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Synthesis of plate powder coated nano sized ZnO by hydrothermal precipitation method

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Abstract : 우리는 마이카, boron nitride, bismuthoxychloride와 같은 판상 분체에 ZnO 나노입자를 코팅한 고 기능성 무기 분체를 합성하였다. 본 실험에서 우리는 수열침전법을 이용하여 합성분체를 합성하였다. 출발물질은 $ZnCl_2$를 사용하였고 침전제로는 hexamethylenetetramine(HMT)와 urea를 사용하였다. 본 실험의 반응변수로는 출발물질의 농도, 침전제 및 반응온도를 변화시켜 실험하였다. 합성물의 형태, 결정성 및 UV-차단능은FE-SEM, XRD, FT-IR, TGA-DTA, in vitro SPF 테스트를 활용해 분석하였다. 본 실험의 결과, 나토입자 크기를 갖는 ZnO는 동일한 최적의 합성조건하에서 다양한 판상 분체의 종류에 관계없이 균일하게 코팅되었다. .

Keywords: *zinc oxide, UV blocking, cosmetics, hexamethylenetetramine, coating*

1. Introduction

Typical UV-blocking materials were used by organic and inorganic materials. Generally, organic UV-absorbers show effective UV-B (290 ~ 320 nm) absorption property, but doesn't show with modest UV-A (320 ~ 400 nm) absorbing ability. Also, they posed a safety problem when used at high concentrations. Inorganic UV blockers act mechanism with blocking vibration, diffraction, reflection and so on. The fine powders of cerium oxide, titanium oxide and zinc oxide have ideal characteristics for use as a broad-spectrum inorganic UV radiation blocking material. In many inorganic UV blocking materials, titanium oxide fine particles have been used and it has the best blocking ability of inorganic UV blocking materials[1,2]. The titanium oxide fine particles not only blocked UVA and UVB but also had drug-proof property. On the other hands, zinc oxide had a lower refractive index. Zinc oxidehas little impurities, anti-bacteria, and deodorization as well as good blocking ability in broad spectrum. Also, zinc oxide has been used in a wide variety of technological applications including sensor devices, electro-luminescent devices, semiconductor devices, piezoelectric materials, and optical waveguides, as a catalyst.

We used coating base with many characteristics such as ultra-fine and plate type particle materials that used in the cosmetic industry. These materials were mica, boron nitride and bismuthoxychloride. We used hydrothermal precipitation method

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because it synthesized ultra-fine particles that metal salts and precipitation materials were mixed with liquid stats and then, we gained metal oxide materials by heating procedure. This method could control the morphology, size and distribution of synthesized composites with many kinds of variables, such as the concentration of zinc chloride, precipitation, sorts of precipitation materials, reaction time, reaction temperature, and nuclear generation agent[3-13]. We analyzed composite powder's shape, crystallization and UV-blocking ability with FE-SEM, XRD, FT-IR, TGA-DTA, and *in vitro* SPF test.

2. Experimental

The pretreatment carried out mica, boron nitride (the following BN) and bismuth-oxychloride(the following BOC) with dilute hydroxy chloride for 2hr. And then, after drying at 100℃ for 24hr, we used pretreated-base-powders. The pretreatment worked the decomposition of organic materials and impurities in coating base materials. And it was easy to coat procedure with attaching the hydroxy group.

We used starting zinc chloride($ZnCl_2$) as salt. Weused two kinds of precipitation materials for testing effect of precipitation kinds. First precipitation material used HMT, so to speak, hexamethylenetetramine ($C_6H_{12}N_4$). Second precipitation material used urea(NH_2CONH_2).

A chemical reaction formula as first precipitation material HMT. A chemical reaction formula as second precipitation material urea.

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4\ NH_3$$
$$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

We used a waterbath for controlling a constant temperature and stirrer for homogeneous mixing. We mixed starting salt material and precipitation material with aqueous states for 1hr. After then, mixed solution was stirred with keeping with 80℃ for 1hr. Adding ammonium hydroxide (NH_4OH) as nuclear generation material, we varied the reaction time. Thereacted material was filtered and washing with warm distilled water and then, was filtered again. After upper process, dried at 100℃ for 24hr. We varied the starting salt material concentrations from 0.05M to 0.2M. For evaluating the effect of precipitation concentration, we varied HMT concentration from 0.05M to 0.2M and varied urea concentration from 1M to 5M. Table 1 showed the experimental condition and variables.

