Nitrogen-Doped Graphene Supported Pd@PdO Core-Shell Cluster for C-C Coupling Reaction

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Nano Res., Just Accepted Manuscript • DOI: 10.1007/s12274-014-0492-1
http://www.thenanoresearch.com on May 5, 2014

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## Nitrogen-Doped Graphene Supported Pd@PdO Core-Shell Cluster for C-C Coupling Reaction

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The well-dispersed Pd@PdO core-shell clusters on N-doping graphene (NDG) due to the influence of nitrogen for nucleation and growth kinetics of metal nanoparticles. The Pd@PdO-NDG catalysts exhibit high performance and well structure stability for the C-C cross coupling reaction.
ABSTRACT
The introduction of nitrogen significantly decreases the metal particle size and improves the performance for metal-based graphene-supported catalysts. In this work, the density functional theory is used to understand the interaction between nitrogen-doped graphene and Pd@PdO clusters. The experiments suggest that small size Pd@PdO clusters (1-2 nm) uniform grow on nitrogen-doped graphene sheet by facile oxidation-reduction method. The nanoscale interaction relationship between nitrogen-doped graphene and Pd@PdO clusters is investigated through X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectra (XAS). The composite catalysts are applied in Suzuki-Miyaura reaction to achieve high yields and well structure stability. These results have potential impact in advanced design and optimization of future high performance catalyst materials for cross coupling reaction.

KEYWORDS
Graphene, Nitrogen-doped, Pd cluster, catalyst, Suzuki reaction

1. Introduction
Pd-catalyzed cross coupling reaction is one of the most important methods for the C-C bond forming in organic chemistry [1-4]. Moreover; its outstanding importance has been demonstrated by the Nobel Prize in chemistry 2010. However, to realize the practical application of Pd catalysts in C-C cross coupling reaction such as Suzuki-Miyaura reaction, several important improvements still await to be made, e.g., reduction of the Pd particle size, increase of the catalyst stability, and a decrease of the amount of Pd used [5, 6]. Especially, Pd clusters, the sizes of which range from sub-nanometer to about 2 nm,
could greatly improve their catalytic properties because of their unique electrical structure, large surface area, and high proportion of surface atoms [7, 8]. Moreover, PdO cluster is also selected as a highly efficient heterogeneous catalyst for Suzuki coupling reactions [9]. However, the surface energy will increase with decreasing particle size, which usually leads to serious aggregation for Pd clusters [10]. Moreover, the morphology and size of Pd clusters may be changed during the Suzuki-Miyaura reaction, which will decrease the catalytic performance. To avoid these problems, the introduction of support materials could effectively stabilize the Pd clusters for enhancing catalytic property. In addition, compared to monometallic nanoparticles, the core-shell type structures such as Pd@PdO could exhibit improved electronic, physiochemical, and catalytic properties since the complex electron interaction between the core and the shell component [11].

Recently, many research works suggest that carbon-based support materials can be doped with heteroatoms such as nitrogen and boron to create strong, beneficial catalyst-carbon support interactions which substantially enhance catalyst activity and stability due to the small particle size and the narrower size distribution of catalyst [12]. For example, the nitrogen-doped Vulcan carbon, the nitrogen atoms significantly mediate the Pd adsorption enhancement on its surface base on the density functional theory study [13]. Graphene is one novel atom-thick two-dimensional graphitic carbon material, has attracted increasing interest due to high surface area and good chemical stability [14-18], which can be also used as an ideal support material for growing and anchoring noble metal Pd clusters for Suzuki-Miyaura reaction [19]. In particular, N-doped graphene (NDG) results in an increase in the conductivity as the nitrogen atoms contribute additional electron density in the parent matrix, which will also influence the metal/NDG interaction behavior [20]. The nitrogen in graphene also plays a significant role in determining nucleation rate and growth process of Pd clusters. However, the direct observation of the spatial relationship between the Pd catalyst and N-doped graphene support is still lacking. Notable, the further understand for the interaction between the nitrogen and metal Pd particle is needed.

