Facile Preparation of Graphene Composite Materials and Their Application

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ABSTRACT

A rapid preparation method of graphene oxide (GO), a promising key material for future technology, has been developed. The most common method for synthesizing GO, namely Hummers' method (oxidation with $KMnO_4$ and $NaNO_3$ in concentrated H_2SO_4), requires long reaction time and large amounts of reagents. We have found that the microwave irradiation of natural graphite flake before oxidation step improved the efficiency of the oxidation process. This facile method provides a greater amount of GO as compared to the original Hummers' method. Our rapid synthetic method would contribute to large-scale production of GO. As an application, we used GO as a functional support material of metal nanoparticles.

Keywords: graphene oxide, rapid Hummers' method, metal nano particle, catalyst, composite

1 APPLICATION OF GRAPHENE OXIDE

GO, readily dispersed in water and/or polar organic solvents, has been used for preparing conductive films, binders for carbon nanotubes and nanohorns, and components of cathodes [1] and/or anodes [2] of lithium batteries. Moreover, the oxygen functionalities of GO allows it to form thin films onto substrates, which is necessary for applications in electronics [3]. Besides the above-mentioned applications share the spotlight with other nanocarbon materials, GO has unique advantages in making composites with inorganic materials and organic polymers due to its large amounts of oxygen functionalities.

As an application of our GO, metal nanoparticles were supported on its surface. The present metal/GO composites showed superior catalytic activities.

2 RAPID HUMMER'S METHOD

The source of graphite used for the synthesis of GO is flake graphite, a naturally occurring mineral that is purified to remove heteroatomic contaminants [4]. Generally, the transformation of graphite into graphene oxide (GO) requires the use of strong oxidizing agents. GO has been synthesized from natural graphite powder by the method reported by Hummers and Offeman [5]. It was found that, an additional graphite oxidation procedure was needed prior to the GO preparation. Otherwise, incompletely oxidized graphite-core/GO-shell particles were always observed in the final product. In order to prevent this phenomenon, Kovtyukhova and Mallouk *et al* developed preoxidation before Hummers' oxidation [6]; graphite powder was put into an 80 °C solution of concentrated H_2SO_4, $K_2S_2O_8$, and P_2O_5. After washing and drying, this preoxidized graphite was then subjected to oxidation by Hummers' method. Despite this process realized a higher yield production of GO, larger amounts of wastes were formed. We have focused on simple pretreatment before Hummers' oxidation, and found that irradiation of microwave successfully shorten the oxidation process. In order to exfoliate and/or partially oxidize graphite, microwave irradiation, a powerful tool for heating, is one of the most costless techniques. Graphite displays strong microwave absorption because of its low resistance, with a dramatic temperature increase to 800-1500 °C, as measured by an infrared thermometer, accompanied by luminous sparks [7]. Liu *et al.* reported the production of carbon nanoscrolls from graphite by microwave irradiation under liquid nitrogen [8]. Additionally, carbon nanotubes can be oxidized under microwave irradiation [9]. Based on these observations, it is supposed that the irradiation of microwave under atmospheric oxygen would expand the lattice distance and increase the oxygen content of graphite.

We initially examined the source of graphite for microwave treatment. When the expandable graphite was exposed to microwave, it explosively expanded in a few seconds, which was not desirable (Figure 1).

Figure 1: The expandable graphite before (left) and after (right) the microwave irradiation for 5 seconds.

Our investigation revealed that natural flake graphite was moderately activated by microwave (2.45 GHz, 700 W, 20 sec) irradiation. The partial oxidation was observed by measuring XPS (Figure 2).
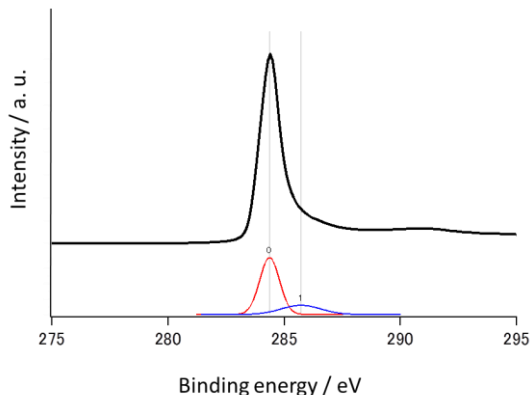

Figure 2: XPS analysis of microwave treated natural flake graphite at C 1s region.

