

Preparation and Electrocatalytic Activity of Gold Nanoparticles Immobilized on the Surface of 4-Mercaptobenzoyl-Functionalized Multiwalled Carbon Nanotubes

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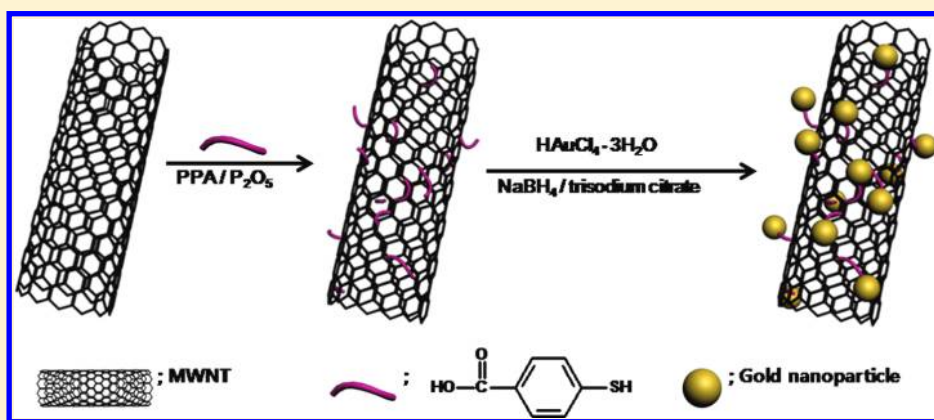
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S Supporting Information

ABSTRACT: Multiwalled carbon nanotubes (MWCNTs) were functionalized with 4-mercaptobenzoic acid in a polyphosphoric acid/phosphorus pentoxide medium to produce 4-mercaptobenzoyl-functionalized MWCNTs (MB-MWCNTs). Gold nanoparticles (GNPs), stabilized by trisodium citrate, were prepared from the in situ reduction of gold(III) chloride trihydrate by sodium borohydride in the presence of MB-MWCNTs dispersed in ethanol. The morphology of the resulting GNP/MB-MWCNT hybrid showed that GNPs were formed with an average diameter of 4.3 nm, and these were uniformly deposited on the surface of the MB-MWCNTs. High-resolution transmission electron microscopy and X-ray photoelectron spectroscopy studies revealed that the GNPs had a well-defined crystal structure. Cyclic voltammetry results showed a high electrocatalytic activity and electrochemical stability of the GNP/MB-MWCNT hybrid in both acidic and basic media.



INTRODUCTION

Carbon nanotubes (CNTs) are known to have excellent mechanical,^{1,2} thermal,³ electrical,⁴ and electrocatalytic⁵ properties. Owing to these unique properties, CNTs have attracted much interest from many areas of science and technology.⁶ Among these areas, CNT-based metal nanoparticle hybrids have been extensively studied because of their potential applications as catalysts,^{7–9} as active materials,^{10–12} in hydrogen and energy storage devices,⁶ and in optical and electronic devices.¹³ Various approaches for the preparation of CNT/nanoparticle hybrids have been suggested, including physical evaporation,¹⁴ chemical reaction with functionalized CNTs,^{15,16} and electrolysis deposition.¹⁷ However, there are still difficulties in being able to disperse metal nanoparticles with a uniform dispersion and regular size on a CNT surface.¹⁸

It is necessary either to attach functional groups or to deposit other nanostructured materials on the surface of CNTs to utilize them as inert base materials for various applications. Functionalized CNTs have been extensively studied for the enhancement of dispersion in processing¹⁹ and/or for further chemical modification.²⁰ Treatment

under harsh conditions in strong (oxidizing) acids, such as sulfuric acid or nitric acid,²¹ or a mixture of these acids²² at elevated temperatures is required to functionalize covalently inert CNTs. Unfortunately, significant damage to the CNT framework has been reported using the common approaches for functionalizing and/or dispersing CNTs,²³ and the oxidized defects formed on the surface of CNTs are most probably the sites that deactivate transition metal catalysts.¹³

We have developed an efficient method to introduce desired organic functional groups to the surface of CNTs in a mild polyphosphoric acid (PPA, 83% assay)/phosphorus pentoxide (P₂O₅) medium as a “direct” Friedel–Crafts acylation reaction.^{24–26} The reaction medium is both mild and nondestructive and plays two important roles for the effective dispersion and functionalization of the CNTs. Thus, a uniform covalent attachment of a desired functional group on the surface of a carbon nanomaterial

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is possible. The first role is that its moderate acidic nature promotes deaggregation to help form a homogeneous dispersion without damaging the CNT, but it is powerful enough to derive efficient functionalization. The second role is the viscous characteristic helping to impede reaggregation after dispersion, which is achieved by applying a shear force under high torque stirring.