Thus, this study uses density functional theory (DFT) to calculate the binding energy between nitrogen-doped graphene and the Pd@PdO clusters. Then we prepared Pd@PdO clusters supported on NDG to further investigate the effect of nitrogen on the growth of Pd@PdO clusters. In general, the Pd nanoparticles supported on reduced graphene oxide exhibit large size (>5 nm) and poor distribution (5-20 nm). In our synthesis process, the high quality and smooth graphene sheets were obtained from expanded graphite by quenching method. This smooth support material is beneficial for the uniform distribution of small size metal clusters. Moreover, the N element in NDG not only could stabilize the embedded Pd@PdO clusters, but also prompt the catalytic activity for Suzuki-Miyaura reaction.

2. Experimental

2.1 The synthesis of Pd@PdO-N doping graphene

All chemical reagents were obtained from commercial sources without further purification. The graphite powder was bought from Qingdao Tianyuan Company. H$_2$SO$_4$ (98%), HNO$_3$ (65%), KMnO$_4$, H$_2$O$_2$, HCl, ammonia, ethanol, and methanol were obtained from Beijing Chemical Co., Ltd. The ethylene glycol, palladium acetate, and polyvinyl pyrrolidone were obtained from Sigma-Aldrich Trading Co., Ltd.

In a typical experimental procedure, briefly, we prepared the expanded graphite (EG) using the H$_2$SO$_4$, HNO$_3$, and KMnO$_4$ as the oxidant and intercalation agent. Then, the single- and few-layer graphene was obtained from EG by quenching method, which is similar to our previous works [17]. For purifying the graphene, we selected the simple density gradient separation method to remove the un-exfoliated EG [21]. The density gradient solution contains the ethanol and ethylene glycol with...
different ratio. After separation process, the graphene sheets were dried, and dispersed in ammonia for following hydrothermal process to obtain N-doped graphene sheets similar to our previous work [22].

Finally, the Pd@PdO-NDG was produced by simple reduction reaction for palladium acetate as follows: 150 ml methanol solution including 0.05 g of N doping graphene and 2.5 g of polyvinyl pyrrolidone (PVP) was sonicated for 15 min to produce homogeneous solution. Then, the solution was transferred to the three necked bottle for the follow reflux procedure. Meanwhile, 20 ml methanol solution of palladium acetate (0.22 mmol Pd(C₂H₃O₂)₂) was added into above solution for continuously stirring and refluxing for 2 hour similar to previous report [23], and the temperature remain at 65 °C. After reduction reaction, the black samples (Pd@PdO-NDG) were separated by high-speed centrifugation, washed with ethanol and distilled water for several times, and dried less than 60 °C. For the further comparation, the Pd@PdO-graphene was obtained by similar method as follows: Firstly, the graphene sheets were also prepared from the expanded graphite by quenching method. Then, 150 ml methanol solution including 0.05 g of graphene and 2.5 g of polyvinyl pyrrolidone (PVP) was sonicated for 15 min to produce homogeneous solution. 20 ml methanol solution of palladium acetate (0.22 mmol) was added into above solution for continuously stirring and refluxing for 2 hour at 65 °C in the three necked bottle. Finally, the Pd@PdO-graphene was obtained after centrifugation, washing, and drying.

2.2 The catalytic experiment
The Suzuki cross coupling reaction procedure: A flask was charged with phenylboronic acid (0.75 mmol), K₂CO₃ (1.25 mmol), ethanol solution of Pd@PdO-NDG (4ml, catalyst 5mg/ml), ethanol (4ml), and different substrate (0.5 mmol). The flask was sealed and stirred in a preheated oil bath (80 °C) for 1 hour. After cooling to room temperature, the mixture solution was filtered, followed by taking 10 μL of the mixture for HPLC analysis. Meanwhile, the purification of mixture solution was completed using petroleum ether and ethyl acetate as eluent in a small column of silica gel. Then, the final pure products were obtained by evaporating the solvent. All the isolated products were analyzed by ¹H NMR spectroscopy. In the recycling test of catalyst for Suzuki-Miyaura reaction, five consecutive cycles were tested. After each cycle, the mixture was diluted with ethanol and shaken. The entire mixture was filtrated and washed thoroughly with ethanol and water to assure the removal of all the products from the catalyst surface. The same amount of dry catalyst and then fresh phenylboronic acid and different substrate solution was added to the catalytic system for the next run.

