



One-step liquid-phase synthesis of platinum nanocatalysts supported on aligned carbon nanotube arrays



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HIGHLIGHTS

- Platinum nanoparticles supported on carbon nanotubes were prepared in liquid-phase.
- Size of platinum nanoparticles can be controlled by changing the synthesis time.
- The nanoparticles were mainly formed on top part of the nanotube arrays.
- The platinum nanoparticles were covered with low crystallinity carbon films.
- The platinum nanoparticles demonstrated promising electrochemical characteristics.

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ABSTRACT

Highly-dispersed platinum nanoparticles supported on vertically aligned carbon nanotube arrays were readily prepared by one-step liquid-phase process. The composites were grown on stainless-steel substrates via electric resistance heating of the substrate in an ethanol solution containing platinum-based organometallic complex as a nanoparticle precursor. The size of platinum nanoparticles on the nanotube surface can be controlled by changing the resistance heating time of the substrate. The nanoparticles were mainly formed on top part of the nanotube arrays, which is attributed to their characteristic reaction field for the formation, i.e., film boiling state. It is also interesting that the platinum nanoparticles were covered with low crystallinity carbon films and immobilized on the nanotube surface. Partial elimination of the films effectively brought electrocatalytic activity for the nanoparticles. This unique one-step process is valuable because it enables the simultaneous preparation of carbon nanomaterials and metallic nanoparticles in a short time.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are attracting much interest as alternative power supplies for stationary power generators, electric vehicles, and portable devices due to their high energy-conversion efficiencies and low environmental impacts. Perfluorosulfonic acid membranes such as Nafion[®] are typically used as electrolytes in PEFCs because of their high proton conductivities and chemical stability. However, these membranes are highly acidic, and thus, materials suitable for PEFC electrocatalysts have been restricted due to the need for high acid resistance, and

chemical and electrochemical stability at their operating temperatures of ca. 80 °C. Therefore, platinum (Pt)-based catalysts supported on carbon are generally preferred because of their high electrocatalytic activity and good durability under such conditions.

Carbon black (CB) has been widely used as the support for Pt-based nanocatalysts. On the other hand, it is suggested that carbon nanotubes (CNTs) [1] are superior to CB in terms of their oxidation resistance, surface area, and gas diffusibility in the electrocatalyst layers [2–6]. With respect to their preparation, composite of metallic nanocatalysts with carbon supports are generally prepared by combination of (i) preparation or synthesis of the carbon support and (ii) Pt supporting process by using wet methods, sputtering, etc. Each process needs strictly controlled preparation conditions with many high-cost chemicals and/or vacuum apparatus.

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Although syntheses of carbon nanomaterials (CNMs) have generally been performed by gas-phase methods, as typified by chemical vapor deposition techniques [7], some condensed-phase synthesis methods have been proposed [8–12]. We have previously developed a one-step liquid-phase synthesis [13–19] of CNMs in alcoholic solutions of organometallic complexes via resistance heating of metallic substrates under ambient pressure. Its outstanding merits are as follows: 1) the simplicity of the process and apparatus and 2) a wide choice of substrates [14], additives [16,18], catalyst precursors [15,18], etc. In the one-step liquid-phase synthesis, it is possible to dissolve various additives to confer functionalities on CNMs. In other words, CNM growth and functionalization is achieved in a one-step process. This paper describes a novel one-step process for the preparation of Pt nanoparticles supported on aligned CNT arrays, which are highly functionalized nanocomposite materials, and its electrochemical performance.

2. Experimental

2.1. One-step liquid-phase synthesis of Pt/CNTs

Commercially available stainless-steel (Japanese Industrial Standards JIS SUS304) substrates ($5 \times 25 \times 0.1 \text{ mm}^3$) were preheated at $500 \text{ }^\circ\text{C}$ for 60 min in air prior to nanocomposite synthesis. Each preheated substrate was fixed between two copper electrodes attached to an aluminium alloy lid, which was then submerged in 200 mL of alcoholic solution in a flask (see Fig. S1 in supporting information). The solution was ethanol (>99.5%, Kanto chemical Co., Inc.) containing 0.1 mM platinum (II) acetylacetonate $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ (= $\text{Pt}(\text{acac})_2$, Wako Pure Chemical Industries, Ltd.), which is a Pt nanoparticle precursor. The substrate was heated via ohmic resistance heating using an alternating current source at $T_{\text{st}} = 800 \text{ }^\circ\text{C}$ (T_{st} : surface temperature of the substrate) for $t_{\text{rh}} = 1\text{--}15 \text{ min}$ (t_{rh} : resistance heating time) in the ethanol solution. The heating-up period for $T_{\text{st}} = 800 \text{ }^\circ\text{C}$ is $\sim 30 \text{ s}$ and temperature was manually maintained by controlling of the voltage (mainly 3–4 V). T_{st} was measured using an infrared thermometer. An inert atmosphere was kept in the flask by flowing Ar gas at a rate of 100 mL/min. A reflux condenser was inserted in the lid so that the gases (such as ethanol vapor and Ar gas) inside the flask were maintained at atmospheric pressure during the synthesis.

