it's Application for Cosmetics

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요 약: 화장품에서 유기 화합물인 OMC (octyl methoxy cinnamate)와 무기 소재인 TiO_2가 자외선 차단제로 가장 보편적으로 사용되고 있다. 그러나 OMC는 skin trouble이 있고, TiO_2는 첨가량에 비해서 자외선 차단 효율이 OMC보다 낮고 입자의 크기효과에 의해 백탁 현상이 나타나는 단점이 있다. 본 연구에서는 이러한 두 성분이 갖는 단점을 보완하는 방법으로 OMC를 나노에멀젼시키고, 이 나노에멀젼-OMC를 나노-TiO_2 미립자로 포집하여 자외선 차단효과를 극대화 하면서, 피부에 OMC가 직접적으로 작용하지 못하도록 하는 방법을 연구하였다. 특히 계면활성제를 boundary로 하는 유기/무기 hybrid nano-material에서 TiO_2 미립자와 OMC-에멀젼이 나노 크기가 되면 백탁 현상이 나타나지 않는 투명한 화장품을 제조할 수 있을 뿐만 아니라 나노-에멀젼 OMC를 TiO_2로 포집하는 과정에서 hydrophilic character를 갖는 레시친으로 TiO_2를 안정화하여 보습성을 더욱 향상시켰다. 합성한 inorganic-organic hybrid nano-material는 TEM을 이용하여 나노 미립자의 morphologies를 규명하였고, UV-Visible spectrometer를 이용하여 자외선 흡수를 측정하였다. 또한 X-ray diffractometer를 이용하여 나노-에멀젼 OMC를 포집하고 있는 TiO_2 미립자가 갖는 특성인 pore의 크기와 구조를 측정하였다. 화장품적인 응용으로서 SPF analyzer 측정결과 기존의 powder-OMC에 비하여 우수한 자외선 차단 효과를 나타내었으며, OMC의 피부 침투도 훨씬 줄일 수 있어 OMC의 피부 부작용을 크게 줄일 수 있을 것이다.

Abstract: Preparations of mesoporous materials using various templates and their applicability have been intensively investigated for many years. We studied on synthesizing mesoporous TiO_2 with pores in which sensitive compounds having weak physico-chemical properties such as thermal or UV irradiation and low solubility in solvent are trapped. Prior to trapping OMC in the pores of mesoporous titania, OMC was nano-emulsified in O/W system using Lecithin. Thereafter the OMC was trapped in the pores of mesoporous titania using sol-gel method. Main focus of this work is to prepare OMC-trapped mesoporous titania and to trace the stability and solubility of nano-emulsified OMC in the pores of mesoporous titania, and compared with that of mesoporous silica. OMC-trapped mesoporous Inorganic-Organic hybrid titania showed higher factors in sun protecting and a skin penetration phenomenon was reduced.

Keywords: *octyl methoxy cinnamate, inorganic-organic nano-hybrid, nano-sized TiO_2, microfluidization*

1. Introduction

Since periodic mesoporous material was synthesized by Mobil researchers in the early 1990s, works in this field have been reported on developing of new materials utilizing various mesoporous materials[1]. The abilities of absorption, adsorption, catalyst of mesoporous materails depend on the physico-chemical characters of the pore such as thickness of pore wall, pore size, and ordered-structures of pore. And these physico-chemical

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characters also depend on the length of non-polar group and intermediates-molecular interactions such as between sol-gel polymers and polar head groups of surfactant, non-polar groups and non-polar groups of surfactant[2].

Modifying the physico-chemical properties of mesoporous materials and applicability have been intensively investigated for many years. Among metal oxide mesoporous materials, mesoporous TiO_2 have been most extensively studied especially. Several research groups have prepared mesoporous TiO_2, as well-known, because TiO_2 have been used in various field such as cosmetics, pigments, polymer, catalyst, optics, etc[3-8]. Recently we reported the preparation of mesoporous silica with pores in which microemulsified OMC were trapped. There were many works on synthesizing of mesoporous TiO_2 using various templates such as glycerol, polyethylene oxide copolymers, and likes, but studies on using Lecithin as template drew less attention, because of relatively more hydrophobic property among non-ionic surfactants despite of using very much in biochemical field[9-11].