2.3 The Density functional calculations
Calculations were performed within the density functional theory (DFT) framework embedded in the Dmol³ code. The exchange-correlation energy was treated with the Perdew-Wang functional of general gradient approximation (GGA) form. DND basis set (double-numerical plus d-DNP basis), which is comparable to Gaussian 6-31G* basis sets, was used in the calculations. For the core treatment, all electrons were explicitly included. Moreover, to avoid spurious interactions between the periodic images along the z axis, a vacuum region with a length of 15 Å was used. The stable configurations were obtained by geometry optimization from the ideal unrelaxed structures. The whole optimization procedure was repeated until the forces on the atoms were less than 0.002 Ha·Å⁻¹ and the energy change less than 1.0×10⁻⁵ Ha·atom⁻¹.

2.4 Characterization Section
The as-prepared products were measured by the powder X-ray diffraction (XRD) pattern using Rigaku D/max-IIIB with Cu Kα radiation.
The morphology and structure of as-prepared products were observed by high-resolution transmission electron microscopy (HRTEM, JEM-2100) with an acceleration voltage of 200 kV. X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a VG ESCALAB MK II with Mg Kα (1253.6eV) achromatic X-ray source. Thermogravimetric analysis was performed on a TG (TA, Q600) thermal analyzer under air with a heating rate of 10 K/min. The metal Pd ions concentration was measured with ICP-AES (Optima-7000DV).

The X-ray absorption data at the Pd K-edge of the samples were recorded at room temperature in transmission mode using ion chambers or in the fluorescent mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (311) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5GeV and a current between 150-210 mA. The photon energy was calibrated with the first inflection point of Pd K-edge in Pd metal foil. Data processing was performed using the program ATHENA. All fits to the EXAFS data were performed using the program ARTEMIS.

3. Results and Discussion

Firstly, the theoretical investigations concerning the adsorption energy, nature of binding, and charge transfer was performed to confirm the effect of N element on the interfacial interactions and the stabilities of systems. The density functional theory (DFT) calculation was applied to evaluate the binding strength between Pd or PdO clusters and NDG. To facilitate a comparison, the adsorption energy between Pd or PdO clusters and the intrinsic graphene sheet was also considered. The numerical results are listed in Table S1 (Electronic Supplementary Material (ESM)). Due to the possible physical adsorptions, it can be found that the adsorption energies between Pd or PdO clusters and graphene are about -2.21eV and -2.29 eV, respectively.
However, when the PdO clusters approaches NDG, the adsorption energy of the system decreases remarkably (-3.61 eV), suggesting the existence of strong covalent chemical adsorption between them. Similar results are also found for the Pd-NDG system. Figure 1(a) and 1(b) shows the density of states (DOS) for Pd@PdO-NDG and Pd@PdO-graphene systems, respectively. The black line in Figure 1(a) represents the total density of states (TDOS) of each element before the Pd@PdO clusters contacting with NDG, while the red line indicates the TDOSs of each element after contacting with NDG. The calculation results indicate the TDOSs of Pd element, which are mainly composed of Pd 4d states [24], shift to lower energy position. Moreover, the TDOSs for C atoms and N atoms are also changed significantly. In contrast, when Pd@PdO clusters adsorbed on graphene, the relevant TDOS of each element is nearly unchanged, as elucidate in Figure 1 (b). Therefore, it can be expected that the interaction between Pd@PdO and NDG is much stronger than that between Pd@PdO and graphene, and N element is rather helpful to enhance the surface chemical adsorption of Pd on the graphene sheet. Furthermore, the strong Pd-graphene support interactions will control the Pd nanoparticle size and dispersion, since the nature of support could govern the nucleation and growth processes during metal particles deposition.

