Systematic analysis of palladium–graphene nanocomposites and their catalytic applications in Sonogashira reaction

Kyoung Hoon Lee a, Sang-Wook Han b, Ki-Young Kwon c, *, Joon B. Park a, *

a Department of Chemistry Education and Institute of Fusion Science, Gyeongsang National University and RINS, Jinju 660-701, Republic of Korea
b Department of Physics Education and Institute of Fusion Science, Chonbuk National University, Jeonbuk 561-756, Republic of Korea
c Department of Chemistry, Gyongginsang National University and RINS, Jinju 660-701, Republic of Korea

Keywords: Palladium–graphene nanocomposites X-ray photoelectron spectroscopy X-ray absorption fine structure Sonogashira reaction Catalysts

A B S T R A C T

Graphene has been modified with palladium nanoparticles (Pd NPs) to develop high performance catalysts for the Sonogashira cross coupling reaction. In this research, graphite oxide (GO) sheets exfoliated from graphite were impregnated with Pd(OAc)2 to prepare Pd2+/GO. Thermal treatments of the Pd2+/GO in H2 flow at 100 °C produced Pd/graphene (Pd/G) nanocomposites. TEM images show that Pd NPs were distributed quite uniformly on the graphene sheet without obvious aggregation, and the mean size of Pd NPs was determined to be less than 2 nm in diameter. Morphological and chemical structures of the GO, Pd2+/GO, and Pd/G were investigated using FT-IR, XRD, XPS, and XAFS. The resulting Pd/G showed excellent catalytic efficiency in the Sonogashira reaction and offers significant advantages over inorganic supported catalysts such as simple recovery and recycling. Finally, deactivation process of the Pd/G in recycling was investigated. We believe that the remarkable reactivity of the Pd/G catalyst toward the Sonogashira reaction is attributed to the high degree of the Pd NP dispersion and thus the increased low coordination numbers of smaller Pd NPs.

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1. Introduction

The homogeneous palladium (Pd) catalyst is known as one of the most efficient catalytic systems for carbon–carbon and carbon–heteroatom bond formations. Properly designed Pd/ligand systems have shown fast reaction rates, high turnover frequency, good selectivity, and high production yields in various C–C and C–X coupling reactions [1–3]. Nonetheless, the use of homogenous Pd catalysts has been limited to a narrow application area since they are difficult to purify and reuse after chemical reactions [1,3]. In particular, the use of ligand-free heterogeneous Pd catalysts is often desirable from the perspective of process development due to their easy handling, simple recovery, and recycling.

A variety of solid-supported metal catalysts with immobilized Pd nanoparticles (NPs) on supports including alumina, silica, zeolite, polymers, and active carbon have been developed [4–10]. Among them, graphene has recently attracted huge attention as a supporting material due to its extraordinary thermal and mechanical stability, high surface area, and ease for surface modification. This implies that graphene has great potential to develop two-dimensional supports to host metal NPs [11–16]. Graphite can be easily converted into graphite oxide (GO) by chemical oxidation according to the Hummers and Offeman method [17], and subsequent thermal or chemical reduction of GO leads to exfoliated graphene sheets [14,18]. If the GO is impregnated with metal precursors and reduced with various chemicals (hydrazine hydrate [11,19], ethylene glycol [20], and SDS [21]) or in H2 environment [22], metal NPs can be prepared on graphene.

Over the last few years, several studies on Pd–graphene synthesis have been conducted; however, a systematic structural analysis of Pd–graphene catalysts has not been reported, and there are only a few examples of catalytic applications [19,20,23]. In the present study, we have exploited graphene as a support for Pd NPs and have selected the Sonogashira reaction as a model reaction to evaluate Pd–graphene (Pd/G) catalysts.

The main purpose of this work is to develop a simple and efficient synthetic route to obtain high performance Pd/G catalysts for C–C coupling reactions and systematically investigate the morphological and chemical structures during the synthetic process and recycling in the Sonogashira reaction. To accomplish this goal, we monitored the chemical synthetic process from graphite to Pd/G using X-ray diffraction (XRD), Fourier transform infrared
spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and transmission electron microscopy (TEM). We investigated catalytic efficiency of the Pd/G in the formation of diphenylacetylene using the Sonogashira reaction of iodobenzene and phenyl acetate. Here, we present that Pd NPs can be homogeneously dispersed on graphene with smaller particle size than any reported in the literature. The resulting Pd/G was shown to act as an efficient catalyst that retained high recyclability for the Sonogashira reaction.

