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Covalently grafted platinum nanoparticles to multi walled carbon nanotubes for enhanced electrocatalytic oxygen reduction

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ABSTRACT

A carbon nanostructure has fabricated from covalently grafted platinum (Pt) to multi walled carbon nanotube (MWCNT) with the assistance of sulfur atom on the MWCNT's sidewall, MWCNT–S–Pt. The MWCNT–S–Pt displays an excellent electrocatalytic performance for oxygen reduction reaction (ORR) than that of an unbonded Pt to MWCNT, MWCNT/Pt. Here we describe a comparative study of the ORR on two MWCNT-supported Pt-based catalysts in aqueous acidic electrolyte. Both MWCNT–S–Pt and MWCNT/Pt catalysts have the compositions of 1.03 and 2.18 at% Pt, respectively. For the characterization, the bonding features have confirmed by the X-ray photoelectron spectroscopic (XPS) and electron microscopy have used to determine the size and shape as well as the distribution of the particle on both catalysts. Electrochemical measurements have performed using the cyclic voltammetry and hydrodynamic voltammetry methods in 0.1 mol l^{-1} $HClO_4$ solution. Kinetic analysis in comparison to unbonded MWCNT/Pt a significant enhancement for the covalently bonded MWCNT–S–Pt has been found. The MWCNT/Pt is unstable at electrode potentials for long term use than that of MWCNT–S–Pt. Ring-current collection measurements for peroxide indicate MWCNT–S–Pt catalyst has a less peroxide yield.

1. Introduction

The fuel cells (FCs) are important environment-friendly power source nowadays with high energy conversion efficiency and low pollution. The slow kinetic rate of the oxygen reduction reaction (ORR) at the cathode is the main challenge that hinders the energy conversion efficiency of FCs [1]. Carbon-supported platinum (Pt) catalysts still serve as the most widely used electrocatalyst in low-temperature FCs [2]. The Pt nanoparticles (NPs) on carbon is one of the most attractive catalysts for many types of industrial reactions such as fuel cell reactions, CO oxidation in a catalytic converter, nitric acid production, and petroleum cracking, etc. [3–5]. Particularly, the design of highly active catalysts for ORR in FCs is one of the great challenges in the field of electrochemical energy conversion [6–8]. Pt usage reduction is an obstacle for the commercialization of FC vehicles because of its high price and limited availability. However, to increase the activity of ORR and decrease the catalysts cost or Pt loading, one strategy is to explore the novel support materials because they play an important role in the dispersion of Pt nanoparticles and facilitate the transportation of reactants/products, which directly improve the catalytic activity and stability of catalysts [9,10].

Recently, carbon nanotubes (CNTs) have been widely studied as an alternative catalyst support for FCs, owing primarily to the unique electrical and structural properties of CNTs [11,12]. Many research groups have reported that the CNT-supported Pt (CNT/Pt) catalysts exhibit increased catalytic activity [13–15] and show high electrochemical stability [16,17]. However, since the surface of the CNT is highly inert because of high graphitization, [18,19] Pt nanoparticles are very difficult to deposit directly and evenly onto such surfaces without active functional groups. On the other hand, Pt particles can be readily detached from a support by ultrasonic or/and high-speed agitation treatment during the preparation of catalyst slurries due to low affinity between Pt and carbon atoms. Therefore, it is difficult to evenly deposit Pt nanoparticles on the surfaces of CNTs and to reinforce the binding strength between Pt and CNTs. Thus far, the most established protocols for catalytic metal immobilization on CNTs include generating functional groups on the external walls, mostly through harsh oxidative treatment, such as refluxing in acid followed by metal deposition on activated CNT walls [20–23]. Such oxidative surface functionalization introduces an avenue for metal precursors to correlate with CNTs and prompts the deposition of metals on the external walls. While this strategy is effective, but satisfactory results are still lacking: the size of the Pt particle on the CNT is difficult to control,

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dispersion of Pt particles remains uneven, most of all, the graphitized surfaces of CNTs are easily destroyed, which reduces the conductivity and durability of CNTs. These drawbacks lead to low output performance for CNT/Pt catalysts in FCs [24]. Thus, to overcome these problems, You et al. [25] have shown that the oxygen molecule can be replaced by other molecule such as sulfur via reduction reaction to make the CNT more conductive and durable after acid treatment and to attach Pt NPs for higher activity via covalent bonding.

Here, we report the synthesis of a multi walled carbon nanotubes (MWCNT)-based Pt catalyst with high ORR activity and stability in acid. We introduce Pt NPs into MWCNT surface through the sulfur atom via covalent bonding (MWCNT–S–Pt). The surface chemical composition and the atomic bonding of MWCNT–S–Pt are examined by transmission electron microscopy (TEM) X-ray powder diffractions (XRD) and X-ray photoelectron spectroscopy (XPS). The covalently bonded MWCNT-based catalyst shows higher ORR activity than that of covalently unbonded catalysts. Subsequently, the electrocatalytic behavior of these MWCNT–S–Pt catalysts supported glassy carbon electrode (GCE) toward O_2 reduction was investigated by employing the cyclic voltammetry, rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) configuration in aqueous 0.1 mol l^{-1} $HClO_4$ acid solutions. The stability and electrocatalytic activity toward the ORR of this newly synthesized composite electrode were also analyzed using Koutecky–Levich and Tafel plots.

2. Experimental

2.1.1. Synthesis of MWCNT–S–Pt

The nanostructure was prepared as described in Ref. [25,26]. Briefly, MWCNT was dispersed in an acid solution of H_2SO_4 and HNO_3 (3:1 by volume) at 80 °C for 3 h under continuous stirring; for formation of functional acid group on the surface of MWCNT (MWCNT–O) and removing metal contamination. The MWCNT was then vacuum-filtered, washed with distilled water, and dried in a vacuum oven at 40 °C for 24 h.

