

Development of a dry process for coating metal nanoparticles on carbon nanotubes

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Abstract

Metal nanoparticles such as platinum (Pt) and gold (Au) decorated CNTs have been thoroughly investigated as electrode of fuel cells and chemical and biological sensors. In these applications, the size and the density of nanoparticles are very important, because the catalyst activation depends on the particle size and the deposition amount. We focused on a dry processing without solutions and attempted to fabricate metal nanoparticles on CNTs by sputtering. In this study, the effect of the crystallinity of CNTs surface on the morphology of Pt film deposited by sputtering process was investigated. To control the crystallinity of CNTs surface, the Ar plasma irradiation was applied to CNTs and the crystallinity of CNTs surface was analyzed by Raman spectroscopy. As results, the I_D/I_G ratio of CNTs surface increased with the Ar plasma irradiation time. This suggested that the crystallinity of CNTs was changed to amorphous carbon with increasing the plasma time. Furthermore, the morphology of Pt on as-received CNTs and plasma-treated CNTs was changed to island shape by annealing at 750 °C. As a result, the particle size on plasma-treated CNTs was smaller with increasing the plasma treatment time. This indicated that morphology of Pt on CNTs related to crystallinity of CNTs surface.

Key words :Carbon nanotubes, Surface modification, Plasma treatment, Nanoparticles, Catalyst

1. Introduction

Carbon nanotubes (CNTs) have become one of the most exciting and well investigated nano-scale materials. The unique properties of CNTs, such as their very large surface to volume ratio, electrical conductivity, heat resistance and chemical stability make them ideal materials for a variety of application. In particular, metal nanoparticles decorated CNTs have been thoroughly investigated as electrode of fuel cells and chemical and biological sensors (Naruse, et al., 2010, Rathod., et al., 2010). Metal nanoparticles such as Pt and Au are used as catalyst in fuel cells. Commonly, because the catalyst activation depends on the particles size and the sufficient surface area of the particles, it is very important to control the particles size and to disperse at high density the particles with the size small. Commonly, metal nanoparticles are deposited onto CNTs in solutions by chemical reduction from a precursor compound, which will be the problems in generation of by-product and effluent. Moreover, to disperse the metal nanoparticles with the size small, it is necessary to reduce the deposited amount because of enlarging the nanoparticle size in firing process. On the other hand, the works relevant to the fabrication of metal nanoparticles on CNTs by using a dry processing without solutions were reported. Zhang et al. showed morphologies of different metals on single wall CNTs by electron-beams deposition (Zhang., et al., 2010). Gingery et al. reported the formation of gold nanoparticles of different deposition rate on multi-walled CNTs by thermal evaporation (Gingery., et al., 2008). Although their works have successfully controlled the nanoparticle size by changing the deposition amount, the density of the particle has not been controlled. On the other hand, Muratore et al. reported the gold particle sputtered under different process parameters (especially metal ion flux and kinetic energy) and the effect of the crystallinity of CNTs surface on the particle size and density of metal nanoparticles on CNTs was discussed (Muratore., et al., 2013). However, after controlling the crystallinity of CNTs surface, the effect of the CNTs surface on the morphology of metal nanoparticle was not discussed circumstantially. Though, as to the modification of CNTs surface, Ahn et al. (2003) and Kyung et al. (2008) reported the effect of the surface treatment techniques such as plasma treatment and Ar neutral beam treatment on the crystallinity of CNTs surface.

In this study, we investigate the effect of the crystallinity of CNTs on the morphology of Pt film deposited by sputtering process. To control the crystallinity of CNTs surface, Ar plasma irradiation was applied to CNTs surface as function of the irradiation time and the crystallinity was analyzed by Raman Spectroscopy. Afterward, Pt was deposited on the as-received CNTs and the plasma treated CNTs and the morphology of Pt film was observed by scanning electron microscopy (SEM). Also, to promote the surface diffusion of Pt atoms on CNTs, Pt deposited CNTs was annealed at 750 °C and the effect of heating treatment on the morphology of Pt film was investigated by SEM and transition electron microscopy (TEM).

