

Surface thiolation of carbon nanotubes as supports: A promising route for the high dispersion of Pt nanoparticles for electrocatalysts

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Abstract

This paper introduces a unique method for achieving high dispersion of precious metal nanoparticles on carbon nanotube supports for electrocatalysts: the surface thiolation of multiwall carbon nanotubes (MWNT). The high dispersion of Pt nanoparticles [i.e., small average particle size (1.5 nm) and narrow size distribution] was obtained by the surface thiolation of MWNT as supports, despite a considerably large Pt load (40 wt% Pt to MWNT) and the use of MWNT with a relatively small surface area as supports to common activated carbon. In particular, EXAFS and XPS data revealed that the interaction between Pt nanoparticles and surface thiol groups on MWNT was the reason for the high dispersion. These highly dispersed Pt nanoparticles showed enhanced and stable electrocatalytic activity in methanol oxidation and oxygen reduction reactions. This result indicates that the surface thiolation of supports is an effective way to obtain highly dispersed precious metal nanoparticles to enhance electrocatalytic activity.

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1. Introduction

Highly dispersed Pt nanoparticles on carbon supports have been used in a number of heterogeneous catalysis applications, including electrocatalysts for fuel cells and catalysts for hydrogenation reactions [1,2]. These catalysis reactions occur entirely on the surface of Pt nanoparticles, so high dispersion is required to elevate catalytic activity and reduce the amount of expensive precious metal used. Notably, the high dispersion is more important in electrocatalysts for fuel cells than in catalysts for organic synthesis or environmental purification, because of the large load (about 20–80%) of precious metal required. The wide variety of pore structures and chemical functional groups on the surface of carbon supports affects the dispersion of Pt nanoparticles [3]. For this reason, various high-dispersion studies have been conducted by modifying the pore structure and chemical nature of the carbon supports [4–9]. Among various carbon supports, carbon nanotubes (CNTs) are very attractive

as electrocatalyst supports. There has been increased interest in the use of CNTs as supports since the first study on such an application in 1994 [10]. CNTs are adequate as supports for various heterogeneous catalysts, especially electrocatalysts, because they have unique physicochemical characteristics, such as good intrinsic conductivity, a pore structure without micropores, durability under corrosive conditions, and mechanical toughness. However, their inert surface nature [11] due to a perfect graphene sheet structure has hindered the high dispersion of precious metal with uniform size distribution using the conventional impregnation method, in which the affinity of the carbon surface for the precursor solution exerts the dominant effect on dispersion in the deposition step [12]. To solve this problem, the surfaces of CNTs have been functionalized with functional groups like carboxyl [13–15], amine [16], and sulfone [17] groups or polymers [18] having a good affinity with precious metal, using various organic synthetic or electrochemical methods.

In this study, we obtained highly dispersed Pt nanoparticles by introducing thiol groups on multiwall carbon nanotube (MWNT) surfaces, using organic synthetic methods based on an amide bond formation. The thiol groups, well-known func-

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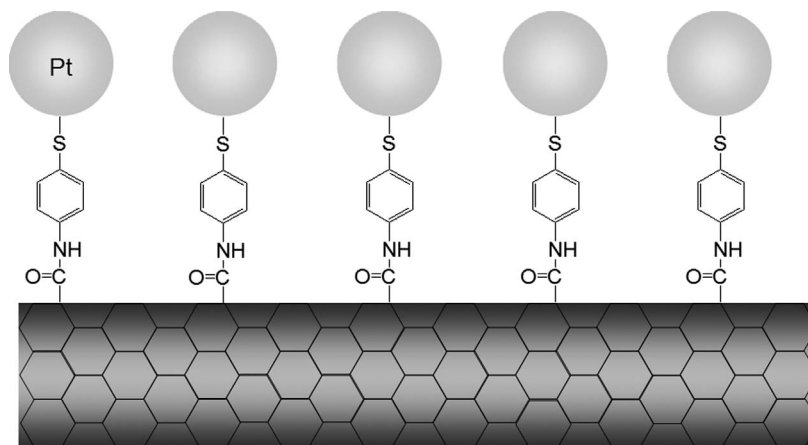


Fig. 1. Schematic illustration of Pt nanoparticles supported on thiolated MWNT.

tional groups forming a spontaneous bond with precious metal surfaces, as in the case of self assembled monolayers (SAMs), were expected to prevent agglomeration among the Pt nanoparticles on MWNTs by a strong interaction with the precious metal (a schematic illustration is presented in Fig. 1).

