THE EFFECTS OF ANILINE AS A STABILIZER FOR Pt NANOPARTICLES DOPED ONTO THE SURFACE OF REDUCED GRAPHENE OXIDE

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1 Introduction
Metal nanoparticles have attracted considerable interest because of their unique performance in electronic, magnetic, optical, catalytic and many other fields [1]. The specific activity of catalysts is strongly related to their size, distribution and support. Highly distributed catalyst particles with a small size and narrow size distribution are ideal for high electrocatalyst activity owing to their large surface-to-volume ratio. Among the possible supports, carbon black (CB) and carbon nanotubes (CNTs) with dispersed metal nanoparticles (NPs) are used widely as electrodes [2]. Recently, graphene, a new two-dimensional nanomaterial composed of sp2-bonded carbon atoms, has attracted a great deal of attention recently due to its excellent properties and potential applications [3]. These remarkable characteristics enable it to be a promising candidate as a new 2D support to load metal NPs, such as Pt, Au, Pd, etc.[4,5]. It is expected that the metal NPs anchored on a graphene sheet potentially exhibit novel catalytic, magnetic and optoelectronic properties. In particular, platinum NPs have been an intensive research subject for the design of electrodes [6], platinum is an important catalyst for many chemical and electrochemical reactions including oxygen reduction, hydrogen oxidation, methanol oxidation and hydrogenations [7]. Well dispersed, small sized Pt NPs are expected to exhibit enhanced activity and selectivity for catalytic reactions [8]. Recently, a graphene oxide (GO) supported platinum hybrid attracted attention due to their promising applications in catalysis for fuel cell reactions, sensors, gas storage, etc [9-11]. Owing to the easy exfoliation and excellent intercalation properties, GO has been used successfully as a host layered material to prepare hybrids of reduced graphene oxide and metal NPs. During the past decades, researchers have made considerable efforts and developed the preparation of size-controlled spherical metal nanoparticles along with their assemblies [12]. On the other hand, the effective attachment of small-sized Pt NPs dispersed uniformly in large quantities onto the surface of graphene nanosheets remains a great challenge [13]. This paper reports a simple process for preparing well dispersed Pt NPs with a small particle size in large quantities loaded on reduced functionalized graphene oxide (Pt NPs/r-fGO), using aniline as stabilizer. Ethylene glycol (EG) was employed as the reducing agent for the functionalized graphene oxide and platinum nanoparticles (Pt NPs) in a single step using the procedure described previously [14]. The main aim was to develop a simple and effective synthetic route that provides well-dispersed Pt NPs with a small particle size in large quantities on the surface of reduced graphene oxide (r-GO). Aniline was used as a stabilizer for the Pt NPs doped in large quantities onto the surface of r-GO to obtain a uniform dispersion of Pt NPs on the surface of r-GO and control the Pt NP size by avoiding agglomeration on the surface of r-GO. Consequently, the use of aniline as a stabilizer for Pt NPs in large quantities enhances the catalytic performance of the hybrid (Pt NPs/r-fGO). A morphological investigation by transmission electron microscopy (TEM) showed that small Pt NPs in large quantities were loaded uniformly on the surface of r-GO using aniline as a stabilizer compared to the Pt NPs deposited on the surface of r-GO without aniline, which confirmed the effect of aniline as stabilizer for Pt NPs. Therefore, the function of aniline as a stabilizer plays an important role in loading Pt NPs on the r-GO surface.

2 Experimentals

2.1 Materials
Graphene oxide was synthesized from graphite flake purchased from Sigma-Aldrich (Product Number 332461). The aniline monomer was obtained from DC Chemical Co. Ltd. (Korea). Hexachloroplatinic acid (H2PtCl6), ethylene glycol (EG), Sulfuric acid (H2SO4), sodium nitrate (NaNO3), potassium permanganate (KMnO4) and all other organic solvents used in this study were used without further purification.

