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# Control of Chemical Reaction of Aluminium Nanoparticles by Silicon Polymer Coating

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#### Abstract

By using silicon polymer, the chemical reaction of Aluminium nanoparticles was controlled, especially, the corrosion reaction was reduced. The coverage of the silicon polymer film on Al nanoparticles was controlled, which changed the chemical reaction rate quantitatively. TEM (Transmission Electron Microscope) analysis indicated that the polymer film of 10 nm thick fully covered Al nanoparticle in the case of 5 mass% polymer coated Al particles in the synthesis. On the other hand, 0.4-1.0 mass% polymer coated Al was partially covered by a film. The AFM-KFM (Atomic Force Microscope-Kelvin prove Force Microscope) demonstrated that the conductivity of the Al nanoparticle was isolated by the polymer. Both the corrosion and H<sub>2</sub> evolution reaction rates were quantitatively reduced by the mass% of polymer coating on the surface of Al particle. This fact suggested that the electrochemical reaction was suppressed by the polymer coating. It was found that the chemical reaction rate of Al nanoparticles could be quantitatively controlled by the coverage of the silicon coating.

Keywords: Polymer; Nanoparticle; Chemical reaction; Aluminium

## Introduction

The nano materials are characterized as a small particle or a tube having at least one side with a length in the nano meter range. Thus, the surface area of nano materials is increased remarkably, enabling them to have dramatically increased surface reaction rates. The size effect of nano materials to increase the reaction rate has been investigated in the fields of catalysis [1-5], sensors [6-8] and batteries [9,10].

As the reaction rate is increased by making the particle nano-sized, then, the deterioration of nano metal should be caused by the corrosion under the atmosphere at high humidity. Moreover, in the case of coastal area, the air bone salt particles are coming from the sea, which make the sever corrosion condition. On the other hand, the film thickness of coating should be very thin because each nanoparticle needs to be coated separately without bonding each other in the synthesis. Thus the coating technique should be very high level. Although it is necessary to prevent the corrosion of metal nano particles, there are few papers on this problem. Several papers show the effect of nanoparticles on the corrosion of the matrix of metals, coatings and composites. However, there very few paper which investigates the corrosion of nanoparticle itself.

In this paper, the control the chemical reaction of Al nanoparticles was tried by using a silicon polymer coating. The chemical reaction of these nano Al was changed by control the coverage of the polymer coating quantitatively. The polymer film on Al was observed by using TEM and AFM in detail. Besides, the corrosion reaction was examined for coated nano Al by the wet and dry test using a NaCl solution. Moreover,  $H_2$  evolution reaction rates were quantitatively examined by changing the mass% of polymer coating. Then, the relationship between the mass% of polymer coating and the reaction rate of the nano metal was discussed. Finally, the chemical reaction reducing mechanism was discussed by changing the coverage of the polymer on nano Al quantitatively.

#### Experimental

## Materials and synthesis

The Al nanoparticles were made by using the atomizing method. Al was melted and dropped through the tandewish, then, atomized in high-pressure water. The size of Al particles were around 300-600 nano meters (nm) in diameter. In order to improve the surface activity, Al surface oxide was completely removed in an acidic solution. Moreover, this process was recognized very important in conducting the synthesis of the polymer only on the metal nanoparticles.

Figure 1 indicates the chemical reaction for the synthesis of silicon polymer on the Al nanoparticle. The silicon polymer was dissolved in an ethanol solution with the Al nanoparticles. After the ethanol was completely evaporated in the vacuum, the silicon polymer was hardened. Thus, the polymer was completely consumed to make the thin film on the nanoparticles. The mass% ratios of the polymer to Al particle in the synthesis were 0, 0.4, 1.0, 3.0, and 5.0%, where the coverage of polymer film on the surface of the nanoparticle was changed quantitatively.

#### Surface analysis for coated Al nanoparticles

To investigate the chemical state of the polymer film in detail, Electron Energy Loss Spectroscopy (EELS) spectra were observed by TEM with the accelerated voltage of 200 kV. Three windows method was used to detect the each peak in this study. Moreover, to investigate the electrochemical reaction, the nano level measurement on the sample was applied by AFM and KFM. Firstly, the ultra-sonication was conducted at 23 kHz for 20 min. in 99.5% ethanol at 30°C where nanoparticles were separated each other. Then, particles were set on a polished Pt plate, then, AFM and KFM measurements were conducted. The surface morphology (AFM) and potential distribution (KFM) measurements were conducted simultaneously by tapping mode using gold coated cantilevers with a spring constant of 2.1 N/m.