2. Experimental

2.1. Surface thiolation of MWNTs

MWNTs were prepared by decomposing acetylene on iron nanoparticles supported on silica at 800 °C, which is a slightly modified method of that described previously [19]. This raw soot containing the MWNTs was heated for 2 h at 450 °C in static air and treated for 12 h with 3 M HCl (Kanto Chemical) at 70 °C. Thiolation of MWNTs was conducted by a method based on the formation of an amide bond [20]. Purified MWNTs (p-MWNTs) were stirred in concentrated HNO₃ (70%, Kanto Chemical) for 15 min to prepare carboxylated MWNTs (c-MWNTs), then chlorinated by refluxing for 12 h with SOCl₂ (Wako) at 70 °C. After the remaining thionyl chloride was evaporated, the thiolated MWNTs (t-MWNTs) were obtained by reacting with NH₂C₆H₄SH (Wako) in dehydrated toluene (Aldrich) for 24 h at 70 °C.

2.2. Electrocatalyst preparation

To support Pt nanoparticles on the MWNTs, we adopted the well-known impregnation method followed by liquid-phase borohydride. A mixture of 20 mg of various MWNTs (p-, c-, and t-MWNTs) and 6.25 ml of 10 mM H₂PtCl₆ (Aldrich) was suspended by sonication in 40 ml of deionized water. Subsequently, this Pt precursor was reduced and supported on MWNTs simultaneously by NaBH₄ (Kanto Chemical) as the reducing agent and washed with deionized water several times. The filtrate was collected to determine an exact load by measuring the Pt residue. After drying, the 40 wt% Pt nanoparticles supported on three kinds of MWNTs – Pt/p-MWNT, Pt/c-MWNT, and Pt/t-MWNT – were obtained. Pt black was also prepared by the same method but without supports.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR), using a Thermo Nicolet AVATAR 360, was conducted to characterize the carboxylation of the MWNTs. Quantitative assay of the introduced functional groups, especially the carboxyl groups, was done using the Boehm titration method [21]. Titration was conducted in the following order. Oxidized MWNTs (50 mg) were placed in 25 ml of 0.01 M NaOH and suspended in a strong ultrasonic homogenizer for 10 min. This suspension solution was stirred for 24 h at room temperature in a closed vessel and then filtered. Subsequently, 20 ml of this filtrate was reacted with the same amount of 0.01 M HCl for 24 h, and then this solution was back-titrated with 0.01 M NaOH. Oxidized and thiolated MWNTs were subjected to zeta potential measurement (ELS-8000, Otsuka) to evaluate a surface charge. The exact Pt load was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 3000DV, Perkin-Elmer). Transmission electron microscopy (TEM; H7100, Hitachi) images were obtained at an accelerating voltage of 100 kV. X-Ray diffractometry (XRD; M18XHF-SRA, MAC Science) analysis was carried out using a Cu-K_α source at room temperature. The average particle size was calculated by the Debye–Scherrer equation using a Pt(111) peak fitted by modified Gaussian function. X-Ray photoelectron spectroscopy (XPS; PHI 5600, ULVAC-PHI) was used to identify the thiolation of the MWNTs and the interaction between the Pt nanoparticles and thiol groups on the MWNTs. Extended X-ray analysis fine structure (EXAFS) data for Pt-L_{III} absorption edges were obtained with transmission mode using the synchrotron radiation of BL01B1, SPring-8, at room temperature. X-Rays were monochromated with two Si(111) planes gratings and detected by two ion chambers, which were continuously purged with a gas mixture of 15% Ar and 85% N₂ in I₀ and 100% Ar gas in I₁. The data reduction was carried out using the ATHENA software. The XANES spectrum was normalized by the Victoreen function, and the radial distribution function (RDF) of EXAFS was obtained by a Fourier transform, in the range of 3–14 Å⁻¹ in *k* space, on *k*³-weighted EXAFS oscillations.

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