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Fabrication of Carbon Nanowalls on Carbon Fiber Paper

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1. Introduction

Carbon nanowalls (CNWs) can be described as self-assembled, free-standing, few-layered graphene sheet nanostructures. The sheets form a self-supported network of wall structures with thicknesses ranging from a few nanometers to a few tens of nanometers. CNWs have been grown by various plasma-enhanced chemical vapor deposition (PECVD) methods, employing microwave plasma, capacitively coupled plasma with H radical injection, electron-beam excited plasma and inductively coupled plasma (ICP) [1]. Among these methods, ICP is relatively simple in structure. Furthermore, the growth rate of CNWs using ICP CVD with CH_4/Ar mixture was rather high compared with other methods [2].

Because of the unique structure of CNWs with high surface-to-volume ratio, CNWs can be potentially used as catalyst support materials for the electrodes of fuel cells. In this application, it is required to support platinum (Pt) nanoparticles as catalysts on the CNW surface.

We have ever developed a method of forming Pt nanoparticles using a metal organic chemical fluid deposition (MOCFD) process employing a supercritical fluid (SCF), where supercritical carbon dioxide (sc-CO_2) is used as a solvent of metal-organic compounds [3]. The SCF possesses attractive properties of both the gas and the liquid phases. Rapid diffusion and permeation are realized by its gas-like diffusivity and viscosity, while its liquid-like density enables dissolution of a wide range of materials. To produce an SCF phase, the temperature and pressure of the material are required to exceed the critical point. The critical point of sc-CO_2 exists at 7.38 MPa (72.8 atm) and 31.1 °C. Among SCFs, the sc-CO_2 is particularly attractive since it is environmentally friendly and safe due to its low toxicity, low reactivity and nonflammability.

Meanwhile, carbon fiber paper has been used as gas diffusion layer in fuel cell application. In this study, CNWs were directly grown on the carbon fiber paper by ICP-CVD employing CH_4/Ar mixture. Furthermore, by using SCF-MOCFD with sc-CO_2, we demonstrated the synthesis of dispersed Pt nanoparticles of 2 nm diameter on the entire surface of CNWs grown on carbon fiber paper for the fuel cell application.

2. Experiments

CNWs were fabricated using ICP-CVD employing Ar/CH_4 mixture [2]. Figure 1 shows a schematic of ICP reactor used for the growth of CNWs. The ICP chamber was 16 cm in diameter and 30 cm in height. A one-turn coil antenna with a diameter of 10 cm was set on a quartz window at the top of chamber. RF (13.56 MHz) power was applied to the coil antenna and plasma was generated in the chamber. The growth experiment was conducted at RF power of 500 W, total pressure of 20 mTorr, temperature of 720 °C, and Ar/CH_4 flow rates of 100/50 sccm.

Figure 2 shows the SCF-MOCFD system employing sc-CO_2 used for the deposition of Pt nanoparticles on the surface of CNW [3]. The MOCFD process was conducted in two high-pressure stainless steel vessels equipped with a compressor, heating units, and a reservoir for the metal-organic compound. As the platinum precursor, we used $(CH_3C_5H_4)Pt(CH_3)_3$:$MeCpPtMe_3$ dissolved in hexane. The concentration of $MeCpPtMe_3$ was 1 wt %, and the quantity of the solution used was 5 mL. In the lower reactor, the pressure and temperature of sc-CO_2 were maintained at 9 MPa and 130 °C, respectively, and the temperature of CNWs was maintained at 180 °C. Pt nanoparticle formation was carried out for 30 min; the vessel was then depressurized slowly in 5 min to atmospheric conditions.

3. Results and discussion

Figure 3(a) shows typical SEM image of carbon fiber used in this study. Figures 3(b)ï 3(d) show SEM images of CNWs grown on carbon fiber by ICP-CVD for 30 min, indicating that CNWs were successfully grown on the carbon fiber paper using ICP-CVD. As shown in Fig. 3(d), CNWs were grown almost vertically on the surface of carbon fibers forming paper structure. The height of CNWs grown on the carbon fiber paper was about 1.5 εm. Raman spectrum of CNWs grown on carbon fiber paper is shown in Fig. 4. The strong and sharp D band peak and Dô band peak suggest a more nanocrystalline structure and the presence of graphene edges and defects, which are prevalent features of CNWs.

Figure 5 shows SEM image of the surface of the CNW supporting Pt nanoparticles after the SCF-CVD. It was found that dispersed Pt nanoparticles of approximately 2 nm in diameter were supported on the surfaces of CNWs grown on carbon fiber paper. The density of Pt nanoparticles on CNW surface was approximately 3×10^{12} cm^{-2}. Figure 6 shows XPS spectrum of the Pt (4f) region of the Pt-supported CNW after the SCF-MOCFD. The presence of two prominent sets of Pt (4f) peaks is further confirmation of Pt being present on the CNW surface. The peak regions in Fig. 6 can be fitted with two sets of peaks at 71.4 eV (4f7/2) and 74.6 eV (4f5/2). These correspond to Pt in the metallic state, indicating that only pure Pt exists without being oxidized on the surface of the CNWs after the SCF-MOCFD.

