고순도로 합성된 나노콜로이드 티타늄옥사이드의 BN 파우더 코팅에 관한 연구

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Synthesis of High Concentrated TiO_2 Nano Colloids and Coating on Boron Nitride Powders

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Abstract

High concentrated TiO_2 nano colloids were synthesized by sol-gel method. Reactions were performed in $TiCl_4/HCl/H_2O$ aqueous solution and the conditions of particles such as shape, size and aggregation, etc. were controlled by polymerization and adsorption of acrylamide in surface of TiO_2 nano particles. And also, aminopropyltriethoxysilane was added instead of acrylamide and compared each other. The prepared colloids were well dispersed and showed the strong absorption peaks at 350nm-370nm which is blue shifted to 20-30nm, compared to macro particles. The obtained techniques from TiO_2 nano colloids synthesis were utilized in coating on boron nitride powders which are nonpolar and isoelectronic materials of carbon. Their surface morphology, structure, thermal stability and U.V

absorption characteristics were examined by SEM(Scanning Electron Microscopy), XRD(X-ray diffraction), TG/DTA(Thermogravimetric and Differential Thermal Analysis), UV-VIS(Ultraviolet-Visible Spectroscopy).corresponding auther(e-mail:shlee6914@hanmail.net)

1. Introduction

TiO_2-based materials have applied to photocatalytic [1-6], cosmetic [7-9] and other various research fields. Recently, as with the other nanoparticle researches have attracted the bunch of interests not only due to their unusual properties compared to the bulk but for their wide spread applications in the practical world, TiO_2 nanoparticle research has been executed intensively.

In general, nanoparticles can be synthesized by reverse micelle [10-13], microemulsion [14-16], electrochemical deposition [17], gas condensation [18-20], sol-gel method [21-26]. The reverse micelle and microemulsion method are proper in making monosized particle but have the limit in low concentration product and involved process to add surfactant in organic solvent. The electrochemical deposition method is good at controlling particle size accurately but has the difficulty in adjusting electrolyte conditions such as pH, composition, temperature, current density, etc. which can have a great to do with the shape of nanoparticle. In the case of gas condensation method, it is possible to take a mass production however the demerits of low uniformity and high cohesion still remain. The sol-gel method is an effective approach for the synthesis of nanoparticle as well as glasses, ceramics, and organic-inorganic composite materials. The advantages of sol-gel techniques arise from the high purity of the metal alkoxide precursors, the molecular homogeneity of the intermediate sols, and the low processing temperatures necessary to prepare materials.

The nanoscale particles have a very large surface to volume ratio and a high surface tension, consequently they are inclinable to agglomerate each other. The particle concentration is becoming higher, the agglomeration is more growing up and this phenomenon can give rise to serious problem in application. Thus it is very important to let the nanoparticles not cohere in the synthesis procedure and for the purpose of solving this cohesion problem several techniques such as self-assembling, polymer coating method have been studied.

In this work we presented the synthesis of high concentrated, well-dispersed TiO_2 nano colloids and its coating on boron nitride powders. High concentrated TiO_2 nano colloids were synthesized by sol-gel method. Reactions were performed in $TiCl_4/HCl/H_2O$ aqueous media under the strong acid condition(pH=2~3) which can make the surface charge of TiO_2 be zero and well dispersed nano colloid, and then particle surface was stabilized with using acrylamide or aminopropyltriethoxysilane. The obtained techniques from TiO_2 nano colloids synthesis were utilized in coating on boron nitride powders which are isoelectronic materials of carbon and has the high dielectric constant and nonpolar property.

2. Experimental

2.1. Synthesis of TiO_2 Nano Colloids

The TiO_2 nano colloids were synthesized by sol-gel method. At first, reagent grade $TiCl_4$ was slowly added dropwise to a flask, kept in a ice bath, containing 6 M aqueous HCl under vigorous stirring to make the resulting solution 2 M in $TiCl_4$, and then complex agent(acetic acid) was added to form stabilized Ti-alkoxide, followed by the addition of ethylacetoacetate for the purpose of controlling the hydrolysis speed of Ti-alkoxide. The addition of ethylacetoacetate makes 4-coordinated Ti-alkoxide form the 6-coordinated compound and retard its hydrolysis rate. After hydrolysis reaction undergoing for 2h at T=80℃, acrylamide or aminopropyltriethoxysilane was added to occur surface reaction on the TiO_2 nanoparticles. The acrylamide is soluble in aqueous solution but it has come to be almost nonsoluble after polymerization, and so it is appropriate to disperse nanoparticles in mixed solution of water and alchol. In the case of aminopropyltriethoxysilane, triethoxy group brings about hydrolysis reaction on the surface of TiO_2 nanoparticles, on the other hand aminopropyl group head for aqueous phase. Thus aminopropyltriethoxy silane has a dispersive property in neutral or basic solution. Finally, nanoparticles were taken by centrifugation after neutralization with sodium hydroxide