As well-known, OMC (as organic sunscreen agent) and TiO_2 (as inorganic sunscreen agent) have been widely used in cosmetic field. But OMC cause skin irritation phenomenon because of skin penetration. In the case of TiO_2, the UV protecting effect of TiO_2 is lower than that of OMC per added amounts by weight, and it shows the whitening problem because of particle size effect of TiO_2. In this work, we prepared OMC-trapped mesoporous Inorganic-Organic hybrid titania using Lecithin as template, and studied the physico-chemical properties of OMC-trapped mesoporous Inorganic-Organic hybrid titania, employing XRD, UV/Visible, BET, TEM, SPF analyzer, TG/DTA, Laser light scattering system. Compared the physico-chemical properties of OMC-trapped mesoporous Inorganic-Organic hybrid titania with that of mesoporous silica, it showed higher factors in sun protecting and a skin penetration phenomenon was reduced.

2. Experiment

2.1. Materials

Titanium (IV) isopropoxide (TPT, 99.9%, Aldrich), tetraethoxy silane (TEOS, 99.9%, Aldrich), hydrogenated lecithin(fat-free soybean lecithin with more than 70% phosphatidyl choline, Lipoid), octyl methoxy cinnamate (OMC, 99.9%, Haaman & Reimer), and cetyltrimethyl ammonium chloride (CTAC, 99%, Aldrich) were used as received, not purified. Also, all other substances were of cosmetic and analytic grade.

Table 1. General Formulation of OMC Nano-emulsion

Part	Ingredient	% by weight
Lipid Phase	Hydrogenated Lecithin	2.0
	Ethanol	10.0
	DEA-cetyl phosphate	1.0
	OMC	50.0
Aqueous Phase	Additive	Qs
	Water	To 100

2.2. Preparation of Nano-emulsified OMC Solution

OMC nano-emulsion was produced by the high-pressure homogenization technique with a Microfluidizer (M110F, MICROFLUIDICS, USA). To a homogenized solution of water phase was added oil phase which was composed of lecithin, ethanol, OMC and additive at 50℃. The crude emulsion was pumped through the interaction chamber of a Microfluidizer at a pressure of 800 bar. This process was repeated up to five times. The general formulation of OMC nano emulsion is summarized in Table 1.

2.3. Preparation of Mesoporous OMC-TiO_2 Hybrids

In this study, mesoporous TiO_2 sample were synthesized in ethanol and water solvent, because the characters synthesized samples depend on the polarity of solvent. We reported on synthesizing of mesoporous silica with pores in which microemulsfied OMC was trapped, preparing process on mesoporous TiO_2 refer to our prior document[12]. The synthesizing process in ethanol solvent is same. Because lecithin is dissolved hardly in water, so CTAC was used with lecithin as template. And only lecithin was used in the case of ethanol solvent. So in the case of ethanol solvent, samples were synthesized using lecithin and CTAC under basic condition.

Lecithin and CTAC were added to 50 mL of water and stirred for 30 min at 60℃ in order to uniform the composition of the solution. The nano-emulsified OMC solution was added to this solution and stirred around

Table 2. Topical Formulations for Determination of Skin Penetration and *in vitro* SPF

Ingredient	% by weight		
	A	B	C
Water	To 100	To 100	To 100
DMDM Hydantoin	0.2	0.2	0.2
Stearic Acid	1.0	1.0	1.0
Cetanol	1.0	1.0	1.0
Glyceryl Stearate/PEG-100	2.0	2.0	2.0
Cetearath-12	1.0	1.0	1.0
Cetyl Octanoate	3.0	3.0	3.0
Dimethicone	2.0	2.0	2.0
Octyl methoxy cinnamate	5.0	-	-
Titanium dioxide	3.0	3.0	-
Nano emulsion of OMC	-	18.0	-
Nano-Hybrid of TiO_2 & OMC	-	-	18.0

30 min at 25℃. Thereafter TPT and ammonia solution were added in this solution, and reacted for 12 h. After reacting, filtered and dried at 80℃. We were synthesized the other one for compare with before synthesis. That is, only nano-emulsified OMC solution except and the other process is same with before synthesis.