In this study, the functionalization of multiwalled carbon nanotubes (MWCNTs) with 4-mercaptobenzoic acid by a “direct” Friedel–Crafts acylation reaction to afford 4-mercaptobenzoyl-functionalized MWCNTs (MB-MWCNTs) was carried out in a nondestructive (oxidative) manner. Gold nanoparticles (GNPs) are known to interact with mercapto groups,²⁷ and thus, they can be stably immobilized onto the surface of MB-MWCNTs without agglomeration occurring.²⁸ These GNP/MB-MWCNT hybrids are expected to exhibit excellent electrocatalytic activity and electrochemical stability.

EXPERIMENTAL SECTION

Materials. All the reagents and solvents used were purchased from Aldrich Chemicals Inc., USA, and were used as received, unless otherwise specified. The MWCNTs (CVD MWCNT 95 with a diameter of ~ 20 nm and a length of 10–50 μm) were obtained from the Hanwha Nanotech Co. Ltd., Seoul, Korea (<http://www.hanwhanotech.co.kr>). The commercial grade platinum on activated carbon catalyst (Pt/C, C2–20, 20% HP Pt on Vulcan XC-72R, E-TEK Division, PE-MEAS Fuel Cell Technologies) was provided by BASF Fuel Cell.

Instrumentations. The Fourier-transform infrared (FT-IR) spectra were recorded using a Jasco Fourier transform spectrophotometer model 480 Plus. All the samples were mixed with dried KBr and pressed to form semitransparent pellets. The FT-IR spectra were collected in the wavelength range from 650 to 4000 cm^{-1} . Raman spectra were performed on a Renishaw Via Raman spectrometer with an excitation wavelength of 514.5 nm. Elemental analysis (EA) was performed using a CE Instruments model EA1110 analyzer. Thermogravimetric analysis (TGA) was conducted in air using a heating rate of 10 $^{\circ}\text{C}/\text{min}$ employing a model TA Q200 analyzer. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Thermo Fisher K-alpha spectrometer employing monochromatic Al K α radiation as the X-ray source. The field emission scanning electron microscopy (FE-SEM) used in this work was collected using an FEI NanoSem 230 microscope. The high-resolution transmission electron microscopy (HR-TEM) employed in this work was obtained using a JEOL JEM-2100F (Cs) microscope operating at 200 kV. The TEM samples were prepared by dipping carbon microgrids containing holes into dispersed samples in ethanol.

Electrochemical Properties. Cyclic voltammetry (CV) measurements were performed using a computer-controlled potentiostat (CHI 760 C, CH Instruments, USA) employing a standard three-electrode cell. Sample/glassy carbon (GC) electrodes were used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (3 M KCl filled) electrode as the reference electrode. Aqueous H_2SO_4 (0.1 M) and KOH (0.1 M) solutions were used as the electrolyte. The MB-MWCNT, GNP/MB-MWCNT, and Pt/C samples were dispersed in water, coated on the GC electrodes, and dried under reduced pressure (0.5 mmHg) for a period of 24 h at 50 $^{\circ}\text{C}$ before testing.

Rotating disk electrode (RDE) and linear sweep voltammetry (LSV) experiments were carried out using an MSR electrode rotator (Pine Instruments, USA) and the CHI 760 C potentiostat.

An aqueous KOH (0.1 M) solution was used as the electrolyte. Either N_2 or O_2 gas was used to purge the solution to achieve an oxygen-free or an oxygen-saturated electrolyte solution, respectively. The sample/GC electrode (3 mm in diameter) dipped in an O_2 -saturated or an N_2 -saturated aqueous KOH (0.1 M) solution was used as the electrolyte, and a scan rate of 10 mV/s was employed. The GC electrode pretreatment procedure and modification are described as follows. Before use, the working electrode was polished with alumina slurry to obtain a mirror-like surface. This was then washed with deionized (DI) water and allowed to dry. The sample (1 mg) was dissolved in the solvent mixture (1 mL) of Nafion (5%) and ethanol ($v/v = 1:9$) under sonication. The suspension (10 μL) was pipetted onto the GC electrode surface and allowed to dry at room temperature.