2. Experiment

Vertically aligned CNTs (VACNTs) were synthesized by chemical vapor deposition using Iron (Fe) and Aluminum (Al) as a catalyst on the copper (20×20×0.1mm) (Figure 1a). Al layer was deposited on the copper substrate using Electron Cyclotron Resonance (ECR) type ion shower equipment followed by a Fe layer. To fabricate the suspension of CNTs, VACNTs/copper were sonicated and dispersed in 5 mL of ethanol. 100 μ L of the mixture was dropped and spin coated onto the copper substrate at 1000 rpm for 30 s (Figure 1b). This coating process was repeated ten times. Figure 1c shows the coated CNTs on copper after for ten times. After the coating process above, Ar plasma was irradiated to modify the CNTs. As for the Ar irradiation treatment, ECR ion shower equipment was again used. Table 1 summarized the conditions for Ar plasma irradiation was performed as a function of irradiation time 5, 15, 25 min. After plasma treatment, platinum (Pt) was deposited onto CNTs by ECR-type sputtering equipment under the condition as shown in Table 2. Deposition rate of Pt was about 4.0 nm / min. Pt was deposited onto all samples of CNTs for 75 s. The samples of Pt deposited CNTs were annealed at 750 °C for 75 s by vacuum heater. The morphology of the CNTs and Pt were characterized by SEM and TEM. Furthermore, the crystallinity of CNTs surface was analyzed by Raman spectroscopy.

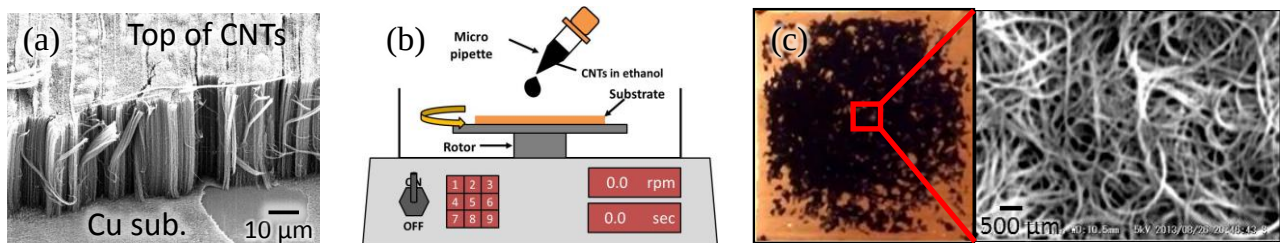


Fig.1 (a) Vertically aligned CNTs, (b) concept Diagram and (c) CNTs/copper substrate

Table 1 Ar plasma irradiation conditions

Acceleration Voltage [V]	750
Ion Current Density [mA/cm ²]	0.30
Vacuum [Pa]	3×10^{-3}
Irradiation Time [min]	5, 15, 25

Table 2 Pt sputtering conditions

Acceleration voltage [V]	1250
Ion current density [mA/cm ²]	0.80
Vacuum [Pa]	3×10^{-3}
Sputtering rate [nm/min]	4.0
Sputtering time [s]	75

3. Results and Discussion

Fig.2 shows a raman spectra of as-received CNTs. We used the characteristic peak at ~1593 cm⁻¹ (G-band) and a peak at ~1368 cm⁻¹ (D-band). As is well known, G-band indicates high crystallinity of hexagonal lattice of graphite

structure and D-band gives an indication of defects in CNTs. Furthermore, the relative ratio of the area of the curves at D-band to G-band (I_D/I_G) can be considered as the level of the disorder degree in the graphite sheets (Gohel, et al. 2005). First, to examine the dispersion of the I_D/I_G ratio among the as-received CNTs, five samples were measured at five spots per one sample. Figure 3 shows the I_D/I_G ratio of as-received CNTs. The average of the I_D/I_G ratio in each sample is about 1.5, which shows the good reproducibility of the prepared CNTs samples.

Figure 4 shows the SEM images of the as-received CNTs and the CNTs treated by Ar plasma irradiation for 5, 15 and 25 min. It can be observed that the CNTs seem to be changed from smooth surface to rough surface with an increase of the Ar plasma irradiation time. To examine the state of CNTs surfaces, the CNTs treated by Ar plasma irradiation for 5, 15 and 25 min was measured by raman spectroscopy. Figure 5 shows the result of the I_D/I_G ratio for the each sample. As a result, the I_D/I_G ratio increased with increasing the plasma irradiation time. This suggests that the crystallinity of CNTs changed to amorphous with increasing the plasma irradiation time. This is in good agreement with the results of figure 4.