2.4. Characterization

The trapped situation of OMC in pore of the inorganic-organic nano-hybrid TiO_2 was confirmed employing thermal gravimetry/differential thermal analysis (TG/DTA, Thermal Instrument, SDT 2960 TA 4000) in 25~700℃ temperature range under heating rate of 1℃/min in air. Bragg's equation $2d\sin\Theta=n\lambda$ is used to get the size and shape of the pore in mesoporous TiO_2. The pore structure of synthesized samples were measured using X-ray diffractometer (XRD, Rigaku, D/MAX 2200 ultima) under the condition of 1^{o} low angle, scanning rate of 1^{o}/minute, and 2Θ angle of 1-8^{o} for measuring. X-ray source is Cu Kα line and wave length is 1.45 Å. After samples were heat-treated at 500℃ for 4 h, the pore size and size distribution were measured using BET apparatus (Micrometritics ASAP2010, ASAP2405, AutoporeIII 9420). In order to measure UV/Visible absorption of OMC, synthesized mesoporous TiO_2 powders (0.01 g) were dispersed in 100 mL of water with supersonication and the absorption were measured in the wavelength range of 200 nm~700 nm using UV/Visible spectrometer (HP, MP8453). To measure the solubility of OMC trapped in the pores with variation of dispersed time; 10, 20, 50, 100 min, 1 g of each samples was dissolved in the 100 mL acetonitrile solvent.

In order to measured of skin penetration and in-vitro SPF, three different types of topical formulations were prepared at the same concentration of OMC and TiO_2; one containing the general OMC, another containing simple mixture of OMC nano-emulsion and nano TiO_2 solution, and the third containing inorganic-organic hybrid of nano sized TiO_2 and OMC. The formula of each sample is shown in Table 2. The skin penetration experiment was carried out in Franz-type diffusion cells. One made sure that the receptor compartment was filled with phosphate buffer below the hairless mouse skin to avoid over-hydration. Six and twelve hours after each application, the skin surface was cleaned and skin cylinders were punched and the OMC penetrated into the skin was extracted and then analyzed using HPLC[13-14].

In vitro SPF data of each sample was obtained from SPF 290s analyzer system (Optometrics, USA)[15].

3. Results and Discussion

Sol-gel reaction of metal alkoxide is composed of three steps, 1) hydrolysis step, 2) polymerization step of sol (gelation), 3) particle growth step. The pore structure of inorganic-organic hybrid metal alkoxide depends on not only interaction of polar head group and sol-gel polymer but also interaction and length of non-polar group in surfactants. The size and structure of pores depend on the kinds of solvent and surfactants, and concentration of surfactants. Hydrolysis step of metal alkoxide is important process in performing of the pore structure as well as stability of surfactant rod micelle. Hydrolysis rate of titanium-alkoxide is much faster than that of silicon-alkoxide. Compared with mesoporous silica, synthesizing mesoporous inorganic-organic hybrid titania with uniform distribution of pore size and periodicity of pore structure is very difficult. In this work, before adding titanium-alkoxide in micro-emulsified OMC solution, small amount of silicon-alkoxide (tetraethoxy silane) was added to stabilize micelles of surfactant and microemulsified OMC.

Figure 1 and Figure 2 are TG/DTA measuring results of pure mesoporous TiO_2 sample (OMC non-trapped

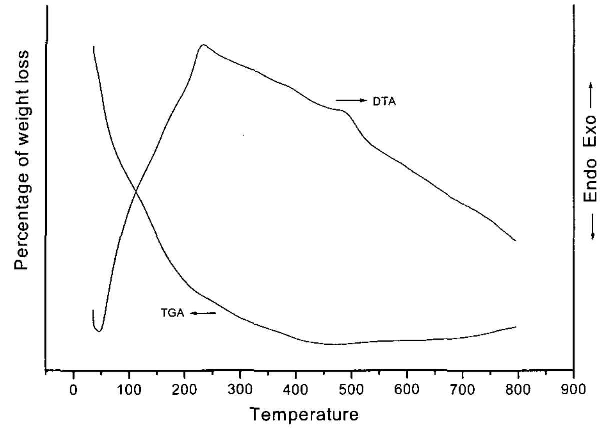

Figure 1. TG/DTA curves of mesoporous TiO_2.