3. Results and Discussion

3.1. The FE-SEM Analysis of the ZnO Coated-particles

The size of synthesized particles had from 20nm to 30nm and the shapes of synthesized particles were rod type, sphere type, and board type. Fig. 1 showed that the higher $ZnCl_2$ concentration, the larger particles quantity of coated materials. When $ZnCl_2$ concentration was 0.1M, the particles of coated materials were sphere type and homogeneous state, but under 0.1M, the particles of coated materials didn't coat ZnO because of early terminating nuclei generation and growth reaction. Over 0.15M, the particles of coated materials were from rod type to board type because of overgrowing the nuclear generation and increasing the particle for priority growth direction. Fig. 2 showed the particles synthesized at different HMT concentration. When HMT concentration was 0.05M(Fig. 2(a)), the particle shape was the middle shape between rod type and sphere type because hydrolysis

Table 1. Synthesis Conditions of Mica, Boron Nitride, Bismuthoxychloride-ZnO Composite

Sample No.	Materials				Reaction Time (hr)	Reaction Temp. (℃)
	Starting Mat.	Precipitation Mat.		Nuclear Mat.		
	$ZnCl_2$ Con. (mol/ℓ)	HMT Con. (mol/ℓ)	Urea Con. (mol/ℓ)	NH_4OH (mℓ)		
SZ 1	0.05	0.1		5	12	80
SZ 2	0.1					
SZ 3	0.15					
SZ 4	0.2					
SZ 5	0.1	0.05		5	12	80
SZ 6		0.1				
SZ 7		0.2				
SZ 8	0.1		1	5	12	80
SZ 9			3			
SZ 10			5			
SZ 11	0.1		1	5	12	90
SZ 12			3			
SZ 13			5			
SZ 14	0.1	0.1		3	12	80
SZ 15				5		
SZ 16				7		
SZ 17	0.1	0.1		5	12	70
SZ 18						80
SZ 19						90
BZ, BOZ 1	0.1	0.1		5	12	80
BZ, BOZ 2	0.2					

reaction of HMT happened slowly and pH of materials increased so slowly. Fig. 2(b) shows when HMT concentration was 0.1M, the particle shape was sphere type and the coating area was increased. But, Fig. 2(c) shows when HMT concentration was 0.2M, the particle shape was changed from sphere type to rod type because nuclei were excessively generated and ZnO grew rod type. Fig. 3 showed the particles synthesized at different urea concentration. Fig. 3(a), (b), (c) were synthesized at reaction temperature 80℃ and Fig. 3(d), (e), (f) were synthesized at reaction temperature 90℃. When Urea concentration was so low, the hydrolysis rate of urea was slow and reaction nuclei didn't make coated-particles(Fig. 3(a)). When Urea concentration was so high, the hydrolysis rate of urea was fast and reaction nuclei made board-type particles(Fig. 3(c)). The higher reaction temperature worked, the smaller coated-areas became. But, HMT as precipitation was better than urea because HMT was the faster hydrolysis rate than

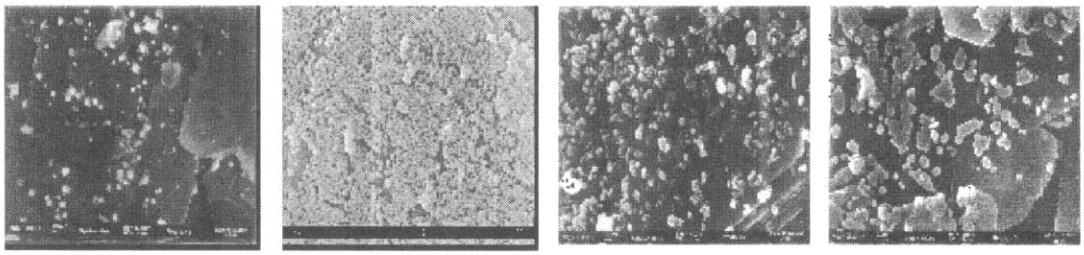

Fig. 1. SEM photographs of synthesized composite from $ZnCl_2$ concentration (a) SZ1, (b) SZ2, (c) SZ3, (d) SZ4.