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Received June 06, 2017; Accepted June 13, 2017; Published June 14, 2017

Citation: Nishimura T (2017) Control of Chemical Reaction of Aluminium Nanoparticles by Silicon Polymer Coating. J Adv Chem Eng 7: 173. doi: 10.4172/2090-4568.1000173

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Figure 1: Schematic diagram of the chemical reaction for synthesis of the silicon polymer coated on Al nanoparticles.

## **Chemical reaction tests**

In order to estimate the corrosion rate of the polymer coated Al nanoparticles, wet and dry corrosion tests were applied in a 0.5 mass% NaCl solution for 14 days (cycles). Only for the first cycle of testing, a 0.5 mass% NaCl solution was dropped on the Al nanoparticles over the platinum (Pt) plate in a chamber kept at 40% relative humidity (RH) and 25°C. Under this condition, the sample was kept and dried for several hours. From the 2nd cycle of the test, pure water was poured on the samples under the same conditions in every 24 hrs. As the NaCl remains on the Pt plate, corrosive conditions have maintained after the 2<sup>nd</sup> cycle of the test. After the corrosion test, the corrosion behaviour of the nanoparticles was observed by SEM. Especially, it was investigated that the corrosion rate was suppressed in proportion to the mass% of the polymer coating.

In the same way, the effect of coating mass% on the volume of the hydrogen  $(H_2)$  evolution reaction on Al nanoparticles was examined. The volume of  $H_2$  evolution reaction for 70 mg of Al nanoparticles was measured in a 0.5M NaOH solution. The evolving  $H_2$  gas was taken into the glass filled with the solution, and the volume was measured by the mess cylinder. Finally, the effect of the mass % of polymer coating on the chemical reaction for the nano Al was discussed in Figure 1.

#### **Results and Discussion**

#### Characterization of coated Al nanoparticles

SEM images of (1) 0.4 mass% and (2) 5 mass% polymer coated Al nanoparticles are shown in Figure 2. Here, 5 mass% means that the weight ratio of polymer is 5 mass% against that of Al particle. The particle diameter is indicated 300-500 nm in the figure. The particle of 0.4 mass% coated Al is partially covered by the silicon polymer. On the other hand, in the case of 5 mass% coated Al; the particle is covered fully by the polymer.

The actual mass% of polymer to Al nanoparticles was measured by the thermo-gravimetric (TG) analysis under an  $N_2$  atmosphere (Figure 3). When the temperature was above 200 degree C, the weight of the nanoparticle decreased due to the epoxy decomposition by melting or evaporation. The weight loss of the 0.4, 1, 3, and 5 mass% coated Al nanoparticle was 0.5, 0.8, 1.8, and 3.2 mass%, respectively, as measured by TG. The weight loss in TG is shown almost the same as the mass% in the synthesis. Thus, the synthesized polymer is kept on the surface

of Al nanoparticle. The mass% of actual polymer coating to Al can be controlled by using the mass% of polymer in the synthesis (Figures 2 and 3).

The TEM images are shown in Figure 4 to investigate the coating film of the epoxy polymer in detail. The 10 nm thick polymer coats uniformly the entire surface of 5 mass% coated Al nanoparticles. Thus, it is thought that the amount of 5 mass% polymers is enough to cover all surface of Al nanoparticle Figure 4.