2.2. TiO_2 Coating on BN Particls

The boron nitride particles were coated with TiO_2 nano colloids by the addition of a known amount of the TiO_2 to an aqueous suspension of boron nitride particles. At first, the boron nitride powders and 1 x 10^{-2} M of cetyltrimethylammonium chloride were added to the volumetric mixed solution of 1:1 water and ethanol, and then dispersed with the vigorous stirring. The 0.1 M of aminopropyltriethoxy silane was added to react with amino group on the surface of boron nitride and give rise to hydrolysis with triethoxy group on the aqueous media. After this reaction, $TiCl_4$ was added slowly with vigorous stirring. The amount of added $TiCl_4$ was 7 w% of boron nitride. Subsequently, let this hydrolysis reaction undergo sufficiently for 2 h at T=80℃. After cooling at room temperature, particles were taken by centrifugation and ethanol washing. Finally, drying at T=110℃ and heat treatment were carried out for 2 h at T=800℃.

2.3. Characterization Methods

The optical absorbance of prepared TiO_2 and TiO_2-coated boron nitride particles were characterized by ultraviolet-visible spectroscopy(UV-VIS, PERKIN ELMER LAMBDA3B) and the morphology and particle size were examined by scanning electron microscopy(SEM, JEOL6400) and transmission electron microscopy(TEM, JEOL JEM3010). The TiO_2 on the surface of boron nitride particles was identified by X-ray diffractomer(XRD, RIGAKU RU200) and the thermal characteristics were investigated by thermogravimetric/differential thermal analyzer(TG/DTA, SEICO SSC5200).

3. Results and Discussion

3.1. TiO_2 Nano Colloids

The TEM images in Fig. 1 show the TiO_2 nano colloids stabilized with acrylamide polymer and aminoprophyltriethoxysilane respectively. In the case of acrylamide treatment, well-dispersed TiO_2 colloids were taken and their particle size ranges 2 to 4 nm. On the other hand, TiO_2 colloids with aminoprophyltriethoxysilane revealed aggregation and the size of agglomeration was around 20 nm.

Fig. 2(a) shows the U.V-visible absorption spectra of TiO_2 nano colloids stabilized with acrylamide and dispersed in the water/alcohol solution as variation of TiO_2 concentration. The TiO_2 nano-colloids solution stabilized with acrylamide shows yellow color because of polymerization of acrylamide monomer and then shows absorption at 420nm wavelength. The absorption and the corresponding bandgap energy of TiO_2 are 380 nm and 3.2 eV for anatase [27] and 390 nm and 3.0 eV for rutile[28]. In this work, the 1:1 diluted sample shows the weak absorption at 420 nm for the acrylamide polymer. The high concentrated colloidal solution has the absorption peak at relatively longer wavelength because of the scattering effect. On the other hand, we can see that the strong and blue shifted absorptions at the less than 360 nm are observed in another more diluted samples and even a 500 times diluted sample shows the strong absorption by quantum size effect. This result indicates that very high concentrated and effective TiO_2 nano colloids are prepared. We confirmed that the TiO_2 contents taken from acrylamide and aminoprophyltriethoxy silane treatment were 20 w%.

The TiO_2 nano colloids stabilized with acrylamide were considered on the process of dispersion in nonpolar organic solvent on the other hand, the aminopropyltriethoxysilane treatment is used for the purpose of measuring the UV-visible absorption in polar solvent and their spectra are indicated in Fig.

2(b).

3.2 ***TiO_2 Coating on BN Powders***

Fig. 3 shows the scanning electron micrograph of boron nitride powders coated with 7 w% of TiO_2 nanocolloids. The TiO_2 nanocolloids are well coated on the lamellar shape of boron nitride powders and this is confirmed by X-ray diffraction identification and UV-absorption properties. The X-ray diffraction pattern as shown in Fig. 4 indicates the formation of TiO_2 crystal on surface of boron nitride after heat treatment for 2 h at

T=800℃. And also, Fig. 5 shows the UV-visible absorption spectra of boron nitride powders. The boron nitride powders coated with TiO_2 exhibits strong absorption of ultra violet but the boron itride itself does not absorb the ultra violet

Fig. 6 shows the TG-DTA curves of boron nitride powders coated with 7 w% of TiO_2 nanocolloids. The DTA peak indicates the endothermic reaction continued to around 1000 ℃ and then, converted to exothermic and the TG peak persist very stable state to around 1000 ℃ and then, shows the sharp rise due to the oxidation. From this result, we can presume that prepared boron nitride powders which are coated with the TiO_2 nanocolloids maintain the thermal stability up to the around 1000 ℃

4. Conclusions

The high concentrated(20 w%) TiO_2 nano colloids are synthesized by sol-gel method. The prepared colloids showed the well dispersion in TEM micrographs and the diluted colloids indicated the strong absorption peaks at less than 360 nm in uv-visible spectra. And also, the technique of coating on boron nitride powders with TiO_2 nano colloids was established. The prepared boron nitride powders showed the thermal stability up to the around 1000 ℃ and the characteristics of TiO_2 in X-ray diffraction and uv-visible spectra according to the formation of TiO_2 crystals on the surface of boron nitride powders.