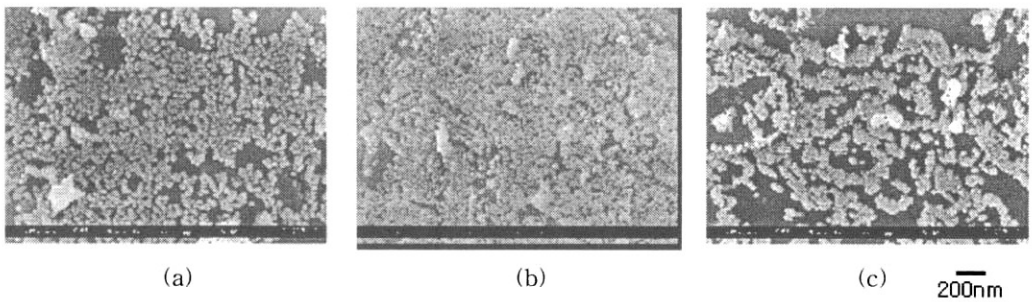

Fig. 2. SEM photographs of synthesized composite from HMT concentration (a) SZ8, (b) SZ9, (c) SZ10.

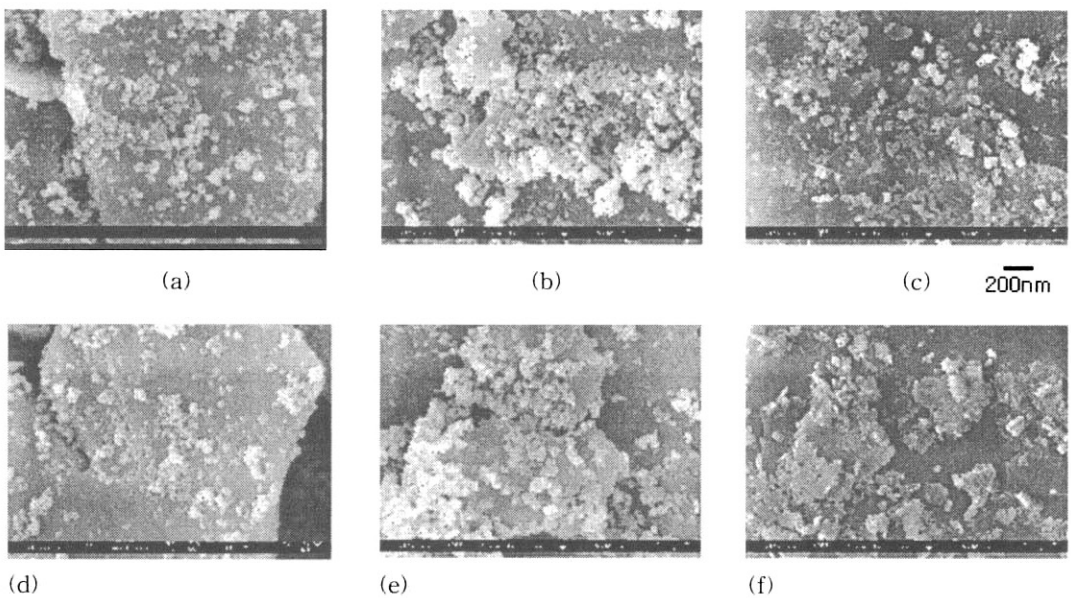

Fig. 3. SEM photographs of synthesized composite from urea concentration (a) SZ11, (b) SZ12, (c) SZ13, (d) SZ14, (e) SZ15, (f) SZ16.

urea and generated many reaction nuclei. Fig. 4 and 5 show the coated-particles of BN and BOC with coating base powder at best coating conditions.

