

SYNTHESIS AND CHARACTERIZATION OF Si OXIDE COATED NANO CERIA BY HYDROLYSIS, AND HYDROTHERMAL TREATMENT AT LOW TEMPERATURE

The purpose of this work was to the application of Si oxide coatings. This study deals with the preparation of ceria(CeO_2) nanoparticles coating with SiO_2 by water glass and hydrolysis reaction. First, the low temperature hydro-reactions were carried out at 30–100°C. Second, Silicon oxide-coated Nano compounds were obtained by the catalyzing synthesis. CeO_2 Nano-powders have been successfully synthesized by means of the hydrothermal method, in a low temperature range of 100–200°C. In order to investigate the structure and morphology of the Nano-powders, scanning electron microscopy(SEM) and X-ray diffraction(XRD) were employed. The XRD results revealed the amorphous nature of silica nanoparticles. To analyze the quantity and properties of the compounds coated with Si oxide, transmission electron microscopy(TEM) in conjunction with electron dispersive spectroscopy was used. Finally, it is suggested that the simple growth process is more favorable mechanism than the solution/aggregation process.

Keywords: Nano-particle, Water glass, Hydro-reaction, Coating method

1. Introduction

Recent nanotechnology and nano-structures have been intensively developed in combination with techniques for the development of synthetic method having a size ranging from several nanometers to a few hundred nanometers, using various types of nanostructure manufacturing processes and applications, such as nanorods and photonic crystal [1-4,16]. In recent years, nano-structures have attracted much attention due to their potential applications in fabricating nanometer-scale devices possessing a variety of interesting functions [5,6]. Among the methods used to coat the nano-structures to protect against wear and to provide corrosion resistance, a number of researchers have used Si oxide to provide functionality to nano-powders for surface treatment [7,8]. Coatings of various types of materials for nanoparticles such as nano-scale structures, nano-rods, and nano-belts and nano-plates have been used [9,10]. These functional surface treatments have gradually extended the range of applications for the purpose of improving the corrosion resistance of nano-compounds, to change the surface appearance, improve the wear resistance, and improve the lubricity of nano-materials, changing a variety of functional properties of the materials. In addition, the sol-gel method, a synthetic method for forming the coating of the film, has often been used. Si oxide can serve as a chemically protective film on the surface in order to improve the chemical durability of the nano-compound and is coated onto the nano-compound using water-glass hydrolysis. Since Si

is an oxide, we significantly modified the surface of the SiO_2 film material which was employed in this study [11,12]. Ceria (CeO_2) has been widely used as a solid ion conductor and as a catalyst carrier, as it is a heat resistant material with a high melting temperature of 2477°C. In particular, ceria has a high chemical resistance in acids and bases and can thus be used in acidic and basic binders/suspensions. Many studies have been carried out on nano-powders to increase their oxidation potential in a state of grain growth and to prevent surface area increase due to further oxidation of the powder surface as well as to improve their chemical durability and control their grain growth.

In this study, the hydrothermal synthesis method is used for the coating of the Si oxide CeO_2 , as it is a simple method with a low cost implementation. Hydrothermal synthesis is then used rapidly and easily for the solvent. Creating the nanostructure in this way was suitable for application in the study. The features of this approach are effective application, and improved degree of coating adhesion of the Si oxide, providing solubility in the solvent by increasing the temperature. The system is pressurized as close to the critical point as possible for most of the material.

2. Experimental

The pH of the water glass ($\text{Na}_2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$) at room temperature was pH = 12~12.5 after placing 0.1 N in the water glass to coat the Si oxide at 80°C. The pH = 10~12 was achieved by

* R&BD CENTER, KTD C&S CO., LTD., INCHEON 21687, REPUBLIC OF KOREA

** DIVISION OF MATERIALS SCIENCE AND ENGINEERING, HANYANG UNIVERSITY, SEOUL 04763, REPUBLIC OF KOREA

Corresponding author: mhkong64@gmail.com

mixing the colloidal solution on ceria (CeO_2) for 10–20 min at 100–200°C using a magnetic stirrer. By hydrolyzing, the water-glass was subjected to hydrothermal synthesis by utilizing the equipment shown in Fig. 1. Also, the mixed aqueous solution was later used as a coating by filtering the solution using filter paper, washing several times, and then drying for 12 hours in a drying oven to provide a Si oxide coating of ceria in a dried rigid state. The solution was then ball milled to become a powdery nano-ceria composite powder. The Si oxide coating process is presented as a schematic diagram in Fig. 2 [13]. In addition, the coated powder was subjected to heat treatment for 30 min at atmospheric pressure to 500°C, to determine the denseness of the surface of the film type and the precipitated microstructures.