2. Experimental

2.1. Materials and methods

High purity graphite powder (99.99%) and palladium acetate (Pd(OAc)$_2$, 99.99%) were purchased from Sigma Aldrich and used as received. Phenylacetate, iodobenzene, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were obtained from Sigma Aldrich. Powder XRD analyses were performed on multi-purpose high performance X-ray diffractometer (PANalytical). The diffraction data were recorded for 2θ angles between 6.0° and 80°. FT-IR analyses were carried out on a Spectrum GX (Perkin Elmer), and samples were prepared in potassium bromide pallets. XPS spectra were acquired using the Mg Kα (hv = 1253.6 eV) radiation (KRATOS, AXIS Nova). TEM measurements were performed using a JEM-2200FS.

Sonogashira reactions were performed using a microwave reactor (Discover system, CEM). X-ray absorption fine structure (XAFS) measurements were performed at Pd K edge (24,350 eV) by selecting the incident X-ray energy with a three-quarter tuned Si(111) double monochromator at 8C and 10C beamlines of the Pohang Light Source (PLS) at room temperature.

2.2. Synthesis of Pd/G nanocomposites

Graphite oxide (GO) was prepared by the oxidation of graphite powder with H$_2$SO$_4$/K$_2$MnO$_4$ according to the method of Hummers and Offeman [17]. Briefly, graphite (2.0 g) was added to concentrated H$_2$SO$_4$ (50 mL) in an ice bath, and Na$_2$SO$_4$ (1.0 g) and KMnO$_4$ (7.0 g) were slowly added under continuous stirring. After 2 h, the suspension was removed from the ice bath and warmed to 35 °C. The whole batch was carefully poured into a 5 L flask in an ice bath, and H$_2$O$_2$ (30%) was added until gas was no longer detected. Then, the suspension was filtered, washed with a 0.1 M HCl solution and distilled water, and centrifuged at 3,000 rpm. The final product (graphite oxide) was freeze-dried and stored in a vacuum desiccator.

Pd NPs dispersed on graphene (Pd/G) were prepared through an impregnation method combined with heat treatment with H$_2$ gas. Typically, GO (0.9 g) was mixed with Pd(OAc)$_2$ (0.21 g) in 90 mL of distilled water, yielding a homogenous, dark yellow dispersion. The resulting suspension was sonicated for 5 min and stirred for 24 h to promote the intercalation of Pd$^{2+}$ with the GO surface. The suspension was filtered and repeatedly washed with distilled water. The filtrate was centrifuged at 3,000 rpm and freeze-dried, yielding Pd$_2$+/GO. The thermal treatment of Pd$_2$+/GO was carried out using a microwave reactor equipped with gas flow controller (Cole–Parmer), quartz tube, and tubular furnace. The Pd$_2$+/GO was collected in a quartz tube and placed inside a tubular furnace. The furnace was sealed and placed to heat at 120 °C with 300 W in a CEM microwave reactor for 10 min. After cooling to room temperature, the proceeding of the reaction was monitored with thin layer chromatography. The product was purified by silica gel column chromatography using hexane as eluent. After separation, the solvent was evaporated in vacuo and product yield was calculated. The recyclability of Pd/G was studied for the same Sonogashira reaction. After each reaction, the Pd/C catalysts were filtered and washed with ethanol for the next run.

2.3. Reaction procedure for Sonogashira reaction using Pd/G catalysts

220 mg of phenylacetate (2 mmol), 112 mg of iodobenzene (1 mmol), 300 mg of DBU (2 mmol), and 50 mg of Pd/G catalyst were placed in a 5 mL microwave reaction flask. The flask was placed to heat at 120 °C with 300 W in a CEM microwave reactor for 10 min. After cooling to room temperature, the proceeding of the reaction was monitored with thin layer chromatography. The product was purified by silica gel column chromatography using hexane as eluent. After separation, the solvent was evaporated in vacuo and product yield was calculated. The recyclability of Pd/G was studied for the same Sonogashira reaction. After each reaction, the Pd/C catalysts were filtered and washed with ethanol for the next run.