2.2 Functionalized Graphene Oxide by aniline monomer (f-GO)

Graphene oxide (GO) was synthesized using the Hummers method [15]. To prepare the aniline-functionalized graphene oxide, 0.2 g of GO was mixed with 4g of aniline in 40 ml of Di-water and dispersed by sonication for 4h. The resulting solution was then washed, filtered and dried at 60°C for 24h.

2.3 Synthesis of Pt NPs/functionlized reduced graphene oxide hybrid (Pt NPs/r-fGO)

Pt NPs were loaded on functionalized graphene oxide (f-GO) sheets by the chemical reduction of hexachloroplatinic acid (H2PtCl6) in an ethylene glycol-water solution. During the reaction, ethylene glycol reduces the f-GO and the Chloroplatinic acid in a single step. In a typical procedure, 50mg of f-GO in 50 ml of Di-water was sonicated for 15 min to obtain a homogeneous solution. Amount of aqueous solution of H2PtCl6 was added to the above solution and sonicated for another 15 min. The mixture was added to 40 ml ethylene glycol in a 250 ml flask. The mixture was first ultrasonically treated for 4 h to ensure a uniform dispersion of H2PtCl6 and f-GO in the ethylene glycol-water solution. The reduction reaction was then performed at 100 °C for 24h with constant stirring. The Pt NPs/r-fGO hybrids were finally separated by filtration and washed several times with Di-water. The resulting product was dried under a vacuum at 60°C for 24h. For comparison, Pt NPs loaded on r-GO without aniline were also produced using the same procedure.

2.4 Characterization

Morphological characterization was performed by transmission electron microscopy (TEM, CM200, Philips, Netherlands) to determine the effect of aniline as stabilizer for the Pt NPs on the surface of r-GO. The TEM samples were prepared by dispersing a small amount of dry powder in ethanol. FT-IR, XPS and FT-Raman spectroscopy were used to characterize the chemical structures of GO before and after functionalization by aniline. X-ray powder diffraction (XRD) was used to determine the crystallinity of r-GO, Pt NPs/r-GO and Pt NPs/r-fGO hybrid. The electrical conductivity and sheet resistance of the GO, f-GO, Pt NPs/r-GO and Pt NPs/r-fGO hybrid were measured using a four-probe with an electrical conductivity meter (Hiresta-UP MCP-HT450, Mitsubishi Chemical, Japan).