Scanning Electron Microscopy (SEM, Hitachi S – 4200) was performed to observe the shape, size, etc. of the coated film on the Si Ceria. The TEM specimens were ultrasonically cleaned by immersing in an acetone solution. X-ray Diffraction Analysis (DMAX 2500 with Cu – $K\alpha$ radiation) was carried out in order to determine the precipitated structure and components of the specimen.

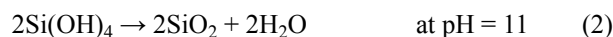
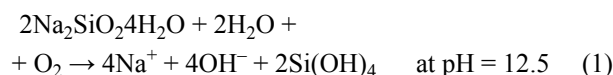
3. Results and discussion

The SEM-EDS analysis results for observing the nanostructure coating and the type of coating of SiO_2 on Ceria show that the Si and the oxide are present on the surface, as shown in Fig. 3.



Fig. 1. Equipment used for hydrolysis and hydrothermal processes

The following formula was used to theoretically verify this.



When a $\text{Na}_2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ was added to the first water-glass solution in the hydrolysis zone outside the neutral area, the alkaline pH = 12.5 is maintained. A $2\text{Si}(\text{OH})_4$ is used as a hydrolysis zone

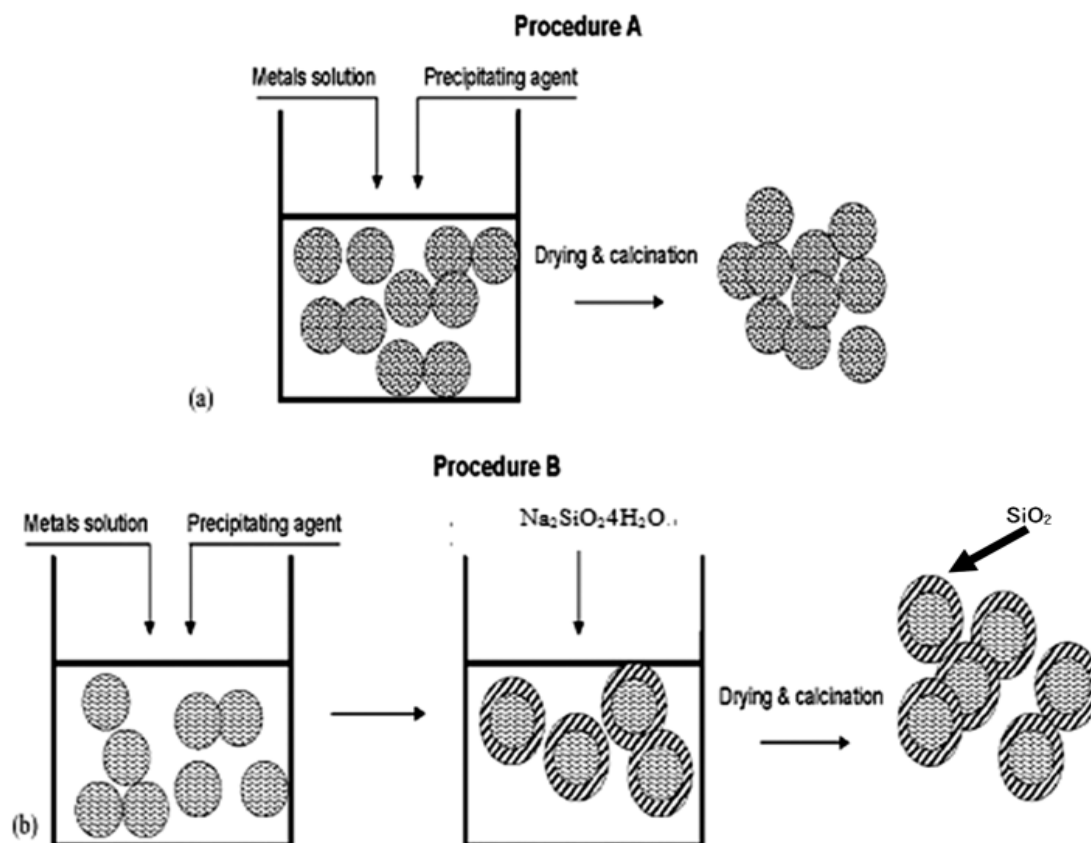


Fig. 2. Schematic illustration of synthesis of Ceria coated with SiO_2 . (a) the simultaneous co-precipitation, and (b) the sequential precipitation of SiO_2 coating process