3. Results and discussion

3.1. Preparation and characterization of Pd/G nanocomposites

Fig. 1 shows XRD patterns obtained from graphite powder, graphite oxide (GO), Pd$_2$+/GO, and Pd–graphene (Pd/G). The graphite powder presents a typical sharp diffraction peak at 2θ = 26.7°, which is characteristic for the (002) plane in hexagonal graphite with a corresponding d-spacing of 3.3 Å. The other peaks indicate (100), (010), (004), and (110) planes of graphite, which is in good agreement with previously reported values [24]. Upon oxidation, the diffraction peak at 2θ = 10.9° disappeared. A broad peak at 2θ = 42.5° indicates that small amounts of graphite phases were still present in the GO. The GO was impregnated with Pd(OAc)$_2$, the characteristic peaks for (002) and (100) planes of GO diminished. The impregnation of metal ions on GO is known to produce metal oxide NPs via bond formation of metallic cations with surface oxygen [19]. Therefore, it is reasonable to consider that the reduced peak intensity in GO resulted from Pd oxide formation of Pd$_2$+/GO with surface oxygen. After Pd$_2$+/GO was calcinated into Pd/G in H$_2$ flow at 100 °C, the 10.9° peak disappeared and a

![Fig. 1. XRD patterns of graphite powder, graphite oxide (GO), Pd$_2$+/GO, and Pd–graphene (Pd/G).](image-url)
broad peak centered at $2\theta = 24.8^\circ$ appeared with a d-spacing of 3.7 Å. This indicates loss of a long-range order in the GO stacked layers, implying that oxygen and water were removed from the GO during intercalation, and most of the GO was reduced into graphene. The peak at $2\theta = 39.1^\circ$ is characteristic for Pd(1 1 1) with face centered cubic structure, and the other peaks exhibit Pd(2 0 0) and Pd(2 2 0) plane, suggesting that the Pd is composed of crystal-line nanostructures on graphene.

For further investigation of the chemical structural changes from graphite to Pd/G, we performed FT-IR spectroscopic measurements. Fig. 2 shows FT-IR spectra for GO, Pd$^{2+}$/GO, and Pd/G. After graphene was oxidized into GO, a strong and broad peak was observed at 3410 cm$^{-1}$ corresponding to a stretching mode of $\nu$-OH groups. The characteristic vibration modes of C=O (1720 cm$^{-1}$), C–O (1380 cm$^{-1}$), and $\nu$-OH (1227 cm$^{-1}$) of carboxyl groups, and C=O (1070 cm$^{-1}$) of carbonyl group were observed. The peak at 1620 cm$^{-1}$ is attributed to ̊C–C stretching of the sp$^2$ character in GO. For Pd$^{2+}$/GO, the peak intensities corresponding to oxygen functional groups significantly decreased. This is relatively consistent with the XRD data, where the Pd$^{2+}$ reacts with surface oxygen to produce Pd oxide and the corresponding XRD peak intensity was reduced. When the Pd$^{2+}$/GO was reduced into Pd/G, most peaks for the oxygen functional groups disappeared. However, traces of C=C and $\nu$-OH groups were present, indicating that the GO was not fully reduced to graphene. It has been reported that although reduction of GO results in removing most of the surface oxygen, a small amount of hydroxyl and ether groups is always retained in the reduced GO [14,18]. To convert GO into completely reduced graphene, rapid heating to higher than 1000 °C is required. However, this extreme annealing condition can induce Pd NPs to be sintered and aggregated, which is not appropriate for our catalytic application of Pd/G since larger particle size will deactivate the catalytic performance in the Sonogashira reaction. (see Section 3.2).