Synthesis of MB-MWCNT. 4-Mercaptobenzoic acid (MBAC, 5.0 g), MWCNT (5.0 g), PPA (83% assay, 200.0 g), and P_2O_5 (50.0 g) were placed in a 500 mL resin flask equipped with a high torque mechanical stirrer and nitrogen inlet and outlet taps. The mixture was stirred under a dry nitrogen purge. The reaction mixture was heated to 130 $^{\circ}\text{C}$ for a period of 24 h. Because of the dispersion of the MWCNTs, the initially dark reaction mixture (MWCNTs) containing a small amount of white powder (MBAC) became black in color as the reaction progressed. At the end of the reaction, the mixture was a shiny, dark brownish black color. The product was poured into distilled water, and the powder-like precipitate was collected using suction filtration and washed with distilled water. The product was Soxhlet-extracted with water overnight to completely remove any residual reaction medium, and also with methanol overnight to remove any unreacted MBAC. Finally, the sample was freeze-dried under reduced pressure (0.05 mmHg) to give a black powder (yield = 8.67 g, 91.76%). Anal. Calcd for $\text{C}_{19.84}\text{H}_5\text{OS}$ (based on percentage yield): C = 81.77; H = 1.73; S = 11.01. Found: C = 80.63; H = 1.37; S = 11.09.

Synthesis of GNP/MB-MWCNT Hybrids. The GNPs were prepared according to a literature method.²⁹ In brief, an aqueous solution containing 18.4 mL of DI water, 0.5 mL of an aqueous 0.05 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution, and 0.5 mL of an aqueous 0.05 M trisodium citrate solution was prepared in a conical flask. Next, 0.6 mL of an ice-cold aqueous 0.1 M NaBH_4 solution was added to one portion of the mixture under vigorous magnetic stirring. The solution turned a red color immediately after the addition of the NaBH_4 solution, indicating the formation of GNPs (see Figure S1 in the Supporting Information). MB-MWCNTs (50 mg) were dispersed in 30 mL of ethanol under ultrasonic agitation for a period of 3 min. Then the resulting black suspension was added to a solution containing colloidal gold (20 mg) at room temperature. The mixture was stirred for 1 day. The homogeneous, well-distributed solution of the GNP/MB-MWCNT hybrid was collected using filtration, washed with water several times, and freeze-dried under a reduced pressure (0.05 mmHg) to give a dark black powder (yield = 48 mg, 69%).

RESULTS AND DISCUSSION

As shown in Figure 1a, the MB-MWCNTs were prepared using a “direct” Friedel–Crafts acylation reaction in a PPA/ P_2O_5 medium. The reaction between the MWCNTs and MBAC typically involved an electrophilic substitution between the sp^2 -hybridized C–H bonds at the defect sites of the MWCNTs and carbonium ($\text{C}^+=\text{O}$) ions generated by the MBAC. The detailed mechanism is shown in Figure S2 in the Supporting Information. Raman spectra displayed that there are no noticeable changes in intensity ratios of D and G bands (Figure S3 in the Supporting