3   CONTROL OF OXIDATION DEGREE

The synthesis of GO with tunable oxidation degrees by simply chemical reactions could provide a significant impact on developing GO as a precursor for large scale production of graphene and serving as a tunable platform for various optoelectronic, physical, biological, and alternative energy applications. As mentioned in the last chapter, the most common methods in synthesizing GO is the Hummers' method. A wide range of structural variations have been reported in literatures, and the interlayer spacing varies from 0.6 nm up to 1.2 nm, depending on synthesis approaches. This fact implies that fine tuning of the reaction conditions enables the control of depending on synthesis approaches. This fact implies that
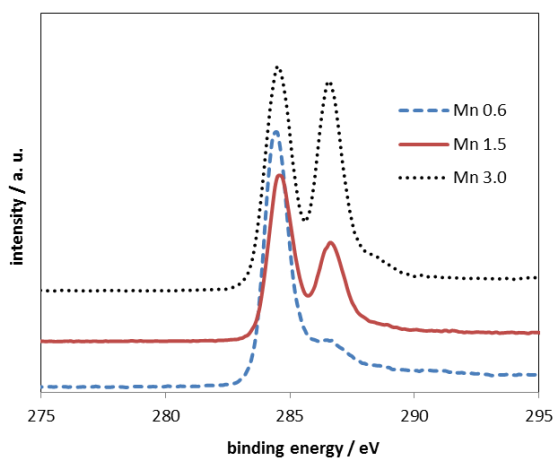

Figure 3: XPS spectra of GO synthesized by changing the amount of $KMnO_4$.

fine tuning of the reaction conditions enables the control of oxidation degree and oxygen functional groups. Lian *et al.* achieved the synthesis of GO with controlling the degree of oxidation by changing the reaction temperature and/or time [9]. We investigated the control of oxidation degree by changing the amount of $KMnO_4$. In the standard oxidation condition, graphite was oxidized by three times its mass of $KMnO_4$. The oxidation degree was determined by XPS analysis (Figure 3). As the amount of $KMnO_4$ was decreased to 1.5 times and 0.6 times mass as a graphite amount, the peak intensity at 284.5 eV increased, meaning that the increase of unoxidized C-C bonds.

4   METAL/GO COMPOSITES

Graphene was found to be a promising support for Pt nanoparticle catalyst [10], which triggered much interest in graphene-supported metal catalysts. In some cases, however, graphene-supported metal catalysts are not preferred. A number of theoretical and experimental studies have shown that, because graphene itself is chemically pretty inert due to the strong sp^2 and π binding between carbon atoms in the graphene plane, the interaction between the metal particles and graphene is quite weak. Consequently, the metal nanoparticles are mobile on graphene [11], which leads to limited application of metal/graphene composite catalysts. It was proposed that defects or mechanical strain in graphene can significantly increase the chemical reactivity of graphene itself and also enhance the interaction between metal nanoparticles [12]. Recently, GO has been attracted much more attention for applications of catalysts. Nanopartcle growth on graphene sheets is an important approach to produce nanohybrids, since controlled nucleation and growth affords optimal chemical interactions and bonding between nanoparticles and graphene sheets, leading to strong electrical and mechanical interactions. Several methods have been proposed to form nanocrystals on graphene sheets, such as electrochemical deposition [13], sol–gel process [14], as well as gas phase deposition [15]. The improved photoelectronic and photocatalytic performance was developed by a TiO_2/GO composite [16]. Another experimental work demonstrated that Co_2O_3/GO showed high stability and catalytic oxygen reduction reaction activity [17], and Pd/GO showed high catalytic activity in Suzuki-coupling reaction [18]. These results triggered our interest in studying metal/GO composites.