In order to investigate electronic structures, XPS measurements for the carbon region (C 1s) were performed as shown in Fig. 3. The C 1s binding energy of graphite has a maximum at 284.7 eV (data not shown) which is a typical peak position for graphite [26]. After oxidation of the graphite into GO, two dominant peaks were observed at 284.7 eV and 286.8 eV. The peak at 284.7 eV is a characteristic peak for C–C bonding of graphite. The other peak at 286.8 eV shows a broad tail to higher binding energy region, which is attributed to emission from the oxidized carbon atoms in the GO. Three components were needed to deconvolute the high binding energy peak (curve fitting was performed using a Gaussian–Lorentzian peak shape after performing a Shirley background correction). They occur at binding energies of 286.8 eV, 287.9 eV, and 289.0 eV, corresponding to the C–OH, C=O, and O=C–O, respectively, which is in good agreement with the FT-IR data presented in Fig. 2. In Pd$^{2+}$/GO, four peaks were still observed at the same binding energy positions, implying that the oxidative structure of GO was retained pretty well after the Pd$^{2+}$ impregnation. However, the relative peak intensity was changed. The high binding energy peak for oxidized carbon atoms decreased by 12% in the normalized peak areas, whereas the peak at 284.4 eV (C–C) increased by 13.2% compared with the GO spectrum. This indicates that bond formation of Pd$^{2+}$ with surface oxygen resulted in the decrease of peak intensity of the surface oxygen functionalities. Specifically, the hydroxyl groups ($\nu$-OH) underwent considerable deoxegenation on the carbon sheet compared with the carbonyl and carboxyl groups. This implies that the Pd$^{2+}$ might preferentially react with the $\nu$-OH functional groups on GO to produce Pd oxide, resulting in the relative increase of the C–C peak intensity. After reduction of the Pd$^{2+}$/GO into Pd/G, a strong peak at 284.7 eV (C–C) was dominant and the peak for oxidized carbon disappeared. The broad tail toward high binding energy indicates that contributions of a variety of different carbon bonding configurations were superimposed.

XPS measurements for the Pd 3d peak were also performed to elucidate the oxidation state of the Pd nanoparticles (Fig. 4). The as-prepared Pd$^{2+}$/GO mainly consisted of +2 oxidation state, as evident from the measured binding energies of Pd 3d$\text{5/2}$ and Pd 3d$\text{3/2}$ electrons at 343.1 eV and 337.8 eV, respectively. After reduction of the Pd$^{2+}$/GO in the H$_2$ (Pd/G) environment, the peaks shifted to lower binding energy by 1.9 eV. The components of Pd 3d$\text{5/2}$ at 341.2 eV and Pd 3d$\text{3/2}$ at 335.9 eV are characteristic for Pd (0).
However, the Pd 3d peak shape became asymmetric on the high binding energy side, indicating incomplete reduction of the Pd$^{2+}$ into Pd. It has been reported that after a metallic Pd foil was etched by argon to remove surface oxide in an ultra high vacuum (UHV), the high binding energy shoulder of the Pd 3d peaks was always observed since Pd can be easily oxidized with low-oxygen base pressure [27]. Similarly, oxidation might occur from air exposure of the sample before XPS measurements even though the freeze-dried Pd/G was stored in vacuum desiccators. The other possibility for the Pd oxidation is that the reduced Pd NPs recombined the residual surface oxygen of the graphene since the graphene was not completely reduced under this preparation condition. At present, it is unclear which process affected the partial oxidation of Pd. Since oxidized Pd NPs are known to have lower catalytic activities in the C–C coupling than metallic Pd NPs [19], more experiments are underway to obtain completely reduced Pd NPs on graphene by adjusting the synthetic conditions.

The morphological changes from graphite to Pd/G were investigated using TEM as shown in Fig. 5. Chemical exfoliation of graphite resulted in a few layered-GO sheets. When the GO was impregnated with Pd(OAc)$_2$, partially aggregated NPs were observed. As we discussed in XRD and XPS sections, the Pd precursors could easily bind with the surface oxygen to produce Pd oxide, which mainly consisted of +2 oxidation state. Therefore, it is reasonable to consider that the NPs dispersed on GO are composed of PdO. It has been reported that the nucleation and growth mechanism depends on the degree of oxygen functionality of the GO, and no metal NPs can be obtained on totally reduced graphene surfaces [11]. This indicates that the oxygen functionality on GO is well prepared and acts as nucleation sites for Pd$^{2+}$ to produce PdO NPs. The average diameter of the PdO NPs was measured to be 7.1 ± 2.3 nm, where more than 50 NPs were randomly chosen and measured in an effort to achieve the desired statistical significance. The mean size of the NPs was 1.4 ± 0.6 nm, and the Pd content in the Pd/G was determined to be 1.6 wt.% using ICP-MS. The stabilization of metal NPs is known to be based on sp$^3$ – sp$^2$ rehybridization of C in the graphene layer via metal–carbon (M–C) bond formation, and the nucleation and dispersion of metal clusters on support are typically dominated by defect sites [28–31]. When the Pd$^{2+}$/GO is calcinated in H$_2$ flow, the PdO NPs are reduced into Pd NPs. The GO is further exfoliated into graphene and sp$^2$ carbon network is restored by hydrogen spillover on Pd NPs and expansion of CO$_2$ evolved between GO sheets during heating, which produces structural defects (dangling bonds) on the surface [12,18,22]. We believe that the defect sites on the graphene are well dispersed and facilitate higher dispersions of Pd NPs with smaller size. The scheme presented in Fig. 5 illustrates the reaction steps involved in the above discussion.