3 Results and discussion

Fig.1 shows the FTIR spectra of graphene oxide (GO) and (b) aniline functionalized graphene oxide (f-GO). In the GO spectrum (Fig.1a), the peaks at 3458, 1624, 1387 and 1116 cm⁻¹ were assigned to the O-H stretching, C=O stretching, C-O stretching and O-H bend vibrations, respectively. When GO was functionalized chemically by aniline (f-GO), the intensity of these peaks decreased significantly, and some of the peaks almost disappeared. The new peaks at 3458 cm⁻¹ and 1315 cm⁻¹ were assigned to the N–H stretching and C-N stretching vibrations, respectively, confirming the presence of the amine groups of aniline on the GO surface. This confirms the successful functionalization of GO by aniline as a stabilizer. For more confirmation, X-ray photoelectron spectroscopy (XPS) was used to characterize the N1s peak of aniline-functionalized GO. Fig. 2 shows the XP spectra of (a) GO and (b) f-GO, the GO has only C1s and O1s peaks, which was attributed to the carboxyl and carbonyl groups after the oxidation treatment, as shown in the Fig. 2a. After being functionalized by the aniline stabilizer, a new peak appeared at 399.9 eV, which was assigned to the nitrogen band (N1s), as shown in Fig. 2b. The intensity of the carbon (C1s) peak increased due to the incorporation of aniline carbon, and the intensity of oxygen group after functionalized graphene oxide decreased due to the elimination of oxygen groups during the chemical reaction between GO and aniline, which confirmed the successful functionalization of GO by the aniline stabilizer. This data confirms the results obtained by Fourier transform infrared (FT-IR) spectroscopy. Fig. 3 shows the XP spectra of (a) Pt NPs/r-GO and (b) Pt NPs/r-fGO. In the XP spectra, there were peaks for Pt 4f, C1s, Pt 4d, N1s and O1s in Pt NPs/r-fGO. The N 1s peak at 402.24 eV was observed only in the Pt
NPs/ r-fGO in the presence of the aniline stabilizer and not in the Pt NPs/r-GO without an aniline stabilizer, this obvious difference was attributed to the nitrogen in the aniline stabilizer. For the aniline-stabilized Pt NPs/r-fGO hybrid, the interaction between aniline and Pt was characterized by the N 1s line of the XP spectra, as shown in Fig. 3a. The peak for N1s at 402.24 eV demonstrated the presence of nitride bonding (Pt–N) between the head-on N atoms of aniline and the surface Pt atoms of Pt NPs [16]. The benzyl rings surrounding the complexed metal core simultaneously separate the particles from each other and promote the Pt NPs to adsorb onto the surface of the r-GO supports through a – interaction. These results confirm the effect of aniline on the stabilization and dispersion of metal NPs on the surface of nanocarbon materials. The Pt 4f line in the XP spectrum showed two pairs of peaks from the spin–orbital splitting of the 4f7/2 and 4f5/2 (Fig. 4). The most intense doublets observed at 71.47 and 74.68 eV were assigned to zero-valent Pt (Pt(0)). This demonstrates that the well dispersed and Pt(0)-dominated catalysts had been prepared successfully using the aniline stabilizer and highly dispersed on the surface of r-GO. The morphological structure, particle size, and metal dispersion of Pt NPs on the surface of r-GO were examined by transmission electron microscopy (TEM). Fig. 5 and 6 respectively show TEM images and histograms of the metal particle size of Pt NPs/r-fGO and Pt NPs/r-GO. Fifty (50) particles were measured randomly to obtain the particle size distribution. The Pt NPs loaded on the r-GO surface in the absence of aniline are shown in the Fig.5 (a, b and c), the Pt NPs on the r-GO are large and not uniform dispersed, with a mean particle size of 2.69; 3.53 and 5.48 nm corresponding to the (10wt%, 30wt% and 50wt% respectively), due to the aggregation of the Pt NPs upon heat treatment and a weak interaction between the r-GO and platinum atoms. The Pt NPs, which were prepared using the aniline stabilizer with a mean particle size of 1.82 ; 2.51 and 3.11nm corresponding to the (10wt%, 30wt% and 50wt% respectively), were dispersed uniformly on the surface of r-GO, as shown in Fig. 6 (d,e and f). These small Pt NPs suggests a strong interaction between r-GO and platinum atoms because there was no aggregation of the Pt NPs upon heat treatment [17]. Therefore, the function of aniline as a stabilizer plays an important role in loading and controlling the size of the Pt NPs on the surface of r-GO. Fig. 7 shows XRD patterns of r-GO, Pt NPs/r-GO and Pt NPs/r-fGO. The peak at 23.68° moved slightly to a higher angle (25.41°) after the deposition of Pt NPs on r-GO, which indicates that GO is further converted to the crystalline graphene, and the conjugated graphene network (sp2 carbon) has been reestablished by the reduction process. Pt NPs are suggested to play an important role in the reduction of GO when using ethylene glycol as a reducing agent [19]. In addition, crystalline platinum showed strong peaks at 39.19°, 55.02°, 67.34°, and 79.81°, which were assigned to the (111), (200), (220), and (311) crystalline planes of fcc Pt NPs, respectively, indicating a face-centered-cubic (fcc) structure. These results confirm that Pt NPs had been dispersed successfully over the surface of functionalized r-GO. Fig.8 shows the sheet resistance and electrical conductivity of the Pt NPs/r-GO and Pt NPs/r-fGO hybrid as a function of the Pt NPs content. In the case, Fig. 8a and 8d show the sheet resistance and electrical conductivity of the Pt NPs/r-GO hybrid, respectively. A clear decrease in sheet resistance with increasing platinum content was observed, suggesting that the Pt NPs yield improved electrical contact between the r-GO sheets [20]. The sheet resistance decreased from 47.3 to 5.86 K / with increasing PtNPs content in the r-GO from 10wt% to 50wt% respectively. Consequently; the electrical conductivities increases from 6.78×10-4 S/cm to 0.61×10-2 S/cm, respectively. The improvement in electrical conductivity might due to the high Pt NPs loading on the surface of the r-GO hybrid. Fig. 8b and 8c show the sheet resistance and electrical conductivity of the Pt NPs/r-fGO hybrid prepared using the aniline stabilizer, respectively. The sheet resistance
in the r-GO decreased from 25.2 to 0.51 K with increasing Pt NPs content from 10wt% to 50wt%, respectively. Consequently, the electrical conductivity increased from 2.51×10⁻³ S/cm to 4.64×10⁻² S/cm, respectively. The electrical conductivity of the 50 wt% Pt NPs in r-fGO hybrid prepared without the aniline stabilizer was seven times higher than that of the 50 wt% Pt NPs in r-GO hybrid prepared without the aniline stabilizer. The difference in electrical conductivity can be related to the morphological behavior, as shown by the TEM images in Figs. 5 and 6. The electrical conductivity of the Pt NPs/r-GO hybrid was lower than that of the Pt NPs/r-fGO hybrid because the electrical contact point is rather insufficient due to the agglomeration of Pt NPs dispersed randomly over the r-GO surface. From this result, the electrical conductivity of the hybrid is strongly dependent on the morphology, such as the small particle size, loading and highly dispersed Pt NPs on the surface of r-GO.