We have succeeded to synthesize Pt, Pd, Rh, Rh, Cu, etc. nanoparticles on GO in solution process (Figures 4 and 5). Controlling of the oxidation degree of GO and the oxidation state of metal species would contribute to the application of metal/GO composites in various fields, such as electrodes, fuel cell catalysts, and catalysts for chemical synthesis.
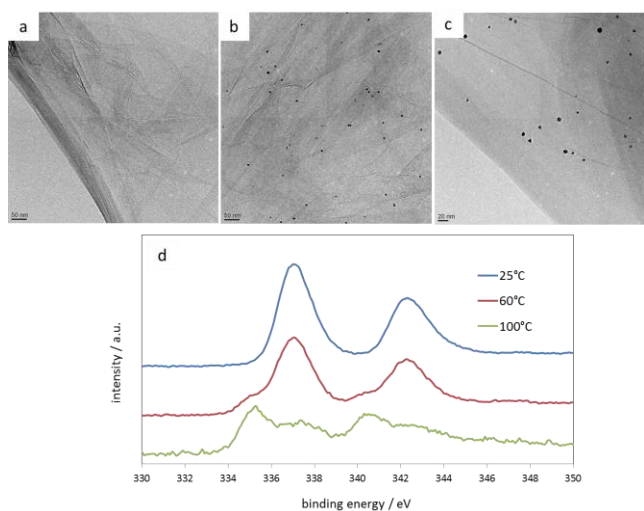
Figure 4: TEM analysis (top) and XPS analysis (bottom) of Pd/GO prepared by changing the reaction temperature; (a) 25 °C, (b) 60 °C, (c) 100 °C.
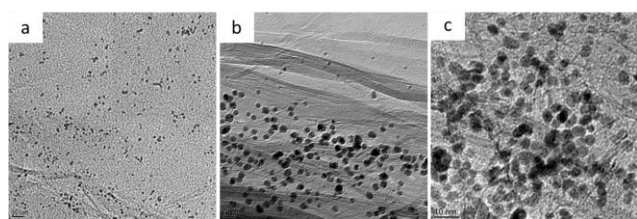

Figure 5: TEM analysis of Pt/GO prepared by changing the reaction conditions; (a) 25 °C with hydrosilane, (b) 100 °C in ethylene glycol, (c) 100 °C in EtOH.

5   METAL/GRAPHENE COMPOSITES

We have developed a new technique for preparing metal–graphene composite materials via intercalation of metal cations into graphene oxide (GO) layers followed by thermal exfoliation [19]. The Pd/graphene composite has a high BET specific surface area of over 500 m^2g^{-1}. TEM observations (Fig. 1a) indicate good dispersion of Pd nanoparticles (average diameter 2–5 nm) and the carbon thin films supporting the Pd nanoparticles consist of mono- and few-layered graphene sheets. TG mass loss analysis revealed that 10.6 wt% of Pd is deposited onto the graphene sheet (Figure 7).
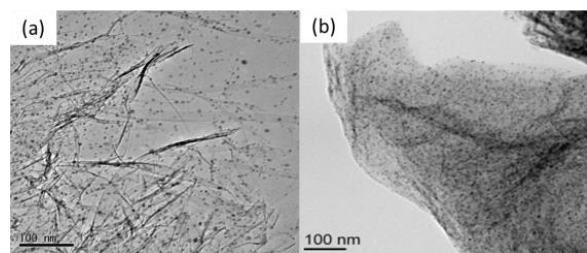

Figure 6: Micrographs of Pd/graphene (1): (a) TEM image of 1 before the reaction and (b) TEM image of 1 recovered after the 2nd cycle and dried in vacuo.
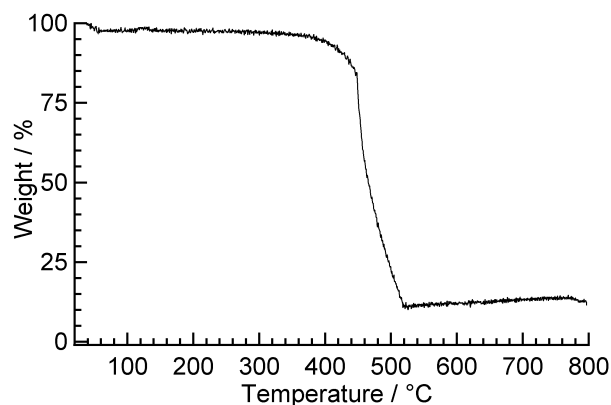

Figure 7: TG mass loss curve for Pd/Graphene.

6   METAL/GRAPHENE FOR CATALYSIS

Previously reported heterogeneous Pd catalysts underwent aggregation of Pd nanoparticles, causing a decrease in product yield when reused as a result of a decrease in the Pd surface area [20]. The Pd/graphene catalyst was found to be recyclable; however, the yield of the product decreased after the third cycle. TEM measurement of catalyst 1 revealed that the Pd particle size did not change before and after the reaction (Figure 6, a and b). This indicates that the catalyst deactivation is not caused by aggregation of Pd. The recovered Pd/graphene catalyst was calcined in air at 300 °C for 30 min, washed with H_2O and EtOH, and dried *in vacuo* to remove impurities adsorbed onto the catalyst. After these catalyst re-activation procedures, the catalytic ability of the Pd/graphene was restored.