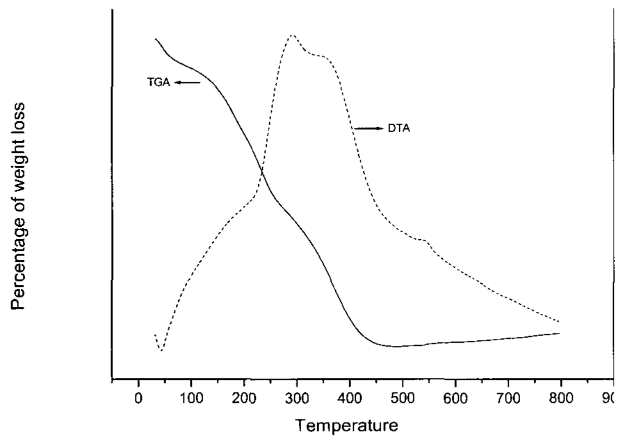

Figure 2. TG/DTA curves of mesoporous OMC trapped-TiO_2.

mesoporous TiO_2, "NOT") and OMC trapped TiO_2 sample (sample name "TOT") respectively. In case of NOT sample, the weight is only decreased rapidly and the exothermic is increased rapidly from 100℃ to 300℃ due to oxidation of templates and solvent in air. And the weight loss in the range 300~500℃ is due to change of titanium oxide from hydroxide form (-OH) to oxide form (-O-). TG/DTA measuring result of TOT sample is not simple. The weight is decreased in the 100~300℃ range because solvent and OMC trapped in rod micelle become oxidation. And due to oxidation of templates such as lecithin interacting between the polar head groups of templates and titania in air, exothermic process shows in 300~450℃ range. In general, the mesopore structure of mesoporous titania decay around 600℃. This decay temperature of meso-pores differs

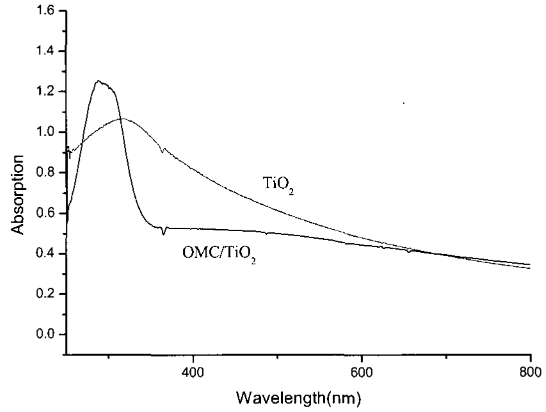

Figure 3. UV/Visible absorption peaks of mesoporous OMC trapped TiO_2 and mesoporous TiO_2.

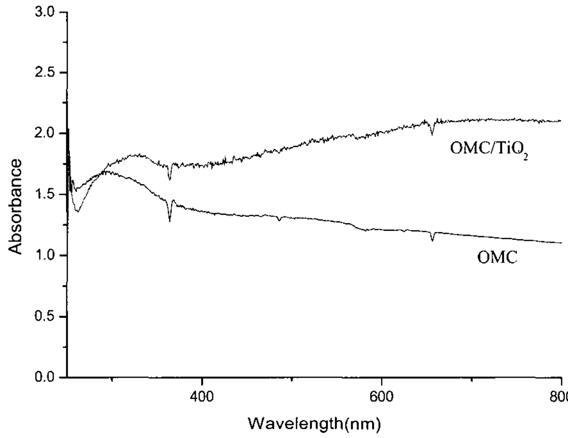

Figure 4. UV/Visible absorption peaks of OMC emulsion (50%) and mixture of OMC/TiO_2.

from the structure and size of the pores. DTA shoulder near 500℃ is evidence that synthesized mesoporous titania in this work have the meso-sized pores and large pore size. We could confirm that nano-emulsified OMC is trapped in pores of mesoporous TiO_2.