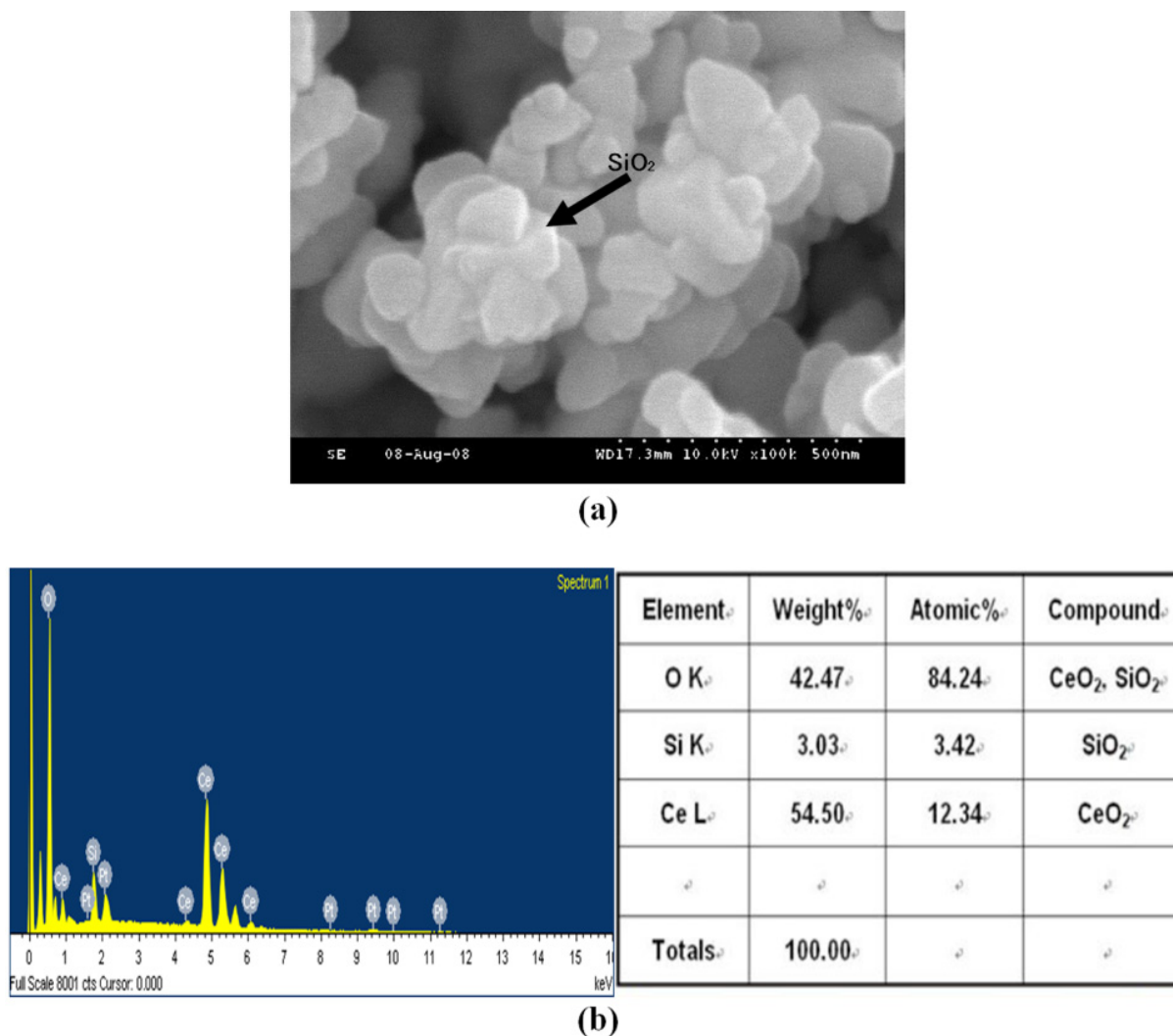


Fig. 3. (a) SEM image and (b) EDS results of SiO₂-coated ceria

and separated to the polymerize coating in the form of a range which is held by pH = 11. And then, oxides of Si single molecules then cover the surface of the nano-compounds [14,15].

In Figure 4, the surface state is shown before and after covering with the Si oxide coating. A change in the size and composition of the SiO₂ was observed due to heat treatment at