The acid treated MWCNT (50 mg) was dispersed in 40 ml tetrahydrofuran and then the 20 ml of 10 wt% NaSH aqueous solution was added for 10 h at 50 °C to produce the thiol groups onto the MWCNT surfaces. The thiolated MWCNT (MWCNT–S) was then vacuum-filtered, washed with distilled water, and dried in a vacuum oven at 40 °C for 24 h.

Finally, the 20 mg MWCNT–S in 30 ml distilled water (DW), 20 mg hydrogen hexachloroplatinate (IV) H_2PtCl_6 in 10 ml DW and 10 ml of 0.2 wt% $NaBH_4$ were mixed together. The mixture was continuous stirred for 24 h at 55 °C to anchor Pt^0 onto the MWNTs. The MWCNT–S–Pt nanostructures were separated from the mixture by vacuum-filtration, washed 5 times with pure ethanol and DW each (total 10 times) after 5 min ultrasonication, and dried in a vacuum oven at 40 °C for 24 h. To obtain the unbonded MWCNT/Pt(s) (the variation of Pt contents has enlisted in supporting information, SI T1), the above procedure was adopted in the absence of NaSH under stirring at room temperature.

2.1.2. Characterizations of physical parameters

Raman spectra were collected with LabRam HR800 UV Raman microscope (Horiba Jobin-Yvon, France), with an excitation wavelength of 514 nm argon ion (Ar^+) laser. All transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDX) were taken by TECNAI model FI-20 (FEI, Netherland). XRD were carried out on a Rigaku D/max-2500, using filtered Cu Kα radiation. X-ray photoelectron spectroscopic (XPS) measurements were performed on a MultiLab 2000 (Thermo Electron Corporation, England) with a 14.9 keV Al Kα X-ray source. The thermal gravity analysis (TGA) was performed on a thermogravimetric analyzer (Perkin-Elmer TGA 7) over a temperature range of 25–800 °C at a heating rate of 25 °C min^{-1}.

2.1.3. Electrochemical measurements

For the electrode preparation, MWCNT–S–Pt or MWCNT/Pt suspension in water (1 mg/ml) was prepared by introducing a predetermined amount of the corresponding sample under sonication. A 20 μl (10 μl × 2) portion of the MWCNT–S–Pt or MWCNT/Pt suspension was then dropped onto the surface of a glassy carbon electrode (GCE, 0.5 cm in diameter) prepolished with 0.05 μm alumina suspension on a polishing cloth (BAS, USA). The Pt loading for all electrochemical experiments can be calculated as 2.66×10^{-5} g cm^{-2} for MWCNT–S–Pt which is much lower than that of MWCNT/Pt (4.44×10^{-5} g cm^{-2}). The ring collection efficiency ($N = 0.18$) was determined using ferrocene solution [27]. All Voltammetric measurements were taken using a three-electrode potentiostat [CHI 700C electrochemical workstation (USA)] in a grounded Faraday cage. Pt wire was used as an auxiliary electrode. A calibrated Ag/AgCl electrode from Bioanalytical Systems Inc. (BAS) in 3 M NaCl solution was used as a reference electrode. All electrochemical measurements, including cyclic voltammograms (CVs), RDE and RRDE voltammograms were performed at room temperature in 0.1 mol l^{-1} $HClO_4$ solutions, which were purged with high purity Ar and oxygen (O_2) for at least 30 min prior to each measurement.

3. Results and discussion

3.1. Characterization of covalently bonded MWCNT–S–Pt nanostructure

3.1.1. TEM and EDX studies

TEM micrographs of MWCNT–S–Pt nanostructures and MWCNT/Pt nanocomposites are shown in Fig. 1. Tubular structures in MWCNT and spherical structures in Pt NPs are clearly evident in both Fig. 1a and b. The TEM image in Fig. 1a shows that the Pt NPs are well-dispersed (but not so many) on the wall of MWCNT to form a pattern with a uniform particle size of about 3–5 nm. These NPs do not aggregate to form larger clusters (Fig. 1a inset). Furthermore, no free Pt NPs (detached from MWCNTs) can be found in the TEM images. On the other hand, MWCNT/Pt composites, however, have an aggregation Pt NPs on outside of the tube surface (Fig. 1b) and most of MWCNT are clean and not been introduced by Pt NPs.

The presence of elements of MWCNT–S–Pt and MWCNT/Pt were also confirmed by EDX spectrum, Fig. 1c, which presents the quantitative microanalysis of components of the MWCNT–S–Pt and MWCNT/Pt, respectively; C, O, Cu, and Pt are in common. However, S peak is shown only in MWCNT–S–Pt spectrum. The peaks of elemental Cu attributed to the TEM grid. It shows clearly the presence of C, O and Pt with S peaks as component elements in MWCNT–S–Pt. Also the peak intensity indicates the corresponding element's population; for instance, the 1.03 and 2.18 at% of Pt have found on the surface of MWCNT–S–Pt and MWCNT/Pt, respectively. The total numerical results of EDX quantitative microanalysis of the MWCNT–S–Pt and MWCNT/Pt are calculated (SI T2). All MWCNT/Pt(s) and MWCNT–S–Pt have analyzed in TGA by using air to decompose all the carbonaceous components (SI F1). The TGA curves show that the dominant weight loss occurs from 300 °C to 570 °C. This is clearly related to the combustion of carbon. A