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Control of Fe catalyst nanoparticle density for carbon nanotube growth using Langmuir-Blodgett deposition of mixtures of Fe nanoparticles and arachidic acid

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ABSTRACT

Vertically-aligned carbon nanotubes (VA-CNTs) have been attracting attention as the electrode material of polymer electrolyte fuel cell. Fe nanoparticles (FeNPs) were used as catalyst for VA-CNT growth. FeNP monolayer film was deposited on substrates by Langmuir-Blodgett (LB) technique. VA-CNTs were synthesized from FeNP LB films by thermal chemical vapor deposition (CVD) method. Number density of VA-CNTs was lowered because of thermal aggregation of FeNPs during thermal CVD. We mixed FeNPs with arachidic acids (C20) as filler molecules, and synthesized VA-CNTs from FeNPs-C20 LB films, therefore we could reduce thermal aggregation and control the number density of FeNPs.

1. Introduction

Recently, global warming has been an important worldwide problem [1]. Global warming has been induced by the increase of greenhouse gas emissions. As the countermeasures, developing clean energy that does not emit carbon dioxide has been an urgent matter. So far recyclable and clean energy, like solar light, wind and biomass have been attracted attention. Among them, fuel cells have been especially expected. Because it has been said that its theoretical electrical efficiency reaches 80% [2]. In addition, the exhaust is only water.

Polymer electrolyte fuel cell (PEFC) that has been expected as the fuel cell for cars has been focused on. High costs derived from Pt catalyst have been large problem [3]. So, there is a need for efficient utilization of a Pt catalyst. As the solution, it has been suggested that vertically-aligned carbon nanotubes (VA-CNTs) are suitable for carrier of Pt catalyst [4]. VA-CNTs satisfy the three conditions that required for carrier of Pt catalyst. Those conditions are the conductivity of protons, the conductivity of electrons and the permeability of gases [5]. It will be able to use Pt catalyst efficiently compared with the carbon black which use as the carrier of Pt catalyst conventionally. In order to improve the permeability of the fuel gas, it is necessary to optimize the number density and diameter of the VA-CNT independently. Conventionally, thin film of catalytic metal material for VA-CNTs growth is prepared by using vapor deposition method or sputtering method so far. But these conventional methods cannot control the number density and the diameter of catalytic nanoparticles independently, so it is required to develop another method.

In this study, we employed the LB technique as the technology for optimization of number density of VA-CNTs. We can deposit the monomolecular thin films of Fe nanoparticles (FeNPs) as the catalytic metal nanoparticles for VA-CNT growth on large substrates directly and easily at low cost. LB technique is superior as a technology to deposit nanoparticles as catalyst for CNT growth.

Next, we synthesized VA-CNTs from the nanoparticle LB films deposited on substrate by thermal chemical vapor deposition (CVD) method. CVD method is suitable for large scale synthesis of VA-CNTs [6]. Arachidic acids (C20) as filler molecules were mixed with FeNPs, because thermal aggregation of FeNPs was occurred by thermal CVD method. To reduce the thermal aggregation of FeNPs, it was necessary to widen the inter-FeNP distance by mixing with C20. Then FeNPs-C20 LB films were prepared, and VA-CNTs were synthesized. FeNPs are dispersed by C20 that have high liquidity. By mixing C20, the inter-FeNP distance was widened and the thermal aggregation of FeNPs was reduced. And we could control the number density of VA-CNT by changing mixture ratio of FeNPs and C20.

2. Experiment

2.1. FeNPs-C20 mixture solution

FeNPs/$CHCl_3$ (1 wt%, 4 nmϕ, SHINKO KAGAKU KOGYOSHO) was diluted 100 times with $CHCl_3$ (Nacalai Tesque) to a concentration of 0.01 wt%. 238 mg of C20 (Nacalai Tesque) and $CHCl_3$ were combined in 100 mL measuring flask. This solution (7.6×10^{-3} M) was diluted

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Table 1
Mixed quantity of FeNPs and C20.

Fe area ratio	FeNPs/$CHCl_3$ (μL)	C20/$CHCl_3$ (μL)
0.0	0	3000
0.05	150	2850
0.1	300	2700
0.2	600	2400
0.3	900	2100
0.4	1200	1800
0.5	1500	1500
0.6	1800	1200
0.7	2100	900
0.8	2400	600
0.9	2700	300
1.0	3000	0

100 times with $CHCl_3$ to a concentration of 7.6×10^{-5} M. Table 1 shows the mixed quantity of FeNPs/$CHCl_3$ solutions mixed with C20/$CHCl_3$ solution used in this study. Fe area ratio is defined by

$$\text{Fe area ratio} = N_{Fe}A_{\text{lim Fe}}/(N_{Fe}A_{\text{lim Fe}} + N_{C20}A_{\text{lim C20}}) \quad (1)$$

where N_{Fe} and N_{C20} are number of FeNPs and C20 molecules, and $A_{\text{lim Fe}}$ and $A_{\text{lim C20}}$ are limited occupied area of FeNP and C20 molecule, respectively. $A_{\text{lim Fe}}$ and $A_{\text{lim C20}}$ are 28.8 nm^2 and 0.22 nm^2 [7], respectively.