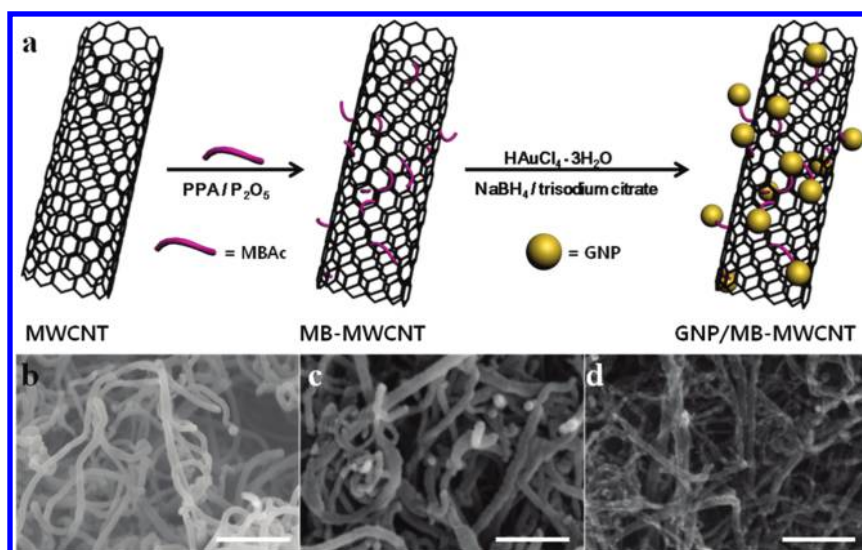


Figure 1. (a) Synthesis of MB-MWCNTs and GNP/MB-MWCNT hybrids, and SEM images of (b) pristine MWCNTs, (c) MB-MWCNTs, and (d) GNP/MB-MWCNT hybrids. Scale bar = 200 nm.

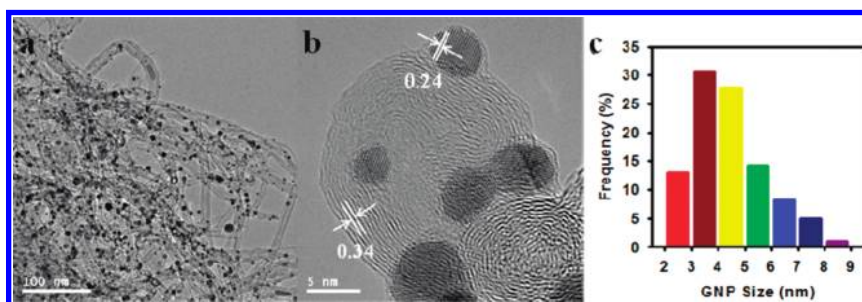


Figure 2. TEM images of GNP/MB-MWCNT hybrids: (a) at low magnification and (b) at high magnification. (c) The size distribution of the GNPs on the MB-MWCNTs. The diameter of the GNPs was determined using the Digital Micrograph software package installed on the TEM machine (see Figure S4 in the Supporting Information).

Information), indicating that the functionalization selectively occurred at the sp²-hybridized C–H bonds. The EA data obtained show that the theoretical and experimental C, H, O, and S contents agree well with the proposal that the reaction to attach mercapto groups (–SH groups, also known as thiol groups) onto the surface of MWCNTs is feasible (see the Experimental Section). It is known that mercapto groups can form stable thiolate–Au bonds,³⁰ and so GNP/MB-MWCNT hybrids were synthesized using a modified literature procedure.³¹

The SEM images show sequential morphological changes on passing from pristine MWCNTs to MB-MWCNTs and GNP/MB-MWCNT hybrids (Figure 1b–d). The MB-MWCNTs have diameters in the range 40–60 nm, whose value is approximately 2–3 times larger than that of pristine MWCNT (~20 nm). This result further supports that the desired functionalization had occurred. SEM images obtained from the GNP/MB-MWCNT hybrids show numerous bright dots that are uniformly distributed on the surface of MB-MWCNTs. This result visually confirms that the GNPs were distributed efficiently on the surface.

Because the GNP/MB-MWCNT hybrids were either in the form of a powder or loose agglomerates, they were dispersed in ethanol. A holey carbon-coated grid was dipped into the sample mixture and then removed to dry in a vacuum oven. TEM images of the GNP/MB-MWCNT hybrids (Figure 2a) show that GNPs were uniformly distributed over the surface of MB-MWCNTs.

No free GNPs were observed in the background on the TEM images, indicating that GNPs were tightly bound to the surface of MB-MWCNTs through strong interactions.

Figure 2b shows a magnified image of the interface between GNPs and MB-MWCNTs. The lattice fringes associated with GNPs have an interplanar spacing of 0.24 nm, consistent with (111) planes of face-centered cubic Au.³² The lattice of the CNTs has an interplanar spacing of 0.34 nm, which is related to the (002) plane of CNTs or graphite.³³

Figure 2c shows the statistical data collected from 300 GNPs, showing the particle size distribution. (See Figure S4 in the Supporting Information. The data were calculated using the Digital Micrograph software program installed in the TEM.) The diameter was in the range 2–8.86 nm, and the average diameter was 4.3 nm. The introduction of mercapto groups on the surface of MWCNTs must have provided anchoring sites for the uniform dispersion and stabilization of GNPs.