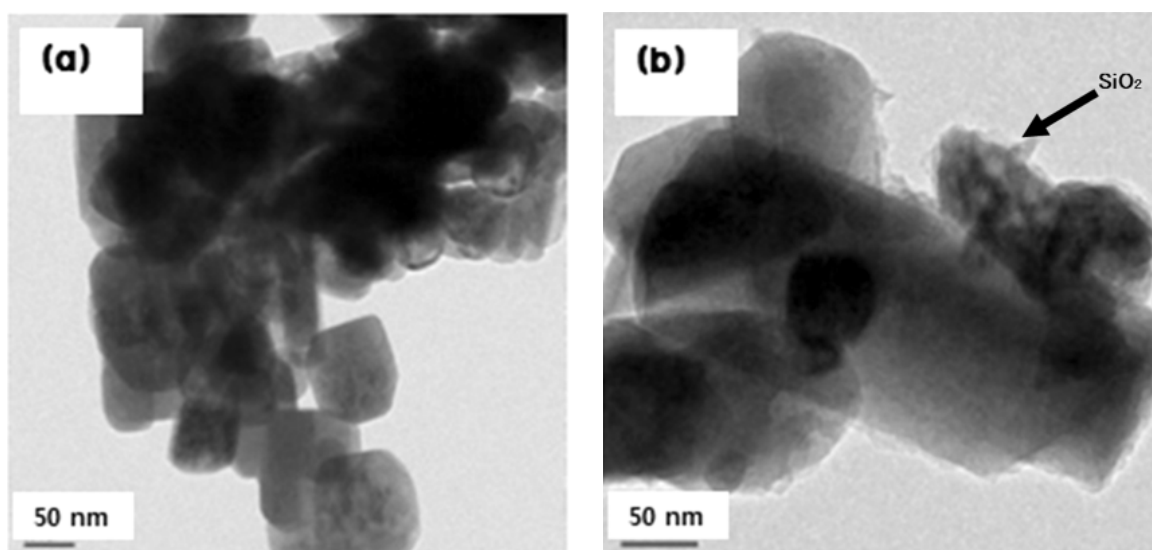


Fig. 4. TEM images of (a) uncoated and (b) SiO₂-coated ceria

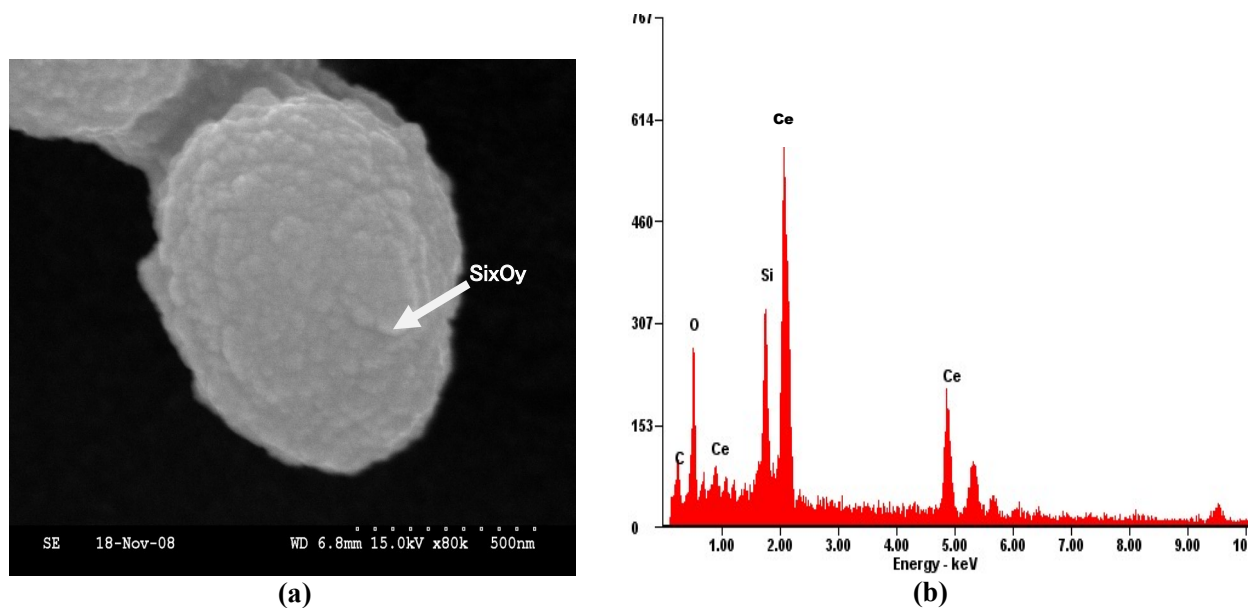


Fig. 5. (a) SEM images and (b) EDS results of SiO_2 coated ceria annealed at 500°C