Figure 1(c) and (d) depicted the electron density differences (EDD) diagrams for Pd@PdO-NDG and Pd@PdO-graphene, respectively. The positive (in blue) or negative (in red) regions indicate where the electron density is enriched or depleted. For the Pd@PdO-NDG (Figure 1c) system, the electron density around N atoms is enhanced, while that around C atoms in N-C bonds is weakened, as compared to the Pd@PdO-graphene in Figure 1(d). Meanwhile, the Mulliken population for Pd in isolated Pd@PdO cluster is about 0.46, and the corresponding values for N and C in the isolated NDG are calculated to be -0.30 and 0.12 respectively. After Pd@PdO cluster contacts with NDG, the Mulliken population of the contacting Pd in Pd@PdO cluster is changed from 0.46 to 0.86, and those of N and C atoms are changed to -0.27 and 0.03, which means considerable electrons transfer between Pd and NDG. The electrons transfer process possibly implies the formation of chemical
bond between Pd@PdO and NDG in Pd@PdO-NDG system. However, when Pd@PdO clusters adsorb on graphene (Figure 1d), the Mulliken change of contacting C atoms varies slightly from 0.00 to -0.05, and the Pd atoms still remain positive (0.46). Therefore, the dopant nitrogen atoms will serve as a mediator to activate nearby carbon atoms, leading to the enhancement of Pd adsorption. Furthermore, due to the large electron affinity of nitrogen, the nucleation and the growth of Pd@PdO clusters on NDG surface will also be influenced, which will result in small-sized, well-dispersed, high-stability Pd@PdO clusters anchoring on graphene as high performance catalyst.

Then, the Pd@PdO clusters anchored NDG for composite catalysts were obtained by facile synthesis method to further proving the theoretical investigation. Firstly, the detailed morphology and structure of as-prepared composite catalyst are characterized using transmission electron microscopy (TEM), and the results are exhibited as Figure 2. The Figure 2 (a) show that graphene within the composite is ultrathin sheet with few folds and crinkles, indicating that graphene obtained from expanded graphite has more stable and flat structure than that graphene from graphite oxide. It is interesting to note that these very small clusters exhibit excellent distribution on the graphene sheets. From the measured particle size distributions as inset in Figure 2 (a), it is clear that average particle size is about 1.8±0.6 nm. Moreover, the high resolution TEM (HRTEM) images (left inset in Figure 2b) show the interplanar spacing of particle lattice is 0.226 nm, which agrees well with the (111) lattice spacing of face centered cubic Pd [25]. Interestingly, the Pd cluster (< 1.5nm) exhibits irregular external structure which is marked by the white arrow possibly due to the part surface oxidation of the Pd clusters to forming PdO (right inset in Figure 2b). In order to compare the role of N element, the Pd-graphene samples are also prepared (Figure S1 in ESM). It is clearly observed that many larger Pd nanoparticles (>10nm) loading on the graphene indicate the nitrogen in graphene could efficiently control the nucleation rate and growth process of Pd clusters. The DFT studies in Figure 1 have shown that carbon substrates forming the C-N defects and the N interstitials can serve as local heterogeneous Pd nucleation sites. Moreover, it can be stated that Pd nucleation preferentially occurs on regions of defective carbon as opposed to well ordered graphitic carbon. The structures of Pd@PdO-NDG were further characterized by X-ray powder diffraction (XRD). The recorded XRD patterns are shown as Figure S2 in ESM, the peaks located at 2θ=26.4, 54.5, and 77.4 are attributed to the (002), (004), and (110) diffraction facets of N-doping graphene, respectively. The peak at 39.4 in Figure S2 correspond to the (111) facets of palladium crystal [26]. However, there is a weak peak at 42.2 could be observed, which is possibly from the (111) facets of PdO. These results also imply the Pd@PdO-NDG composite catalysts are successfully produced. Additionally, the Pd content in Pd@PdO-NDG was investigated by thermogravmetric analysis (TG-DSC) in air (Figure S3 in ESM). On the basis of the TG measurements, it is estimated that the Pd ratio in Pd@PdO-NDG is about 14 wt %, which is also close to the ICP-AES analysis result for Pd content (15.5 wt %).