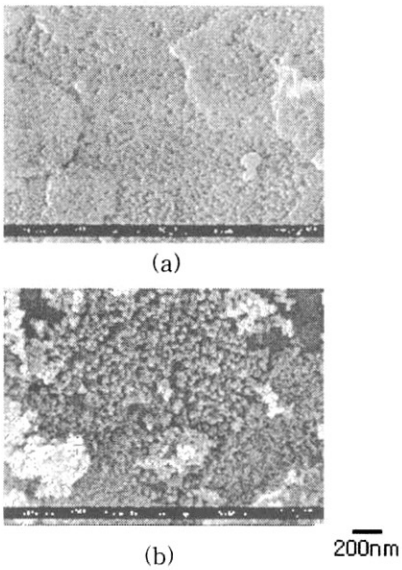

Fig. 4. SEM photographs of synthesized composite from BN-ZnO (a) BZ1, (b) BZ2.

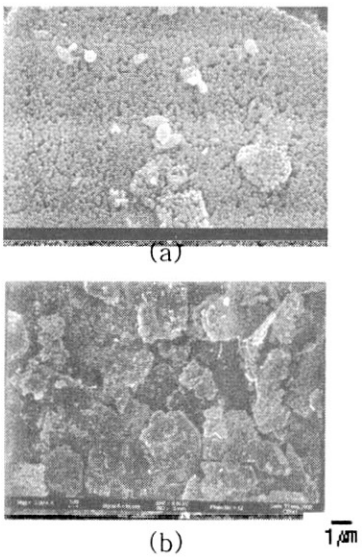

Fig. 5. SEM photographs of synthesized composite from GLO-ZnO (a) BOZ1, (b) BOZ2.

3.2. The Analysis of FT-IR

After coating ZnO on mica, dry at 100℃ and then, sintered at 300℃, 500℃, 700℃. Fig. 6 showed the result of FT-IR at different calcined temperature. Fig. 6 shows Al-O bond at 1070cm^{-1}. 1100 cm^{-1} was piled up 1070 cm^{-1}, and it was larger than other peaks. After sintering at 500~700℃, 3600 cm^{-1}peak proved zinc hydroxy salt radical that was evidence of reaction material as OH^- radical. But, this peak didn't appear at 700℃, because the decomposition of OH and salt in zinc hydroxy salt occurred to reduce the mass at 600℃in TGA-DTA curves. After sintering, ZnO peak generated 480cm^{-1}.

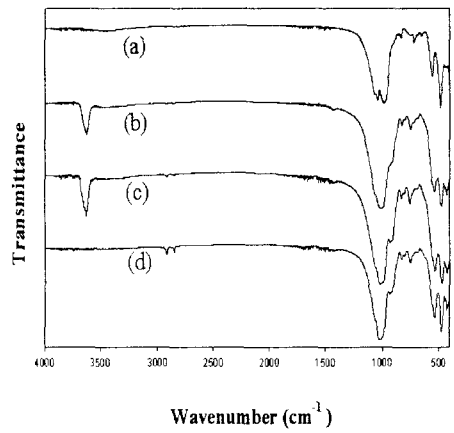

Fig. 6. FT-IR spectra of SZ 4 from (a) pure mica, (b) 300℃, (c) 500℃, (d) 700℃.

3.3. The Analysis of XRD patterns

Fig. 7 shows the XRD patterns of BZ2 specimen in BN-ZnO composites that were made by changing sintering temperatures. This result matched JCPDS value and we knew that the particle structure of this specimen was hexagonal type. Coated-ZnO particles looked like sphere type with FE-SEM in spite of being anisotropy, becausemany nuclei with critical size grew into about 0.5nm to 5nm with first growth. And then first-growth particles formed second-particles of sphere type by equal

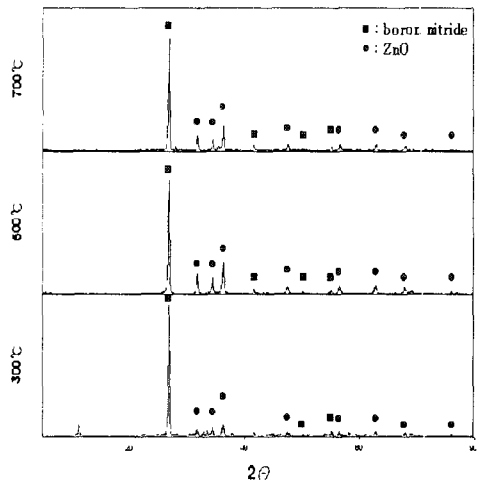

Fig. 7. XRD patterns of BZ 2 from various sintering temperature at300℃, 500℃, 700℃

aggregation. The XRD patterns of SZ4 and BOZ2 was similar to the results of BZ2.