TEM element mapping was used as an additional method to characterize the uniformity of the assembly of GNPs on the surface of the MB-MWCNTs (see Figure S5 in the Supporting Information). The scanning TEM images show the presence of O (C=O) and S (S–H) groups from the mercaptobenzoyl (MB) moiety on the MWCNTs, C from the MWCNTs and MB moiety, and Au from GNPs. The presence of O and S in the elemental mapping images confirms that a significant amount of the MB moieties were present

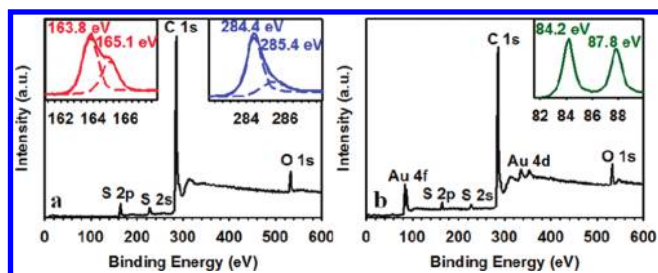


Figure 3. XPS spectra: (a) MB-MWCNTs (the inset shows the S 2p doublet (top left-hand side) and C 1s (top right-hand side)); (b) GNP/MB-MWCNT hybrids (the inset shows the Au 4f doublet).

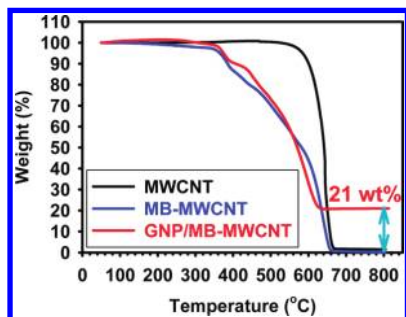


Figure 4. TGA thermograms of the samples using a heating rate of 10 °C/min in air.

on the surface of the MWCNTs. In addition, the Au elemental mapping matched well with the locations of the S element mapping. This result indicates that the GNPs were successfully linked on the surface of the MB-MWCNTs.

To provide further assurance of the existence of Au, S, O, and C in the GNP/MB-MWCNT hybrids, an XPS survey was employed to carry out a surface chemical composition analysis of the samples. The MB-MWCNTs showed significant S 2p, S 2s, and O 1s signals from the MB moiety, and a C 1s signal that was the main contribution from the MWCNTs (Figure 3a). The deconvoluted C 1s peak showed a major C 1s peak occurring at 284.4 eV and a minor peak occurring at 285.4 eV. The former peak was assigned to the carbon occurring in graphite, and the latter peak was ascribed to the carbon atoms present in the C–O group. The C 1s peak in the high-energy region broadened due to the mixing of the sp^2 carbon peak and the peak from carbon atoms bound to sulfur atoms. The peak occurring at 532.2 eV corresponds to O 1s. There was an S 2p peak with a shoulder, and an S 2s peak occurring at 163.8 and 228.0 eV.^{34,35} The S 2p peak was deconvoluted into two separate peaks occurring at 163.8 and 165.1 eV, which are closely related to the –SH states, confirming that the MB had grafted onto the surface of the MWCNTs. These peaks are assignable to the S 2p_{1/2} and S 2p_{3/2} electrons, respectively.³⁶

As shown in Figure 3b, in the case of GNP/MB-MWCNTs, the XPS spectrum showed a strong C 1s peak occurring at 285 eV, an S 2p peak occurring at 164.1 eV, and an S 2s peak occurring at 227.9 eV. New peaks occurring at 84.2 and 87.8 eV are associated with the Au 4f electrons, corresponding to Au 4f_{7/2} and Au 4f_{5/2}, respectively. The emission of 4f photoelectrons from Au was identified by two peaks in the XPS spectra. These were assignable to Au⁰ (occurring at 84.2 and 87.8 eV).³⁷ These are typical values for Au⁰ and strongly indicate the formation of GNPs on the sidewalls of the MB-MWCNTs.