X-ray photoelectron spectroscopy (XPS) could analyze the surface layer element composition, chemical state, and electronic structure of solid catalyst materials. Thus, XPS technology is also used to further study the electronic structure change and the nitrogen doping effect (Figure 3). Meanwhile, the Pd-graphene was also studied as a reference. Figure 3 (a) shows the high-resolution Pd 3d spectra. For the Pd-graphene, the two peaks located at 335.8 and 341.2 eV can be assigned to Pd 3d5/2 and Pd 3d3/2 of metallic Pd (0), respectively [27]. But, the shoulder peaks at 337.8 eV and 343.2 eV are appeared, which are consistent with the reported values for Pd (II) samples, confirmed the existence
Figure 3 The high-resolution XPS spectra of Pd 3d (a) and N 1s (b) for N-doping graphene, Pd-graphene, and Pd@PdO-NDG. Comparison of the Pd K-edge XANES spectra for Pd@PdO-NDG and Pd foil (c). Fourier transform of $k^2$-weighted EXAFS data for the same sample Pd@PdO-NDG (d) and the inset is structure scheme of Pd@PdO clusters.

of PdO species on the surface of Pd. Interestingly, for Pd@PdO-NDG, Pd peaks obviously shift toward higher binding energy compared to that of the Pd-graphene. Normally, this kind of shift is induced by the change of electronic structure or coordinated environment [16, 28], which due to the presence of strong interactions between Pd@PdO and NDG, and small size effect of Pd@PdO clusters. In the Pd@PdO-NDG system, the nitrogen atoms with more electrons change the electron density around carbon atoms leading to the adsorption energy enhancement of Pd on graphene sheets based on the above theory investigation results, which is beneficial to the growth of Pd@PdO clusters on graphene sheet. In addition, according to the XPS result, the nitrogen concentration is about 4.0 atom %. Furthermore, it is observed that three different types of nitrogen in N doping graphene including the pyridinic nitrogen (398.3 eV), pyrrolic nitrogen (399.6 eV), and sp$^3$ C-N bond (401 eV) in Figure 3 (b). However, for Pd@PdO-NDG, the pyrrolic nitrogen (399.9 eV) is primary composition [29]. The pyrrolic nitrogen atoms donate $\pi$-electron density in carbon network of graphene lattice and contribute to the sp$^2$ character of the graphene network. Therefore, we consider the metal Pd@PdO connects with the pyrrolic nitrogen to forming the stable chemical adsorption structure. Moreover, the pyrrolic nitrogen peak also transfers toward the high energy which further proves the strong interaction between NDG and Pd@PdO.

To supporting above analysis, the X-ray absorption spectra measurements (XAS) were also performed, which were sensitive to valence and local structures.
of investigated elements [16, 30]. Figure 3(c) displays the Pd K-edge of X-ray absorption near edge structure spectra (XANES) for Pd@PdO-NDG together with reference spectra of Pd foil. For the Pd foil reference, the absorption threshold resonance, appearing between 24360 and 24380 eV corresponds to the electronic transitions that arise from the 1s state to the unoccupied 4p states above Fermi level [31]. The second (24385 eV) and third (24435 eV) peaks correspond to 1s→dp and 1s→dsp transitions, respectively. The absorption threshold resonance position and intensity is sensitive to changes in electron occupancy in the valance orbital and ligand field environments of the absorber. However, the Pd K-edge for Pd@PdO-NDG show a distinct shift toward higher energy relative to the reference spectra of Pd foil, which is in accord with results from XPS measurement. This kind of shift is normally induced by change of metal's electronic structure. This shows the presence of strong interface interaction and electron transfer between Pd@PdO and nitrogen-doped graphene. Furthermore, the spectrum of Pd@PdO-NDG also exhibits a small feature at 24372 eV, indicating the presence of Pd (II). In contrast, the intensity of the metallic Pd peak at 24370 eV decreases significantly, indicating the oxidation of Pd clusters for the Pd@PdO, which is also in agreement with the XPS results. Additionally, the Fourier transform of \( k^2 \)-weighted EXAFS data for Pd@PdO-NDG are exhibited in Figure 3 (d) along with reference data for bulk metallic Pd. The results show the first-shell Pd-O signal and the Pd-Pd signal, indicating that the Pd (II) ion was formed directly on the surface of Pd clusters, in good agreement with the XANES and XPS results. The structural parameters derived from the Pd K-edge EXAFS data analyses are shown in Table S2 in ESM. The Pd-Pd coordination number in Pd foil is found to be 9.7±0.5. However, for Pd@PdO-NDG, coordination number is decreased to 2.1±0.2, reflecting a decrease in the average coordination number, as expected in the case of small sized Pd clusters. The coordination number derived from XAS is a nonlinear function of particle diameter, and it has been widely used in EXAFS analysis to determine the size of the nanoparticles. Therefore, based on the Pd crystal cell parameters and physical model, the particle diameter of Pd@PdO clusters is about 1.5 nm with approximate surface single layer PdO structure (Table S2), which is very close to the HRTEM results, and the simple structure sketch of Pd@PdO is also listed as inset in Figure 3 (d). Furthermore, the detailed structure schematics for Pd@PdO-NDG and Pd@PdO-graphene are shown as Scheme S1 in ESM. It is believed that introduction of nitrogen into the graphene support network can also potentially increase utilization of noble-phase metal through improvements in dispersion, catalytic activity, and durability.