3.4. The Analysis of TGA-DTA

Fig. 8 shows the TGA-DTA peak of BZ2. The major mass reduction at 180℃ was occurred by the decomposition of water and organic materials. The mass reduction at 450℃ and 650℃ were occurred by the

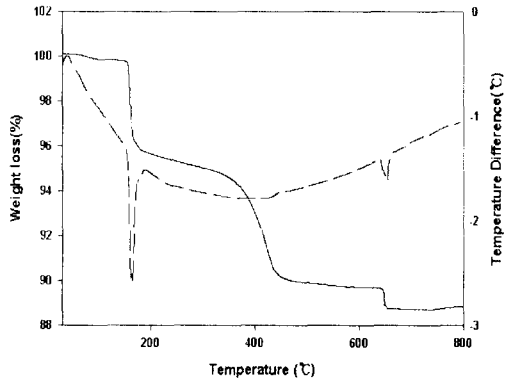

Fig. 8. TGA-DTA curve of synthesized composite from BZ 2.

decomposition of OH^- and Cl^- radicals in hydroxy-salt.

3.5. The Analysis of *In-vitro* SPF test

Table 2 showed the results of in vitro SPF and UVA blocking ability. The results were important to compare relatively uncoated specimens (sample A, B, C) and ZnO coated plate type materials(sample D, E, F). The result of *in-vitro* SPF test were not useful to determine an absolute value but useful to compare with others. The results of *in-vitro* SPF were increased over 10 by coating or

Table 2. The results of in vitro SPF and UVA blocking ability

Sample No.	UVB blocking ability	UVA blocking ability	
	In vitro SPF	Critical Wavelength (nm)	UVA/B ratio
Sample A (Pure mica)	1.23±0.02	385.2	0.590±0.025
Sample B (Pure BN)	2.62±0.07	379.3	0.555±0.005
Sample C (Pure BOC)	7.60±0.71	386.9	0.726±0.009
Sample D (ZnO coated mica)	12.90±1.70	389.6	0.872±0.006
Sample E (ZnO coated BN)	13.90±0.09	390.2	0.936±0.007
Sample F (ZnO coated BOC)	19.60±0.70	387.7	0.946±0.005

non-coating. In specially, BOC had relatively high SPF data because it had relatively higher reflexive index and covering ability than mica and BN.

4. Conclusion

In this study, hydrothermal precipitation method was used to synthesis functional inorganic composite powder having narrow ZnO coated plate particle distribution. The optimal coating condition was determined by variation of concentrations of starting material, precipitation materials, nuclear formation material, reaction time and reaction temperature.

1. We used HMT and urea as precipitation agent. This study showed that HMT possessedsuperior characteristics of precipitation agent than urea. Because the hydrolysis rate of HMT was more fast than that of urea, the reaction could be happened as uniform and simultaneous.
2. When the reaction temperature was increased, the rate of hydrolysis grow up, then the amount of coated ZnO was increasing and the shape of coated ZnO maintained sphere type. But, when the reaction temperature be more than 90℃, the rate of hydrolysis so high, then the shape of coated ZnO was needle type.
3. The coated ZnO particle maintained the original shape after calcinations of 700℃. From XRD data, hexagonal ZnO was synthesized at 300℃, and pure ZnO was synthesized at 700℃.
4. According to *in-vitro*UV blocking test, the functional composite powder sample was higher than non-coated powder beyond decuple. Because UVA/B ratio above 0.8, we could confirm that this sample possessed the blocking ability of broad spectrum.

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