2.2. Surface pressure, FeNPs-C20 LB film

L film was prepared with our laboratory made LB trough. A surface pressure sensor of the Wilhelmy type [8] as shown in Fig. 1 was attached to the LB trough for π-A isotherm measurement. The trough was filled with distilled water (Nacalai Tesque). The temperature of the subphase was 295 K. Then 3000 μL of the solutions prepared in Table 1 were dropped on the water surface. After 6 min for volatilizing $CHCl_3$, the molecules on the surface of sub phase were compressed with barrier to prepare L film while the surface pressure was measured. The LB film was deposited on SiO_2/Si substrates by raising and lowering three times at 30 to 40 mN/m. And the LB film was transferred to a Transmission Electron Microscope (TEM) grid (with supporting film of elastic carbon, Okenshoji) through horizontal adhesion method.

2.3. Thermal CVD method

VA-CNTs were synthesized from FeNP LB films and FeNPs-C20 LB films on the SiO_2/Si substrates by thermal CVD method. Table 2(a) shows the process condition of thermal CVD for VA-CNT growth.

2.4. TEM and SEM

The structural morphology of annealed L film of FeNPs deposited on TEM grids was characterized by TEM (HITACHI H-7650) at 100 kV. Table 2(b) shows the process condition for annealing.

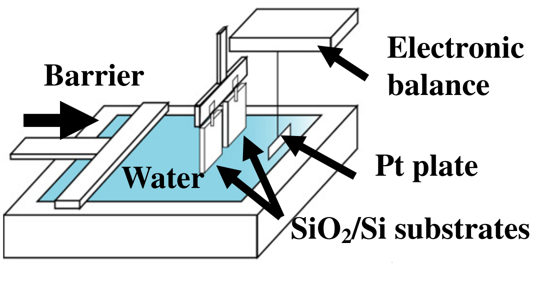

Fig. 1. Laboratory made LB trough.

Table 2
(a) Thermal CVD and (b) annealing process condition.

Process	Temperature	Ar+H_2(4%)	Ar	C_2H_2	Pressure
(a)	923 ~1073 K	180 sccm	–	40 sccm	103 kPa
(b)	1023 K	–	220 sccm	–	103 kPa

A part of VA-CNTs which have been synthesized on the SiO_2/Si substrates following the procedure shown in Section 2.3 was removed by a pair of tweezers. The cross section of VA-CNTs and the FeNPs at the hid area of VA-CNTs were characterized by Field Emission-Scanning Electron Microscope (FE-SEM) (JEOL JSM-6330) at 5 and 15 kV, respectively

3. Results and discussions

3.1. π-A isotherms

Fig. 2 shows π-A isotherms of the pure and the mixed film of FeNPs and C20. The shapes of π-A isotherms are changed by Fe area ratio. In case of the sample of C20 (Fe area ratio was 0.0), its surface pressure did not rise at the start of compression. When C20 was compressed further, the surface pressure rose steeply. We postulate that C20 molecules were in a close-packed structure at the surface pressure. On the other hand, in case of the sample of Fe area ratio 1.0, its surface pressure had already risen before compression, and the slope of the surface pressure was affected by compression. It seems that surfactants which contained in the original solution of FeNPs as dispersants influence the π-A isotherms. The shape of π-A isotherm of Fe area ratio 0.1 was similar to that of C20 (Fe area ratio was 0.0). The more the Fe area ratio increased, the more the shapes of π-A isotherms were similar to the shape of π-A isotherm of Fe area ratio 1.0.

The shape of the π-A isotherm changes depending upon the Fe area ratio, which is considered to be due to the low liquidity of FeNPs. Fig. 3 shows schematic packing images of FeNPs at Fe area ratio 1.0. It seems that FeNPs are clustered like Fig. 3(a) at low surface pressures. The surface of FeNP is modified by hydrophobic protective layer which thickness is about 1 nm. Fig. 3(b) shows the packing model that takes into account the protective layer in initial compression. It seems that FeNPs are compressed while the protective layer collides.

Fig. 4 shows the limited occupied area by each Fe area ratio. Experimental data were calculated from π-A isotherms in Fig. 2. Theoretical calculation were defined by

$$\text{theoretical limited occupied area} = (A_{\text{lim Fe}}N_{Fe} + A_{\text{lim C20}}N_{C20})/N_{Fe} + N_{C20}. \quad (2)$$

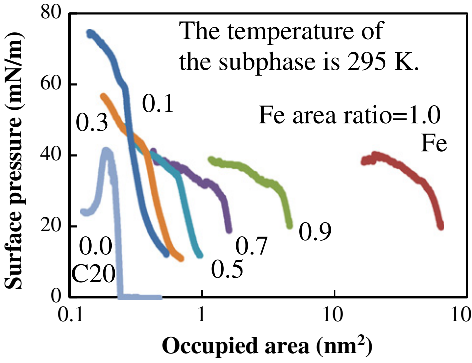

Fig. 2. π-A isotherms of the pure and the mixed film of FeNPs and C20.