The chemical elements in the polymer of 5 mass% coated Al was estimated by the EDS (Electron Dispersive Spectroscopy) spectrum in Figure 5. The elements of Al, Si, O and C were detected with the Cu from the mesh. In order to estimate the chemical state of Al, Si, C, O, the EELS spectra were obtained for the polymer film of 5 mass% coated Al in Figure 6. In the case of Al-L spectrum, a sharp peak is shown at 80 eV, which is similar to that of Al<sub>2</sub>O<sub>3</sub>. On the other hand, Al-L spectrum has a shoulder around 75 eV, moreover, Al-K spectrum has a little broad style. Thus, the state of Al is not exactly Al<sub>2</sub>O<sub>3</sub>, but the oxidized state. In the case of Si-L spectrum, a sharp peak is indicated at 110 eV, besides, a sharp peak is shown at 1870 eV in Si-K, which is similar to that of SiO<sub>2</sub>. Besides, a strong peak is indicated at 540 eV in O-K spectrum, and a broad peak at 565 eV, which shows that the polymer is the oxidized state. The state of Si is thought an oxidized one similar to SiO<sub>2</sub>. This result corresponds to the reaction of synthesis of the silicon polymer in Figure 1. A strong peak is shown at 284 eV in C-K EELS spectrum, which is thought to reflect  $(1s \rightarrow \pi^*)$  transition. Besides, a broad peak is observed at 290-300 eV, which is thought to reflect (1s  $\rightarrow 6^*$ ) transition. Figure 7 indicates EELS mappings of elements for 5 mass% coated Al, where (a) Al-L, (b) C-K, (c) Si-L and (d) O-K. The polymer film on Al particle has the high concentration of O. However, the concentration of Al is very low on the particle due to the high thickness of Al particle. On the other hand, the concentration of Si is high on the particle, which is caused from the thin polymer film. Thus, the high concentration of O-K in the film is thought to reflect the chemical bond of silicon polymer. Thus, the chemical state of the silicon polymer film was shown by the EELS measurement.

#### Effect of coating film on the chemical reaction

Figure 8 indicates AFM and KFM (potential distribution) results conducted by the tapping mode. The 0 mass% (uncoated) Al particle represents a half globe in KFM image, which is almost the same as the AFM one. The 1.0 and 3 mass% coated Al particle display broken shapes in KFM images, which is different from half globe shapes in AFM. Therefore, in the case of 1.0 and 3 mass% coated Al; the potential around the Al particles is partially isolated from the Pt plate by the polymer coating. Thus the coverage of the polymer suppresses the electrochemical reaction. In other word, the corrosion reaction of metal particle can be suppressed by the coverage of the polymer film (Figure 8).

The effect of coating mass% on the volume of the hydrogen ( $H_2$ ) evolution reaction on Al nanoparticles is shown in Figure 9. The evolution volume (V  $H_2$ ) of  $H_2$  for Al of 70 mg nanoparticles was evaluated in a 0.5M NaOH solution. From the Figure, the V  $H_2$  for each sample increases according to the test time. After 300 s, the 0, 0.4, 1.0, 3.0 and 5 mass% coated Al has V  $H_2$  of 14, 9, 4.5 and 0.2 and 0 mL, respectively. Thus, V  $H_2$  is less as the coating mass% increases. Therefore, the  $H_2$  evolution reaction was suppressed in proportion to the mass% of polymer coating (Figure 9). In order to estimate the effect of coating film on the chemical reaction, a wet and dry corrosion test with a NaCl solution was performed. The Al nanoparticles was put into a 0.5 mass% NaCl solution on Pt plate in a chamber at 40% Relative

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# Citation: Nishimura T (2017) Control of Chemical Reaction of Aluminium Nanoparticles by Silicon Polymer Coating. J Adv Chem Eng 7: 173. doi: 10.4172/2090-4568.1000173



Figure 2: SEM image of (1) 0.4 mass% and (2) 5 mass% polymer coated Al nanoparticles.



Figure 3: Thermo Gravimetric (TG) analysis for the silicon coated Al nanoparticles.









Figure 6: EELS spectra of (a) Al-L, Si-L, (b) Al-K, Si-K, (c) C-K and (d) O-K for 5 mass% polymer films on coated Al



Figure 7: EELS mapping for 5 mass% polymer films on coated Al. (a) Al-L, (b) C-K, (c) Si-L and O-K.



Figure 8: AFM and KFM images for (1) 0%, (2) 3% and (3) 5% silicon coated AI nanoparticles.