Table 2: Recycling experiments with Pd/graphene catalyst.[a]

cycle	1	2	3	4	5	6[b]
yield / %	quant.	97	98	58	34	88

[a] Bromobenzene (0.20 mmol), phenylboronic acid (0.22 mmol) , K_2CO_3 (0.3 mmol), catalyst (1 mg), EtOH (0.25 mL), H_2O (0.25 mL). [b] The catalyst was calcined at 300 °C for 1 h, washed, and dried, then reused.

We tried to confirm the formation of Ph–Pd–Br species using ESI-MS. Pd/graphene (5 mg, Pd content: 0.009 mmol) and bromobenzene (2 mg, 0.013 mmol) were heated in EtOH and H_2O for 30 min. After filtration, the solution was analyzed by ESI(+)-MS using MeOH:H_2O = 1:1 as the eluent. We observed peaks with m/z = 201 and 265, corresponding to Ph–Pd–OH and Ph–Pd–Br species, respectively. This suggests that the Pd was leached by forming Pd(II) with bromobenzene.

In an actual reaction system, Pd would be partially released from and captured on the graphene surface. After

the reductive elimination, the formation of Pd(0) causes the redeposition of Pd on the support. Graphene's sheet structure would prevent aggregation. Other supports such as activated carbon has high surface area, however, the pore size of activated carbon would be too small for Pd(0) to disperse, causing aggregation (Figure 8). This point needs further experiments and discussions to clarify the reason.
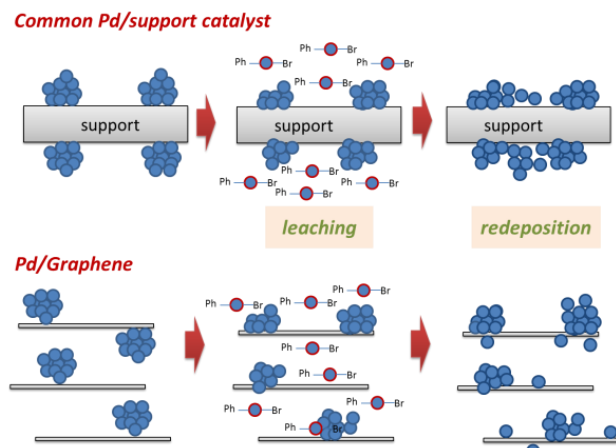

Figure 8: Superiority of graphene as a support material.

7 METAL/GO FOR CATALYSIS

Palladium on activated carbon (Pd/C) is widely used as a heterogeneous hydrogenation catalyst in both laboratory and chemical industry because of its high catalytic activity and ease of handling. Unfortunately however, Pd/C shows less chemoselectivity: when several reducible functionalities are present, mixtures of reduced products could be obtained [21]. When Pd/GO prepared from $Pd(OAc)_2$ at room temperature was used as a catalyst, the olefin moiety of chalcone (**1**) was selectively reduced to give **2a** (Table 1, Entry 1). On the other hand, the use of commercial Pd/C produced a mixture of **2a**, **2a′** and **2a″** (Entry 2). The Pd/GO catalyst showed excellent selectivity even if the reaction was performed in 5 atm of H_2 (Entry 3) or at 60 °C (Entry 5).

Table 1: Reduction of chalcone (**1a**)[a]

Entry	H_2/atm	Catalyst	Yield/%[b]		
			2a	**2a′**	**2a″**
1	1	Pd/GO	>99	0	0
2	1	Pd/C	5[c]	87[c]	3[c]
3	5	Pd/GO	>99	0	0
4	5	Pd/C	0[c]	85[c]	14[c]
5[d]	1	Pd/GO	>99	0	0

[a] Pd (0.1 mol%), **1a** (0.3 mmol), H_2O (1.5 mL), EtOH (1.5 mL) were mixed and stirred under H_2 atmosphere. [b] The yields were determined by GC. [c] The yields were determined by ^1H NMR. [d] Reaction was performed at 60 °C.

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