5. References

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Figure 1. Transmission electron micrographs of TiO_2 colloids stabilized with acrylamide polymers(a) and amino-rophyl-triethoxysilane(b).

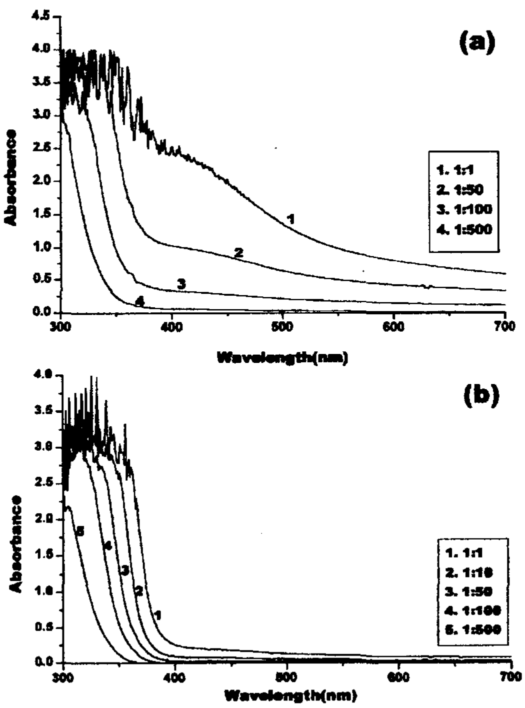

Figure 2. UV-visible absorption spectra of TiO_2 nano-colloids disperced in the aqueous/alcohol solution as variation of concentration of TiO_2. The TiO_2 solution is synthesized by the method of stabilization with acrylamide(a) and aminopropyl triethoxysilane(b).

Figure 3. SEM micrograph of the BN powders coated with 7 w% of TiO_2

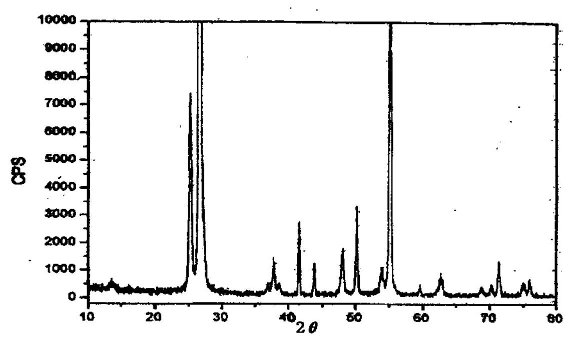

Figure 4. XRD pattern of the BN powders coated with 7 w% of TiO_2.

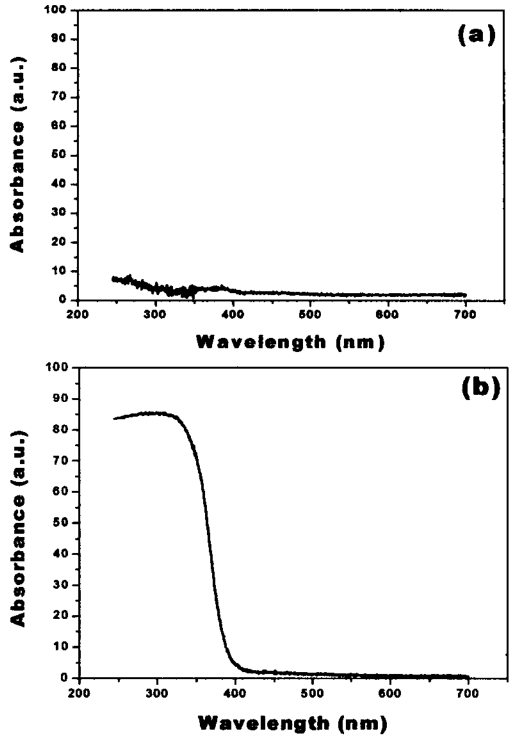

Figure 5. UV-visible absorption spectra of BN powders.

(a) Non-coated, (b) coated with 7 w% of TiO_2.

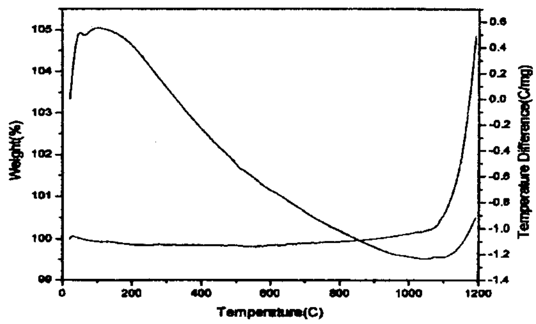

Figure 6. TG-DTA curves of the BN powders coated with 7 w% of TiO_2