The detailed local structural properties of the Pd NPs were examined using XAFS measurements at the Pd K edge. Figs. 6a and b show XANES and EXAFS spectra of Pd(OAc)$_2$, Pd$^{2+}$/GO, Pd/G, and Pd foil. In general, the XANES can describe the chemical balance state and the local structural properties of X-ray absorbing atom, whereas EXAFS...
whereas Pd/G has a mixed structure of Pd and the local structural properties around the Pd atoms of Pd. The XANES spectra demonstrate that the chemical balance state and the disorder (|FT(k)|^2) of 3.0–11.5 Å were reduced by a factor of 2 for a better comparison to the other values of those of the Pd foil. The EXAFS data were analyzed using the IFEFFIT [33] code and standard procedures [34]. The small oscillations (EXAFS) above the absorption edge were extracted from the XAFS spectra using AUTOBK codes (a part of IFEFFIT). Fig. 7b shows the magnitude of Fourier transformed EXAFS. The EXAFS demonstrates that the local structural properties around Pd atoms of Pd^2+/GO are similar to those of Pd(OAc)_2, whereas Pd atoms of Pd/G have middle values of those of the Pd^2+/GO and the Pd foil, suggesting that the Pd NPs of Pd/G have Pd–O bonds as well as Pd–Pd bonds. In order to determine the local structural properties around Pd atoms of the samples, the XAFS spectra were analyzed using the IFEFFIT [33] code and standard procedures [34]. The small oscillations (EXAFS) above the absorption edge were extracted from the XAFS spectra using AUTOBK codes (a part of IFEFFIT). Fig. 7b shows the magnitude of Fourier transformed EXAFS. The EXAFS demonstrates that the local structural properties around Pd atoms of Pd^2+/GO are similar to those of Pd(OAc)_2, whereas Pd/G has a mixed structure of Pd^2+/GO and Pd foil. The XANES and EXAFS agree well with the XPS data that the Pd NPs of Pd/G are partially oxidized. However, it is still unclear whether the Pd NPs are composed of Pd oxide or locally oxidized near the surface surrounded by oxygen atoms.

The quantitative local structural properties around Pd atoms were obtained by fitting the EXAFS data to EXAFS theoretical calculations [35], as shown in Fig. 7. In these fits, the bond length, coordination number, and disorder (σ^2, including structural disorder and thermal vibration) were varied. The coordination number and the disorder are determined by using a k-weight fit [36]. Table 2 summarizes the fitting results. EXAFS from Pd^2+/GO shows that a Pd atom is surrounded by 5.3 ± 0.3 oxygen atoms with the Pd–O bond length of 2.125 ± 0.005 Å, as shown in Fig. 7a. There were no further atomic shells observed around a Pd of Pd^2+/GO. The EXAFS and the TEM images (Fig. 5) strongly suggest that amorphous Pd–O clusters formed into lumps. After the Pd^2+/GO was calcinated, a Pd atom of Pd/G has only 2.0 ± 0.3 oxygen atoms at 2.186 ± 0.008 Å and 3.1 ± 0.3 Pd atoms at 2.722 ± 0.003 Å as the first and the second neighboring atoms, as shown in Fig. 7b. The bond length and the disorder (σ^2) of the Pd–O pairs on Pd/G are quite similar to those of the Pd^2+/GO, meaning that the oxygen atoms directly bond with the Pd atoms. In order to compare the bond length and the disorder of Pd–Pd pairs on Pd/G to those of a Pd foil, EXAFS from a Pd foil was analyzed. Fig. 7c shows the best fit of EXAFS data from a Pd foil to the EXAFS theoretical calculation [35]. It is known that Pd has an Fm3m space group with a lattice constant of 3.89 Å. The bond length of 2.740 ± 0.002 Å with the disorder of 0.005 ± 0.001 Å^2 for Pd–Pd pairs is determined from the fit. The bond length corresponds to the Pd lattice constant of ~3.88 Å. EXAFS shows that the distance and the disorder of Pd–Pd pairs on Pd/G are comparable to those of Pd foil. This finding is evidence that there are Pd clusters on the Pd/G. Based on the mean coordination numbers of the Pd–O and Pd–Pd pairs of Pd/G, it is predicted that a core Pd atom is surrounded by 12 Pd atoms and an outer Pd atom has two oxygen bonds. In the scenario, the mean diameter of Pd NPs on graphene is estimated to be 0.98 nm which agrees well with the TEM result (Fig. 5). The EXAFS clarifies that only the near surface Pd NPs on Pd/G are locally oxidized (see Table 1).
3.2. Catalytic activity of Pd/G in the Sonogashira reaction