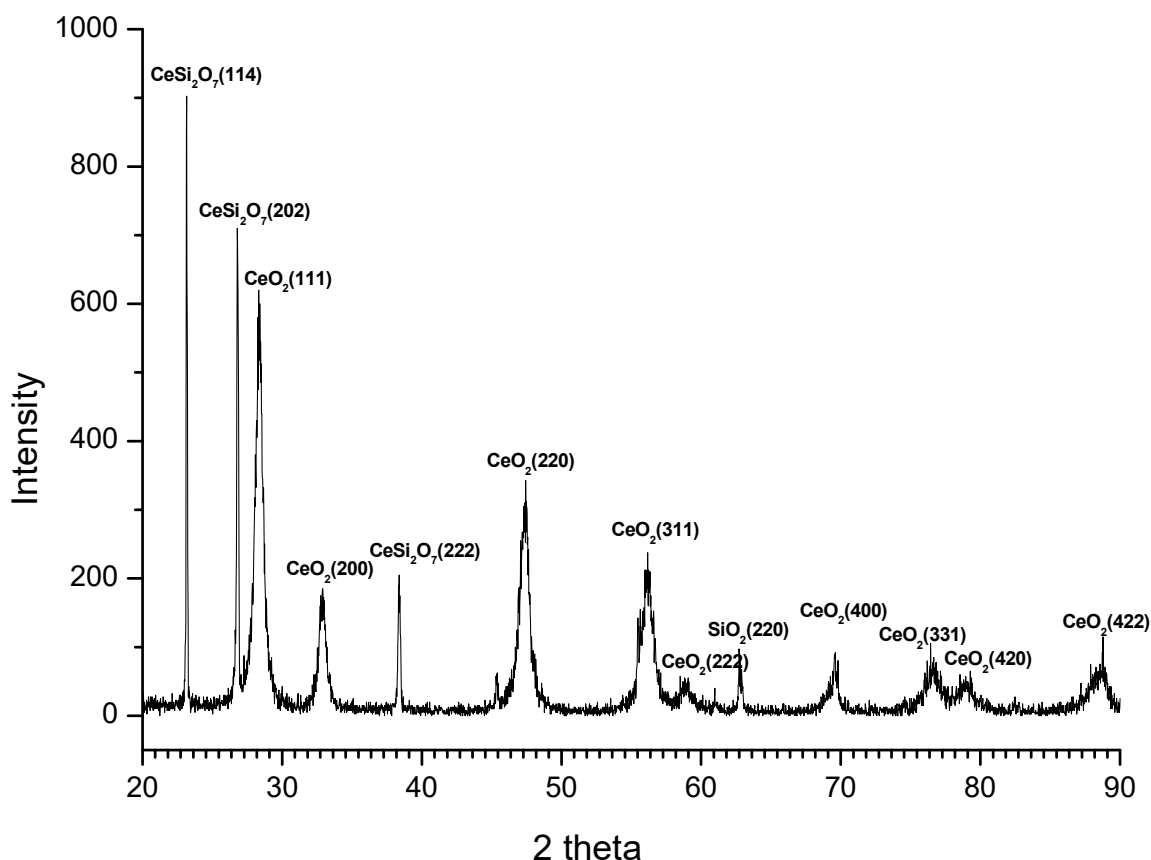


Fig. 6. XRD pattern of CeO_2 nano particles coated with SiO_2 and annealed at 500°C

a high temperature for the coated Ceria. In the observation results shown in Fig. 5, the SEM images show that after heat treatment at 500°C for 30 min, the grain growth and the level of 500 nm were maintained even without the glass film covering the surface. The state of the particle after heat treatment at 500°C for 30 min showed a rapidly increased size with the existing thickness of 500 nm. The result shows that the protective function of the Si

oxide was weak in accordance with the temperature increase. That is, the XRD analysis results shown in Fig. 6 demonstrate that the components of the composite qualitatively CeSi_2O_7 at 500°C . It can be seen that the CeSi_2O_7 composite coating film is formed after heat treatment for 30 min. This demonstrates that as a new compound, CeSi_2O_7 is generated by heat treatment showing that the SiO_2 reacts with the outer surface of CeO_2 nano-powders.

4. Conclusions

In this study, it was confirmed that a water glass solution of Ceria nano-powder formed by hydrolysis and hydrothermal synthesis was impregnated in an aqueous solution to form a film thickness of the SiO₂ coating of 5~50 nm. CeO₂-SiO₂ nano-powder was shown to be an effective composite coating film that can be formed at high temperature through heat treatment at 500°C. Finally, it is suggested that the simple growth process is a more favorable mechanism than the