The practical application of Pd@PdO-NDG catalysts in C-C cross coupling reaction such as Suzuki-Miyaura reaction were tested using phenylboronic acid and different substrate in the presence of stabilized Pd@PdO-NDG catalytic. Table 1 gives the reaction conditions and results for the different substrate. As shown in Table 1, both these reactions can be successfully performed under these conditions, providing a complete conversions of 100% and high yields of 96% of the corresponding Suzuki reactions products after 1 h at 80 °C, respectively. Among them, the No.3 shows a slightly lower yield rate, which still higher than that of other Pd catalysts at same time in previous reports due to the small size Pd@PdO clusters with high ratio surface atoms [32]. On the contrast, Pd@PdO-graphene catalytic with relatively big and aggregated nanoparticle exhibits low yields for the Suzuki-Miyaura reaction, and the detailed results are shown as Table S3 in ESM. N-dopant induced alteration of catalyst electronic structure, influencing the catalytic reaction. For example, one study showed that C–N surface species interactions with a decorating Pt nanoparticle phase result in a shift to higher binding energy components which may...
Table 1. The Suzuki coupling reactions with the catalyst Pd@PdO-NDG

<table>
<thead>
<tr>
<th>Entry</th>
<th>R1</th>
<th>X</th>
<th>Reaction time</th>
<th>1st Cycle Yield (a) (%)</th>
<th>2nd Cycle Yield (a) (%)</th>
<th>3rd Cycle Yield (a) (%)</th>
<th>4th Cycle Yield (a) (%)</th>
<th>5th Cycle Yield (a) (%)</th>
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<tbody>
<tr>
<td>No.1</td>
<td>NO₂</td>
<td>Br</td>
<td>60 min</td>
<td>96</td>
<td>93</td>
<td>93</td>
<td>92</td>
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<tr>
<td>No.2</td>
<td>CN</td>
<td>Br</td>
<td>60 min</td>
<td>95</td>
<td>94</td>
<td>90</td>
<td>89</td>
<td>85</td>
</tr>
<tr>
<td>No.3</td>
<td>OCH₃</td>
<td>Br</td>
<td>60 min</td>
<td>90</td>
<td>86</td>
<td>84</td>
<td>82</td>
<td>80</td>
</tr>
</tbody>
</table>

*Experiment conditions*: phenylboronic acid (0.75 mmol), K₂CO₃ (1.25 mmol), different substrate (0.5 mmol), ethanol solution of Pd@PdO-NDG catalyst (4ml, 5mg/ml), ethanol (4ml), 80 °C, 60 min. The yield is determined by high-performance liquid chromatography (HPLC) and ¹H NMR.