The Sonogashira reaction is one of the most widely used synthetic protocols for carbon–carbon or carbon–heteroatom bond formations. Specifically, microwave-assisted solvent-free Sonogashira reactions have been demonstrated to be an effective approach in organic synthesis due to maximization of substrate loadings, increased selectivity, toxic solvent-free condition, and easy separation for recycling [37–40]. We investigated the catalytic activity of Pd/G in the formation of diphenylacetylene using the Sonogashira reaction of iodobenzene and phenyl acetate (Fig. 8). When the Pd/G was used as the catalyst, reaction yield reached as high as 89%, whereas the Pd$^{2+}$/GO yield was only 54% (Table 2). The highly dispersed metal NPs on supports with smaller diameter are known to have higher catalytic activity due to the advantages of increased low coordination numbers in Pd NPs and larger surface area, resulting in larger number of active sites [41,42]. Therefore, the high catalytic activity can be attributed to smaller particle size less than 2 nm and higher dispersion. The size-dependent electronic structural change may also contribute to increased catalytic efficiency [43,44].

One of the important properties of heterogeneous catalysis is to easily remove catalysts from the reaction mixture and to recycle them for subsequent reactions until the catalysts are deactivated. The recyclability of Pd/G was studied for the same Sonogashira reaction. As shown in Table 2, the Pd/G can be easily recycled up to five times. The catalytic activity was retained until the third recycling, but it dropped in run 4 and 5, showing 55% and 46% conversions, respectively. Evidence for the deactivation of the Pd/G catalyst can be obtained from TEM images. Fig. 8b and c indicate TEM images of Pd/G after the third run of the Sonogashira reaction, clearly showing that the Pd NPs are sintered and agglomerated after the reaction. The average particle diameter was determined to be 13.2 ± 4.1 nm. This result suggests that the deactivation of Pd/G in recycling is attributed to the formation of sintered and agglomerated Pd NPs on graphene.

Many correlated aspects have been considered to explain catalytic activity and deactivation including quantum size effects such as layer thickness [43], under-coordinate effects of metal NPs as sites for binding of substrates [41,42], and electronic effects associated with metal NPs-support interactions [45,46]. Among them, the size of NPs and their size distribution (dispersion) could be an easy way to explain the difference in catalytic efficiency. From this point of view, the high surface area of Pd NPs with higher dispersion is expected to increase reaction binding sites and their catalytic activity. We consider that the size increase in Pd NPs after the cross coupling reaction reduces the number of the under-coordinated Pd atoms in NPs, resulting in deactivation of the nanocatalysts.

4. Conclusions

An efficient synthetic route was developed for even dispersion of Pd NPs on graphene sheets with a particle size less than 2.0 nm, which is the smallest reported value in Pd–graphene catalysts. We show that the presence of oxygen functionalities on GO provides reactive sites for Pd precursors, and Pd$^{2+}$/GO can be directly reduced and exfoliated into Pd/G in H$_2$ flow without any reducing agent. The surface defects on graphene act as nucleation and growth sites for Pd NPs and facilitate higher dispersions of Pd NPs. Since only the surface of Pd NPs on graphene was partially oxidized, the Pd/G showed excellent catalytic efficiency in Sonogashira reaction and offers significant advantages over conventional inorganic supported catalysts such as simple recovery and recycling. This approach is of considerable interest and importance, as it offers a facile way to synthesize Pd NPs with easy control of size by thermal treatments.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2012-0003300). The XAFS data were taken at the 8C and 10C beamlines of PLS.

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