2.2. Characterization

After the synthesis, the as-prepared deposits on the substrates were observed under a scanning electron microscope (SEM; Hitachi S-5000), and their Raman spectra were obtained using a laser Raman microscope (JASCO NRS-3200) with an Ar laser (excitation beam wavelength: 532 nm). Pt nanoparticles on CNT walls were also analyzed via an X-ray photoelectron spectroscopy (XPS, JEOL JPS-9010MC). The deposits were dispersed in acetone via ultrasonification, and the specimen on a grid was observed under a transmission electron microscope (TEM; Hitachi H-9500) with an energy dispersive X-ray spectrometer (EDX). As electrochemical characterization for the composite, potential cycling (i.e., cyclic voltammetry) was performed by a potentiostat (ALS Model 2325 Bi-Potentiostat). The stainless-steel substrate with the composite was cut and directly used as the working electrode for the measurement. A reversible hydrogen electrode (RHE) and a Pt wire were used as reference and counter electrodes, respectively. The measurements were performed in N_2 saturated 50 mM H_2SO_4 solution at room temperature.

3. Results and discussion

3.1. Synthesis of Pt/CNTs

Preheating of stainless-steel substrates leads to the formation of an Fe-rich oxide layer on the substrates' surface [13], which brings the generation of a large number of Fe catalyst nanoparticles that served as sites for CNT growth during resistance heating in the ethanol solution. Fig. 1, column (a) shows the SEM images of multi-walled CNTs (MWCNTs) grown on the substrate surface in the ethanol solution via resistance heating for $t_{\text{rh}} = 1, 5, \text{ and } 15 \text{ min}$. Before the observation, the deposits were partially removed from the surface by tweezers to make it possible to compare their morphologies. The alignments and lengths of the MWCNTs gradually improved with increasing t_{rh} . For $t_{\text{rh}} = 5\text{--}15 \text{ min}$, however, the length of aligned CNT arrays (ACNTAs) remained nearly the same ($\sim 10 \mu\text{m}$), indicating that the lifetime of the precipitated Fe catalyst particles for CNT growth is approximately 5 min. Fig. 1, column (b) shows the respective high-magnification SEM images of those in column (a) (top part of ACNTAs). A significant number of metallic nanoparticles was observed, particularly when $t_{\text{rh}} = 5 \text{ min}$ and 15 min. In addition, the size of the nanoparticles gradually increased with increasing t_{rh} . Interestingly, there was a tendency that the nanoparticles were mainly observed on the top part of the ACNTAs, i.e., the farthest part from underlying steel substrate.

TEM images of the composites can be seen in Fig. 2 (a). MWCNTs had somewhat meandering shapes and their outer diameters were approximately 20 nm. Many metallic nanoparticles were observed on the CNT walls and their elementary analysis using TEM-EDX clarified that the metallic nanoparticles were Pt-based compounds (see supporting information Fig. S2). This result indicated that the origin of the nanoparticles was $\text{Pt}(\text{acac})_2$ contained in the ethanol solution. The diameters of the Pt nanoparticles (D_{Pt}) ranged from 1 to 8 nm with an average diameter $D_{\text{Pt}}^{\text{av}} = 4.8 \text{ nm}$ for $t_{\text{rh}} = 5 \text{ min}$ and 3–11 nm with $D_{\text{Pt}}^{\text{av}} = 7.0 \text{ nm}$ for $t_{\text{rh}} = 15 \text{ min}$ (Fig. 2(b)), respectively. As can be seen in the high-magnification TEM image in Fig. 2(a) ($t_{\text{rh}} = 15 \text{ min}$), the nanoparticles were often covered with low crystallinity carbon films with thickness of 1–3 nm. On the other hand, Fe nanoparticles as minor by-products were also observed in the interior of MWCNTs, which were presumably separated from the substrate surface during CNT growth [13].

Pt-based nanoparticles on MWCNT walls with $t_{\text{rh}} = 15 \text{ min}$ were analyzed using XPS; Pt $4f_{7/2}$ (lower binding energy) and Pt $4f_{5/2}$ (higher binding energy) peaks were observed, as shown in Fig. 3(a). Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks for the nanoparticles appeared at 71.1 eV and 74.4 eV, respectively, indicating that Pt was deposited as Pt metal (Pt(0)) [3,20]. Small peaks appearing at 77–80 eV were attributed to Pt oxides [20]. The Raman spectrum of the composite ($t_{\text{rh}} = 15 \text{ min}$) is shown in Fig. 3(b). The G-band, which is assigned to the in-plane vibration of carbon atoms in graphene sheets, appeared at $\sim 1580 \text{ cm}^{-1}$, and the D-band, which is attributed to defects and dangling bonds in the sheets, appeared at $\sim 1340 \text{ cm}^{-1}$. The intensity ratio ($I_{\text{D}}/I_{\text{G}}$) of the D- and G-bands [21,22] of the composite was approximately 2.1, which is much larger than that ($I_{\text{D}}/I_{\text{G}} = 1.2$) of ACNTAs prepared from ethanol without $\text{Pt}(\text{acac})_2$ with $t_{\text{rh}} = 15 \text{ min}$ [13] (see supporting information Fig. S3). Such a large $I_{\text{D}}/I_{\text{G}}$ value for the composite is presumably attributed to the presence of low crystallinity carbon films on Pt nanoparticles as observed by TEM.

3.2. Formation mechanism of Pt/CNT

With respect to formation mechanism of the composite, we have focused on the characteristic reaction field near the substrate

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