solution/aggregation process. And then, I have achieved the protection of chemical corrosion against to strong acid or strong bases by the nano-ceria coated with Si oxide. As well, I have acquired anti-abrasive properties by CeSi₂O₇ composite layers.

REFERENCES

- [1] Y. Zhang, K. Suenage, C. Colliex, S. Iijima, *Science* **281**, 973 (1998).
- [2] R. Zhang, Y. Lifshitz, S. Lee, *Adv. Mater.* **15**, 635 (2003).
- [3] Y. Li, Y. Bando, D. Golberg, Y. Uemura, *Appl. Phys. Lett.* **83**, 3999 (2003).
- [4] Y. Yin, Y. Lu, Y. Sun, Y. Xia, *Nano Lett.* **2**, 427 (2002).
- [5] Y. Wang, Z. Tang, X. Liang, N. Liz-Marzan Kotov, *Nano Lett.* **4**, 225 (2004).
- [6] M. Ahmad, T. Khan, G. Ali, J. Akhter, *Rev. Adv. Mater. Sci.* **51**, 427 (2006).
- [7] H. Gleiter, *Prog. Mater. Sci.* **33**, 223 (1989).
- [8] Y. Lu, *Mat. Sci. Eng. R.* **16**, 161 (1996).
- [9] M. Meyers, A. Mishra and D. Benson, *Prog. Mater. Sci.* **26**, 43 (2010).
- [10] R. Ormerod, *Chem. Soc. Rev.* **32**, 17 (2003).
- [11] A. Hetznecker, H. Kohler, U. Schonauer, U. Guth, *Sensor and Actuators B: Chemical* **99**, 373 (2004).
- [12] E.C. Ziemath, B.Z. Saggioro, J.S. Fossa, *J. of Non-Crystalline Solids* **351**, 3870 (2005).
- [13] X. Li, Z. Cao, Z. Zhang, H. Dang, *Applied Surface Science* **252**, 7856 (2006).
- [14] Z. Guo, F. Du, G. Li, Z. Cui, *Inorganic Chemistry* **45**, 4167 (2006).
- [15] Q. Fang, X. Liang, *R.S.C Adv.* **2**, 5370 (2012).
- [16] Y. Liu, G. Zhao, D. Wang, Y. Li, *National Science Review* **2**, 150 (2015).