Figure 3 and Figure 4 are UV/Visible absorptions of mesoporous TiO_2 and inorganic-organic hybrid TiO_2 with OMC trapped pores respectively. Compared with pure mesoporous TiO_2, mesoporous TiO_2 with nanoemulsified OMC exhibits absorption in wide wavelength range of ultraviolet and high UV protection effect. Figure 5 is UV/Visible absorptions of suncream samples prepared with only nanoemulsified OMC, TiO_2 powder/nano-emulsified OMC, mixture of nano TiO_2 solution and nanoemulsified OMC, and inorganic-organic hybrid TiO_2 with OMC trapped pores. Also

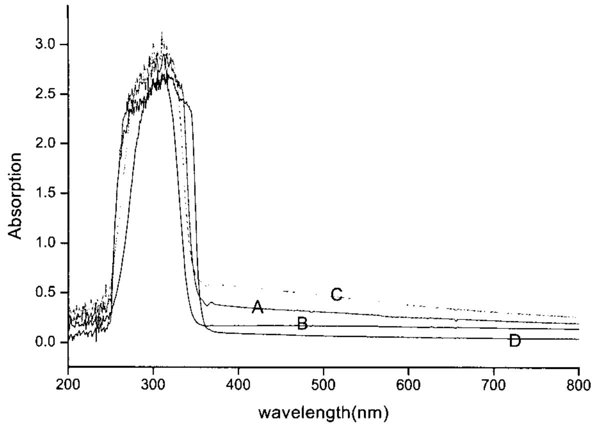

Figure 5. UV/Visible absorption peaks of sun cream prepared with synthesized samples.
A; mixture of TiO_2 powder (50 nm particle size) and emulsified OMC,
B; mixture of TiO_2 nano solution and emulsified OMC,
C; OMC trapped mesoporous TiO_2,
D; emulsified OMC (7%)

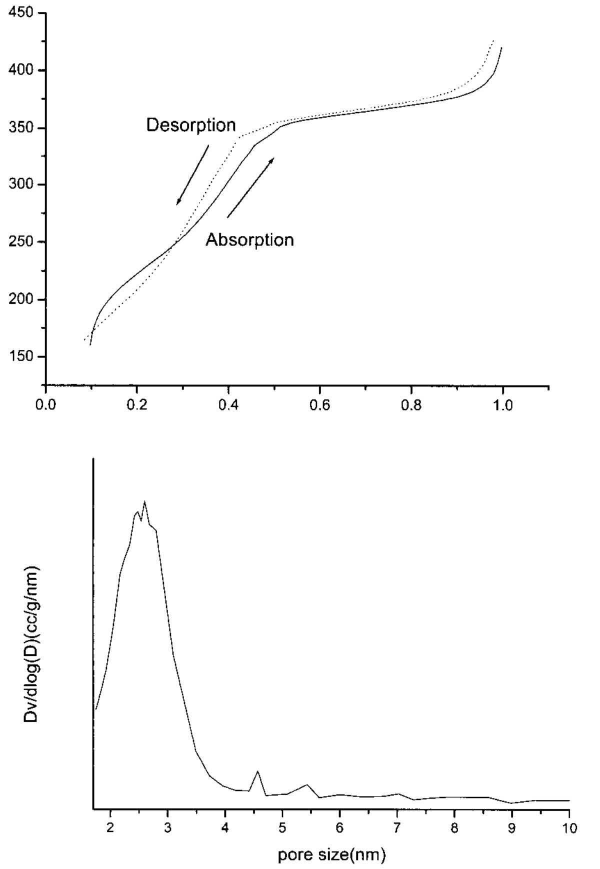

Figure 6. N_2 adsorption and desorption isotherms and pore size distribution of mesoporous TiO_2 at 500℃.