Humidity (RH) and 25°C. SEM images of the Al nanoparticles after the corrosion test at each day are indicated in Figure 10. The shape of the 3 mass% polymer coated sample keeps the initial one after 14 days, showing that it is not subjected to the corrosion. This corrosion prevention is caused by the coverage of polymer which isolates Al particles from the Pt plate. On the other hand, the shape of 0 mass% (uncoated) samples is partially changed at 7 days, and continues to be corroded, yielding to a slender-shape at 14 days. The corrosion is thought to start from the bare (no polymer) position of a metal and the electrochemical reaction keeps in that region. Finally the galvanic corrosion between Al particle and Pt plate is thought conducted for 14 days. Thus, the Al nanoparticle changes in the shape according to the polymer coating mass% after the corrosion test (Figure 10).

The effect of the coating mass% on the sizes of the Al nanoparticles after a wet and dry NaCl corrosion test was estimated in Figure 11. The size of the Al nanoparticles was normalized by the supposition that the initial diameter for particles was 100%. The initial sizes of diameters (D) were measured for 20 particles in SEM, where the volume (V1) was calculated as (4/3) (D/2)<sup>3</sup>. After the corrosion test, the long (L) and short (S) diameters were measured, where the volume (V2) was (4/3) (L/2)  $(S/2)^2$ .

The normalized size (SN) is identified as following:

 $\mathrm{SN}{=}(\mathrm{average\ size\ of\ V2\ for\ 20\ particles})/(\mathrm{average\ size\ of\ V1\ for\ 20\ particles})$ 

The normalized size (SN) of 0 mass% (uncoated) Al decreases remarkably with time in the corrosion test, showing that the corrosion rate is very high. However, the SN of the 3 mass% coated Al is hardly changed. Thus, the corrosion is thought prevented by the polymer film in the case of 3 mass% coated Al. After 14 days, the SN of the 0, 0.4, 1.0 and 3 mass% coated samples are 80, 85, 91, and 97%, respectively. Therefore, the SN after 14 days shows higher value as the coating mass% increases (Figure 11).

The effect of the polymer coating mass% on the reaction rate of Al nanoparticles in the corrosion and hydrogen  $(H_2)$  evolution test are summarized in Figure 12. The corrosion rate for each coated sample was calculated using the supposition that the amount of corrosion of 0 mass% Al at 14 days was 100%.

The rate (RC) of corrosion (C) for each coated sample at 14 days was calculated as:

RC (%)=(C of each mass% coated Al)  $\times$  100 / (C of 0 mass% Al)

In the same way, the rate of the  $H_2$  reaction was determined by the supposition that the volume of 0 mass% Al at 300 s was 100%. It is shown from the Figure that both rates are reduced as mass% of polymer coating increased. This fact indicates that electrochemical reactions on the Al particles under these conditions are suppressed by the polymer coating. Moreover, a quantitative relationship between the reaction rate and mass% of coating was established.

The reaction rate of Al nanoparticles was able to be quantitatively changed by the mass% of polymer coating. Besides, the mass% of actual polymer coating on a metal can be controlled by the mass% of polymer against that of Al in the synthesis. Therefore, the reaction rate can be controlled by the synthesis using the change of mass% of polymer. In this way, the synthesis is able established using only the mass% ratio of polymer to metal in the synthesis. Finally, it can be said that the chemical reaction of nano metals can be controlled by the silicon polymer coating (Figure 12).

#### Conclusions

The silicon polymer coating was conducted to control the chemical reaction of Al nanoparticle. The 5 mass% polymers coated Al particles in the synthesis were observed by TEM to be fully covered by a polymer film of 10 nm thick. The 0.4-1.0 mass% coated Al was partially covered by a film. The potential around the Al particles showed a lower value by polymer coating in AFM-KFM, indicating that the conductivity of the nano Al was isolated by the silicon polymer. As the mass% of polymer coating increased, the reaction rates for both the corrosion and H<sub>2</sub> evolution tests were reduced. Therefore, the chemical reaction on the Al particles was quantitatively suppressed by the polymer coating.



Figure 10: SEM images of (a) 5% and (b) 0% coated Al nanoparticles subjected to a wet and dry corrosion test for 0, 7 and 14 days.



120 100 📥 rate (H2) Reaction rate / % 80 ---corr 60 40 20 0 0 1 2 3 4 **Coating mass%** 

**Figure 12:** Effect of the polymer coating mass% on the reaction rate of Al nanoparticles in the corrosion and hydrogen ( $H_2$ ) evolution test.

Thus, the chemical reaction rate of a nano metal could be controlled by a polymer coating in the synthesis.

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