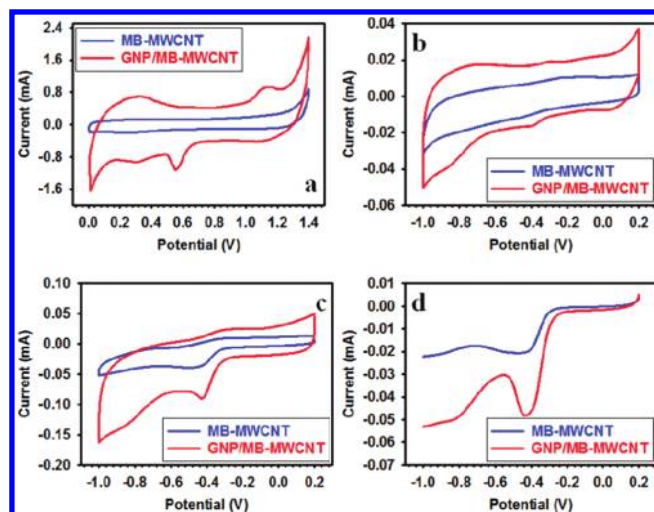


Figure 5. CV curves of MB-MWCNTs and GNP/MB-MWCNT hybrids on GC electrodes using a scan rate of 10 mV/s: (a) in an O₂-saturated 0.1 M aqueous H₂SO₄ solution; (b) in N₂-saturated 0.1 M aqueous KOH solution; and (c) in an O₂-saturated 0.1 M aqueous KOH solution. (d) LSV in an O₂-saturated 0.1 M aqueous KOH solution.

The degree of functionalization and the amount of GNP loaded could be quantitatively estimated using TGA. The powdered samples were subject to TGA using a heating rate of 10 °C/min in air. Pristine MWCNTs, MB-MWCNTs, and GNP/MB-MWCNT hybrids showed temperatures where 5% weight loss ($T_{d5\%}$) in air occurred at 584, 365, and 374 °C, respectively (Figure 4). This confirmed that the organic pendants on MB-MWCNTs were covalently attached to the surface of MWCNTs from the change in inclination of the baseline around 380 °C in air. The amount of organic moiety on the MB-MWCNTs could be estimated from the weight loss occurring at 380 °C and was approximately 15 wt % of the MB moiety. This result agrees well with EA results (see the Experimental Section). The char yields of the MWCNTs and GNP/MB-MWCNT hybrids at 800 °C were 1.5% and 21%, respectively, while MB-MWCNTs showed values close to 0%. This result indicates that the residual amount of pristine MWCNT was because of catalytic residues (1.5 wt %). After functionalization to MB-MWCNTs, the impurities were nearly eliminated in a mild acid treatment.³⁸ Hence, the residual amount of GNP/MB-MWCNT hybrids at 800 °C should be associated with the GNPs, and this amount was 21 wt %. This is a strong indication that GNPs were successfully anchored to the surface of MB-MWCNTs and that the residual value at 800 °C was attributable to the amount of GNP loaded.

The deposition of GNPs on the surface of MB-MWCNTs greatly influenced their electrochemical properties. The higher electroactive surface area of CNT-based nanomaterials always shows a higher electrocatalytic activity.^{39,40} CV was performed in an O₂-saturated 0.1 M aqueous H₂SO₄ solution in the potential range 0–1.4 V versus Ag/AgCl, employing a sweep rate of 10 mV/s. In this way, CV was used to estimate the electroactive surface of the modified electrodes. The CV curves recorded for MB-MWCNTs and GNP/MB-MWCNT hybrids coated on GC electrodes are shown in Figure 5a. While MB-MWCNTs showed almost no redox activity, the GNP/MB-MWCNT hybrid showed a distinct oxidation peak occurring at 0.55 V

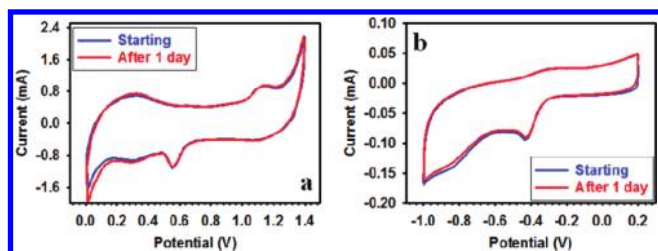
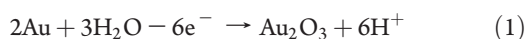


Figure 6. (a) Electrochemical stability measurements on GNP/MB-MWCNT/GC electrodes using continuous CV at a scan rate of 10 mV/s: (a) in an O_2 -saturated 0.1 M aqueous H_2SO_4 solution; (b) in an O_2 -saturated 0.1 M aqueous KOH solution.

and a reduction peak occurring at 1.15 V. According to eq 1,⁴¹ these oxidation peaks are associated with the formation of an oxide monolayer on the GNPs.