4Conclusions

A simple one step method was developed to load small sized Pt NPs (~ 3 nm) in large quantities (50wt %) on reduced functionalized graphene oxide using an ethylene glycol solution as the reducing agent and aniline as the stabilizer for Pt NPs without damaging the graphite structures of the r-GO. The morphological investigation confirmed the effect of aniline on the stabilization and dispersion of Pt NPs on the r-GO surface. The aniline-functionalized graphene oxide was confirmed by the appearance of a new peak at 399.9 eV, which was assigned to the nitrogen band (N1s) using XPS analysis. The formation of the Pt NPs and their existence in the hybrid were confirmed by XPS and XRD analysis. The four-point probe investigations revealed higher electrical conductivity and lower sheet resistance of the Pt NPs/r-fGO hybrid prepared using the aniline stabilizer compared to the same weight percentage of the Pt NPs/r-GO hybrid without aniline. The Pt NPs loading on the surface of r-GO with uniform dispersion has a great effect on the electrical conductivity. The enhancement of the electrical conductivity of the hybrid prepared using the aniline stabilizer originated from the morphological structure, such as the small particle size, uniform dispersion in large quantities of Pt NPs and good interfacial interaction between the Pt NPs and r-GO hybrid. Consequently, the resistance decreased in the case of highly dispersed Pt NPs on the surface of the r-GO using aniline stabilizer.

Reference

Figure Captions

Fig. 1. FT-IR spectra of (a) GO and (b) f-GO.

Fig. 2. XP spectra of (a) GO and (b) f-GO.

Fig. 3. XP spectra of (a) Pt NPs/r-GO and (b) Pt NPs/r-fGO hybrid.

Fig. 4. XP spectra of Pt 4f region for Pt NPs/ r-fGO hybrid.

Fig. 5. TEM images and histogram of the Pt NPs of Pt NPs/r-GO hybrids in the absence of aniline with different weights of Pt NPs loaded on the r-GO surface: (a) 10wt%, (b) 30wt%, and (c) 50wt%.
Fig. 6. TEM images and histogram of Pt N of Pt NPs/r-fGO hybrids in the presence of aniline as a stabilizer with different weights of Pt NPs loaded on the surface of r-GO: (d) 10wt%, (e) 30wt%, and (f) 50wt%.

Fig. 7. XRD patterns of (a) r-GO, (b) Pt NPs/r-GO, and (c) Pt NPs/r-fGO hybrid composite.

Fig. 8. Sheet resistance of (a) Pt NPs/r-GO, (b) Pt NPs/r-fGO, and electrical conductivity of (c) Pt NPs/r-fGO, (d) Pt NPs/r-GO as a function of the platinum content in the r-GO hybrids.