Pt-supported CNWs grown on the carbon fiber paper will be well suited to the application for the electrodes of fuel cells. The electrocatalytic activity will be investigated.

References

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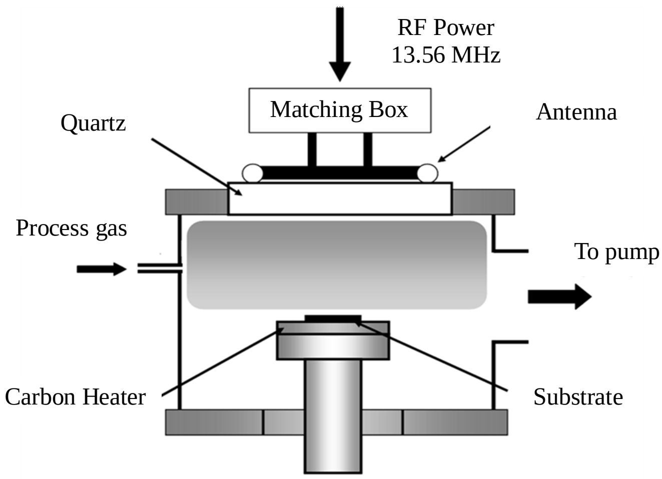

Fig. 1 Schematic of ICP system used for the growth of CNWs.

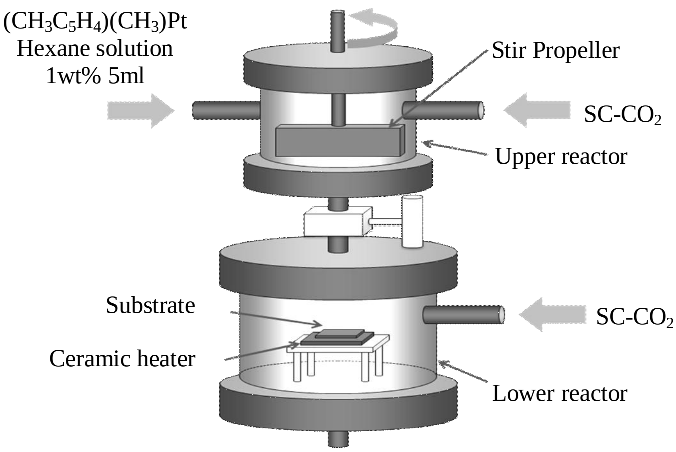

Fig. 2 Schematic of SCF-CVD system used for the preparation of Pt nanoparticles.

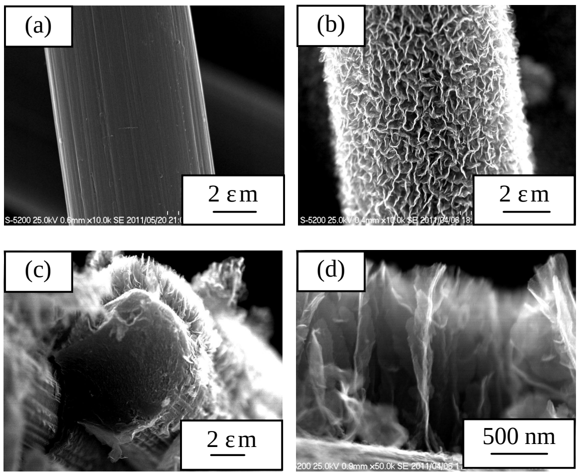

Fig. 3 (a) SEM image of carbon fiber forming paper structure. (b)ï (d) SEM images of CNWs grown on carbon fiber.

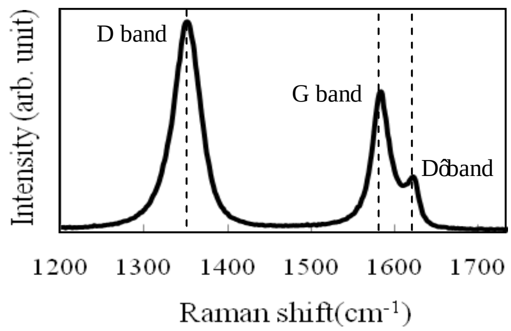

Fig. 4 Raman spectrum of CNWs grown on carbon fiber paper.

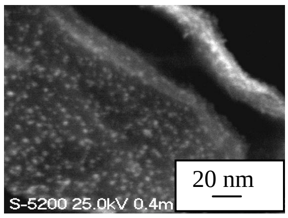

Fig. 5 SEM image of Pt-supported CNW on carbon fiber paper.

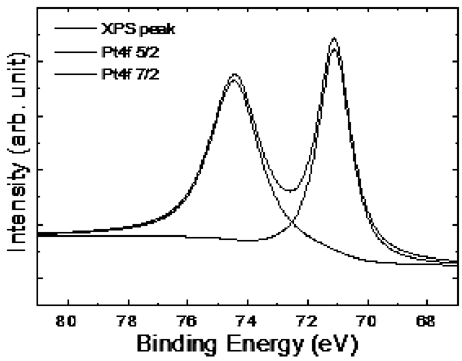

Fig. 6 XPS spectrum of Pt-supported CNW after SCF-MOCFD.