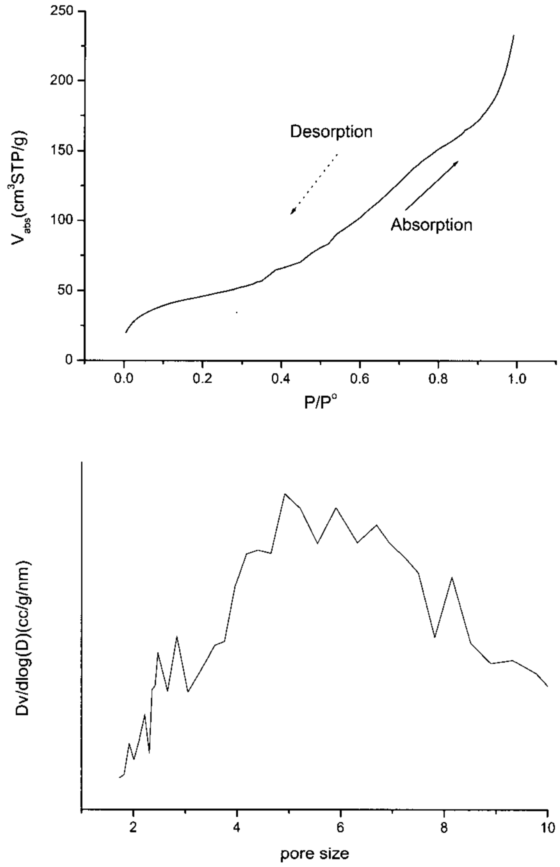

Figure 7. N_2 adsorption and desorption isotherms and pore size distribution of OMC trapped TiO_2.

inorganic-organic hybrid TiO_2 with OMC trapped pores exhibits the highest UV/Visible absorption than that of other samples.

Nano-emulsified OMC trapped in pores of TiO_2 is encapsulated and immobilized by complicated physical forces such as interaction between the molecules and capillary phenomenon. To understand these effects, it is interested in comparing solubility of OMC with that of silica in acetonitril solvent, which was trapped in the rod micelle of inorganic-organic nano-hybrid TiO_2. Solubility results are not showed here, but OMC trapped in the rod micelle of inorganic-organic nano-hybrid TiO_2 is more stable than that of silica.

Figure 6 and Figure 7 are N_2 adsorption results of pure mesoporous TiO_2 and hybrid mesoporous TiO_2 with trapped OMC respectively. After samples were heat-treated at 500℃ in air condition, N_2 adsorptions of samples were measured using BET apparatus. It is exhibits for pure mesoporous TiO_2 2~4 nm pore size

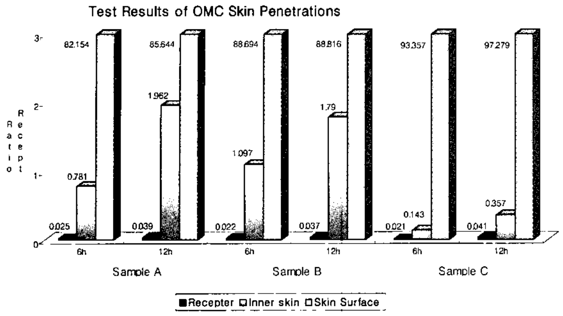

Figure 8. Skin penetration effect of octyl methoxy cinnamate.

Table 3. Skin Penetration of Octyl Methoxy Cinnamate with Change of Penetration Time

	Sample A		Sample B		Sample C	
Penetration time	6 h	12 h	6 h	12 h	6 h	12 h
Skin Surface	82.15	85.64	88.69	88.82	93.36	97.28
Inner Skin	0.781	1.962	1.097	1.79	0.143	0.357
Receptor	0.025	0.039	0.022	0.037	0.021	0.041

Table 4. *In-vitro* SPF Data of Topical Formulations

	Sample A	Sample B	Sample C
In-vitro SPF	8.96	8.36	9.61

distribution, 2~10 nm pore size distribution for hybrid mesoporous TiO_2 with trapped OMC. It is not showed here, but these results were confirmed from XRD measured results.

Figure 8 and Table 3 are skin penetration test results of OMC samples. It exhibits that skin penetration of OMC trapped in pore of hybrid TiO_2 is the slower than that of other samples, and was hardly penetrated into skin. *In-vitro* SPF results are shown in Table 4. Also inorganic-organic hybrid TiO_2 with nanoemusified OMC have the highest sun protection factor value, compared with those of other samples.

We confirmed from this research that our results could be useful in developing new advanced materials, and our encapsulation method could used to deliver stably other critical molecules as well as OMC in mesopores of mesoporous materials.

4. Conclusion

This study was very useful in synthesizing mesoporous inorganic-organic hybrid nano-materials, with which nano-emulsified OMC was trapped stably in rod micelle. Titania synthesized by our method has ordered-pore structure, and the trapped OMC in pores of hybrid TiO_2 maintained stability for long time. Also OMC-trapped mesoporous inorganic-organic hybrid titania showed higher factors in sun protecting and a skin penetration phenomenon was reduced.

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