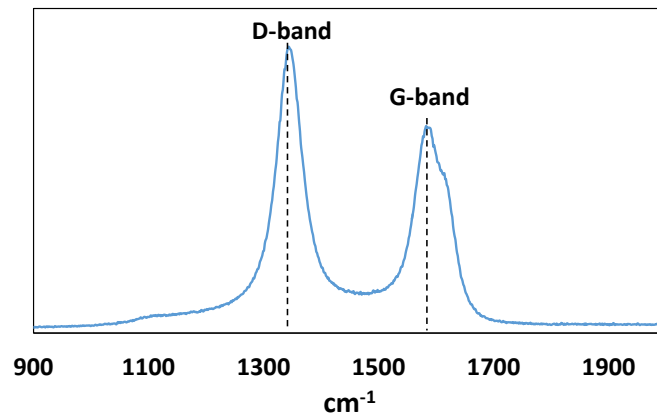


Fig.2 Raman spectra of as-received CNTs

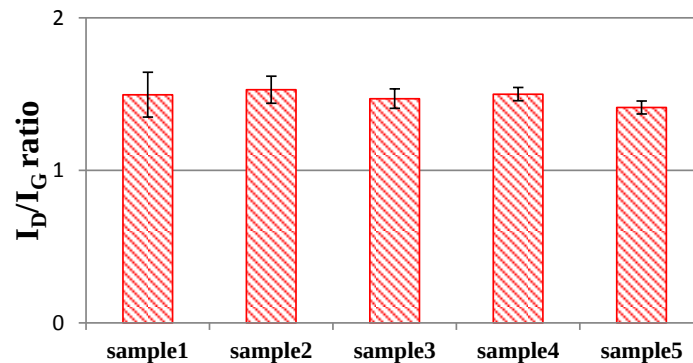


Fig. 3 I_D/I_G ratio of as-received CNTs

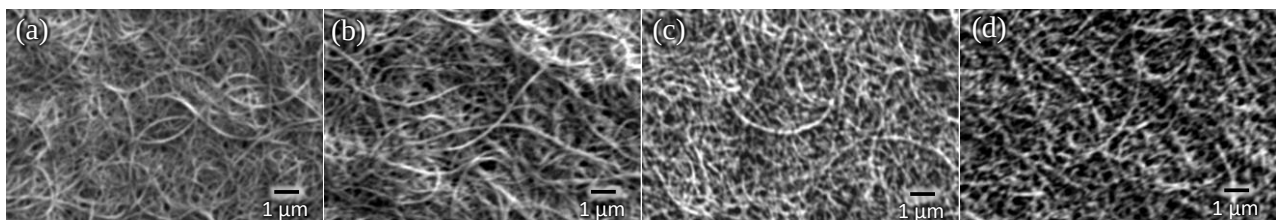


Fig.4 SEM image of the CNTs before and after Ar plasma irradiation : (a) as-received CNTs (b) CNTs irradiation for for 5min (c) CNTs irradiation for 15 min (d) CNTs irradiation for 25 min

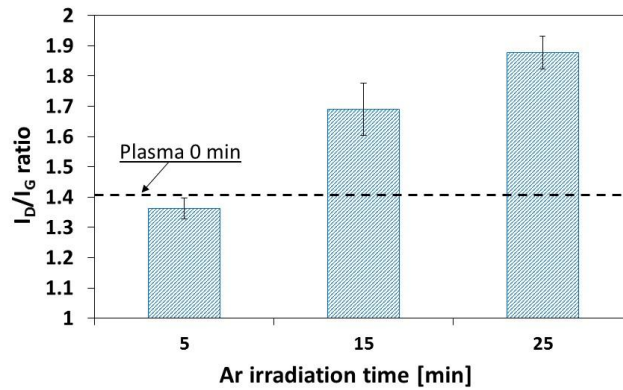
Fig.5 The I_D/I_G ratio of CNTs after Ar plasma irradiation