Compared with MB-MWCNTs, the peak current of the GNP/MB-MWCNT hybrids was significantly increased, illustrating that the GNP/MB-MWCNT electrode possessed a much higher electrocatalytic activity.

Figure 5b shows the CV curves of the MB-MWCNTs and GNP/MB-MWCNT hybrids on GC electrodes in an N_2 -saturated 0.1 M aqueous KOH solution using a scan rate of 10 mV/s. Featureless voltammetric currents within the potential range -0.3 to -0.6 V were observed. In contrast, a marked catalytic reduction of oxygen by the MB-MWCNTs and GNP/MB-MWCNT hybrids occurred at potentials of -0.48 and -0.43 V, respectively, when the electrolyte solution was saturated with O_2 in the alkaline electrolyte (Figure 5c). This result indicates that GNP/MB-MWCNT hybrids have an excellent electrocatalytic activity for oxygen reduction reactions (ORR), which is a superb performance in an acidic medium compared with a commercial Pt (20 wt %) on activated carbon catalyst (see Figure S6 in the Supporting Information).

The electrocatalytic properties of the MB-MWCNTs and GNP/MB-MWCNT hybrids for ORR were also investigated using LSV in an O_2 -saturated 0.1 M aqueous KOH solution using a scan rate of 10 mV/s. The corresponding results are shown in Figure 5d. The peak current density of the MB-MWCNTs and GNP/MB-MWCNT hybrids was -0.02 and -0.048 mA/cm², respectively. The peak current density of the GNP/MB-MWCNT hybrids, together with the positive shift in the onset potential for the oxygen reduction (Figure 5d), was 2.4 times higher than that of MB-MWCNTs. This result implies that the GNP/MB-MWCNT hybrids possess a higher electrocatalytic activity for ORR than for MB-MWCNTs. This increase in the electrocatalytic activity can be attributed to the uniform dispersion of the GNPs on the MB-MWCNTs, which provides a higher active surface area.

The electrochemical stability under ORR conditions of the GNP/MB-MWCNT hybrids was investigated in O_2 -saturated 0.1 M aqueous H_2SO_4 and KOH solutions for 1 day using sequential CV. There were no obvious changes in the onset potential or in the kinetic current after continuous ORR reactions for a period of 24 h (Figure 6), indicating that the catalytic sites of the GNP/MB-MWCNT hybrids were stable in both acidic and basic media.⁴ The electrocatalytic stability of GNP/MB-MWCNT supposes to be originated from the formation of stable thiolate–Au bonds that prevent aggregation of GNP during electrochemical reaction.³⁰ In addition, unlike oxidized CNTs in strong acids, no additional

oxygenated groups, which are known to deactivate transition metal catalysts,¹³ were introduced to the surface of MB-MWCNT.

CONCLUSIONS

The functionalization of MWCNT with MBAC is indeed a useful approach to introduce a thiol functionality, which provides stable anchoring sites for GNPs. The resulting MB-MWCNTs were used to support GNPs to afford GNP/MB-MWCNT hybrids, which were characterized using several analytical techniques, such as EA, FT-IR, Raman, TGA, and XPS to confirm the functionalization of the MB moiety and the deposition of GNPs. The morphology of the GNP/MB-MWCNT hybrids was studied using SEM and TEM, showing that the GNPs were uniformly distributed on the surface of the MB-MWCNTs. The GNP/MB-MWCNT hybrids showed distinct redox peaks with a much higher electrocatalytic activity and electrochemical stability than MB-MWCNTs in both acidic and basic media. Furthermore, the GNP/MB-MWCNT hybrids displayed a superb electrocatalytic performance for ORR in acidic medium compared to commercial Pt/C catalyst. This result suggests that our new design of a GNP/CNT-based ORR catalyst can be used in energy conversion applications for enhanced performance.

ASSOCIATED CONTENT

S Supporting Information. GNP synthesis, proposed functionalization mechanism, TEM images, EDX, Raman spectra, and CV of Vulcan 72XR. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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