Figure 6a shows the SEM images of the CNTs on which Pt was deposited, while figure 6b shows the SEM images of the CNTs annealed at 750 °C. Here, when temperature against melting point is higher than 0.5, bulk diffusion of thin film arise. Because we deposit Pt on CNTs and cause bulk diffusion of Pt film, annealing temperature was 750 °C in this study. Since the explanation only by our experimental observation was not enough, I have add the reference by C. Muratore et. al. (2013). They also reported the formation of nanoparticle on CNTs by using annealing. Since we are sure that the Pt was deposited on the surface of CNTs before annealing, the highest possibility of the migration of Pt particles might be occurred according to the Muratore's report. To examine the morphology of Pt in detail, the morphology was observed by TEM. Figure 7 shows the TEM image of the annealed CNTs on which Pt was deposited. Figure 7a, 7b and 7c were the TEM images of the CNTs treated by plasma irradiation for 0, 5 and 25 min, respectively. The arrows labeled Pt in the figure indicate the Pt that was deposited on CNTs which could be observed like tube. As results, the morphology of Pt on as-received CNTs seems to be the continuous film and Pt film covered the CNTs surface. On the other hand, the morphology of Pt on plasma-treated CNTs seems to be island shape. Moreover, the particles size and the dispersion of the particles size are smaller with increasing the plasma treatment time. This seems to be because the surface energy of CNTs surface increased by decreasing the crystallinity (the I_D/I_G ratio as shown figure 5) and the morphology of CNTs changed by bombardment of Ar plasma ions. Generally, as-received CNTs surface that arise from the strong sp^2 bonding and near perfect network are non-reactive nature. Therefore, Pt atoms deposited on CNTs possess a high mobility as they only weakly interact, leading to agglutinate easily and grow up largely. On the other hand, because the crystallinity of CNTs decreased with increasing plasma treatment time, we consider that surface energy of CNTs increases. Also, the surface morphology of CNTs was changed with increasing plasma treatment time from TEM images (Fig.7). In sum, increase of surface energy and surface roughness migration on the CNTs of Pt atoms was restrained. Felten et al. (2007) also reported that the Au clusters evaporated on CNTs are preferentially located in regions covered by an amorphous layer. Therefore, the particles size and the dispersion of the particles size seem to be smaller with increasing the plasma treatment time, indicating that the crystallinity of CNTs surface and surface morphology of CNTs are very important factor to control the size and density of Pt nanoparticles.

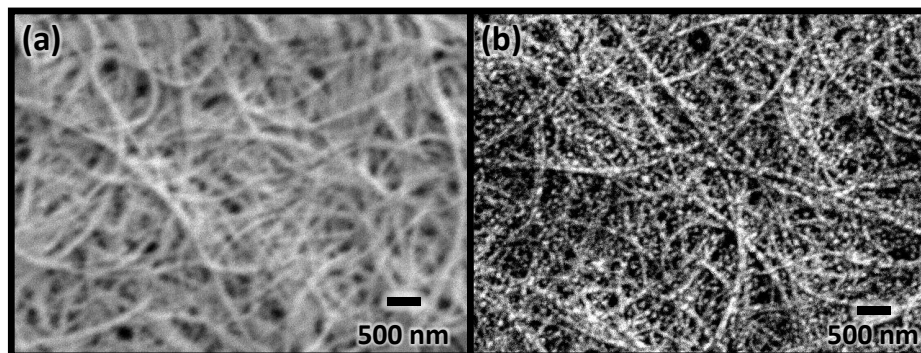


Fig.6 SEM image of the Pt deposited on CNTs treated by plasma for 5 min : (a) before annealing (b) after annealing

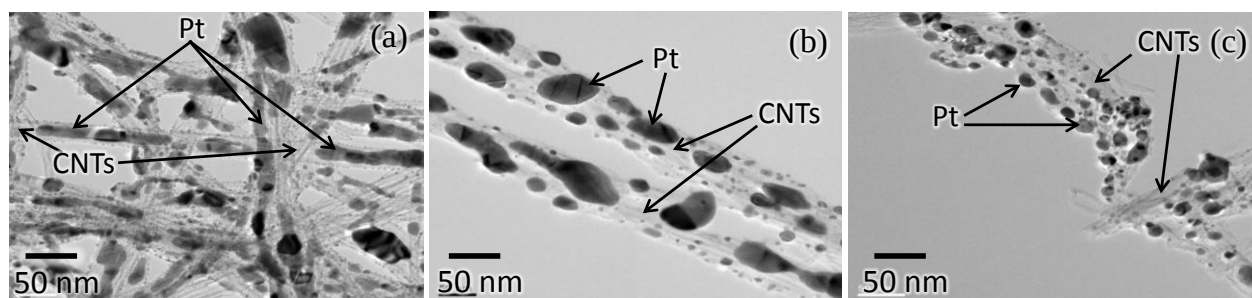


Fig.7 TEM Image of the CNTs after annealing at 750°C : (a) as-received CNTs (b) CNTs irradiated for 5 min (c) CNTs irradiated for 25 min

4. Conclusion

In this study, the effect of Ar plasma irradiation on the formation of Pt particles on CNTs was studied. The I_D/I_G ratio of CNTs surface increased with the Ar plasma irradiation time. The crystallinity of CNTs was changed from sp^2 bonding to amorphous carbon by plasma treatment. Moreover, the particles size and the dispersion of the particles size on CNTs were smaller with increasing the plasma treatment time. This indicated that the crystallinity on CNTs surface is very important factor to control the size and density of Pt nanoparticles. In the future, the effect of the deposited amount of Pt on the morphology of Pt nanoparticles will be investigated. Moreover, the catalyst activation of Pt nanoparticles fabricated by dry process will be examined by cyclic voltammetry.

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