decrease the specific interaction between the Pt surfaces and detrimental strongly adsorbed intermediates resulting in the catalytic enhancement [33]. Moreover, the pure products for Suzuki reaction were analyzed at detail by the ¹H NMR, and the results were listed in the ESM. Suzuki coupling reaction is composing of the oxidation-addition reaction, the transfer of negative ion toward the metal Pd (II), and the reduction-eliminating reaction [34]. During the reaction, the formation of chemical bond between the metal Pd and the support material could enhance the structure stability of metal Pd@PdO resulting in the excellent catalytic performance. In general, the dopant nitrogen atom could serve as a mediator to activate nearby carbon atoms, leading to the enhancement of Pd adsorption. Therefore, large numbers of small-sized, well-dispersed Pd@PdO clusters are obtained which have more catalytic active centers for coupling reaction. Furthermore, the PdO clusters also possess highly efficient heterogeneous catalyst for Suzuki coupling reactions [35]. In this work, the PdO layer presented on the surface of catalyst exhibits high reactivity active. This is attributed to the strong bonding interaction between the surface atoms of catalytic and the reaction substrates molecule [36]. The Pd@PdO core-shell structure also enhances the catalytic stability. In fact, the experiment shows that the Pd@PdO-NDG catalytic performance is still high after five cycles for Suzuki coupling reaction. To further confirming the structure and morphology change of Pd@PdO-NDG catalyst during the Suzuki reactions, the HRTEM measurements were completed for typical sample after Suzuki coupling reactions (Figure S4 in ESM). The results show that large number of highly uniform Pd@PdO clusters on the NDG could be obtained similar to above TEM analysis. No significant changes could be found indicating the substrate material efficiently connects with the Pd clusters. Meanwhile, the XRD patterns of typical product Pd@PdO-NDG after Suzuki coupling reactions also show that the structure and the oxidation state of catalyst have hardly changed (Figure S2 in ESM). Additionally, the Pd (II) peaks and the Pd (0) peaks for the catalysts before and after Suzuki reaction in XPS spectra are further analyzed to prove the structure stability of Pd@PdO core-shell (Figure S5 in ESM). The result exhibits that the peak intensity of Pd (II) and Pd (0) is remained before and after Suzuki reaction, implying unchanged oxidation state for Pd@PdO catalysts. Meanwhile, the Pd@PdO-NDG catalyst can be re-used for Suzuki reaction without larger loss of its catalytic activity and selectivity. The above results strongly suggest that the stable PdO@Pd core-shell structures on NDG display high activity. The nitrogen has an
4. Conclusions

In summary, the introduction of N-doping graphene could modify nucleation and growth kinetics during Pd@PdO catalyst deposition, which results in smaller Pd@PdO particles, uniform dispersion, and enhanced catalyst durability. Furthermore, the Pd@PdO-NDG catalysts exhibit high yields and well structure stability for the C-C cross coupling reaction. N-doping graphene offers new opportunities for heterogeneous catalysis with different metal clusters.

Acknowledgements

This work was supported by the Key Program Projects of the National Natural Science Foundation of China (No 21031001), the National Natural Science Foundation of China (91122018, 21371053, 51372071), the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No 708029), Special Research Fund for the Doctoral Program of Higher Education of China (20112301110002), the Cultivation Fund of Industrialization for Scientific and Technological Achievements of Heilongjiang Province (1253CGZH13), the Application Technology Research and Development Project of Harbin City (2013AA7BG025). The authors thank beamline BL14W1 (Shanghai Synchrotron Radiation Facility) for providing the beam time.

Electronic Supplementary Material: Supplementary material (the TEM images, XRD pattern, and TG-DSC of products; the adsorption energy calculation for the composites and the 1H NMR spectroscopic analysis of the Suzuki reaction products) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-***.***.

References


Electronic Supplementary Material

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Supporting information to DOI 10.1007/s12274-****-****-# (automatically inserted by the publisher)

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Table S1. Calculated adsorption energies for Pd-NDG, PdO-NDG, Pd-graphene, and PdO-graphene systems.

<table>
<thead>
<tr>
<th></th>
<th>Graphene Energies (Hatree)</th>
<th>Metal clusters Energies (Hatree)</th>
<th>Metal–Graphene Energies (Hatree)</th>
<th>Adsorption Energies (eV)</th>
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<tr>
<td>Pd-Graphene</td>
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<td>-24741.179</td>
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<tr>
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<td>-65130.442</td>
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<td>-65130.442</td>
<td>-70109.201</td>
<td><strong>-3.60912</strong></td>
</tr>
</tbody>
</table>

Figure S1 TEM image of the Pd-graphene, Inset: the HRTEM images for the Pd nanoparticles on graphene.
**Figure S2** XRD patterns of Pd@PdO-NDG before and after the Suzuki reaction.

**Figure S3** TG-DSC curves recorded for the as-prepared samples Pd@PdO-NDG at 1000°C in air.
Table S2. Fit structural parameters derived from Pd K-edge XANES for Pd@PdO-NDG and Pd foil.

<table>
<thead>
<tr>
<th>Shell</th>
<th>N[^a]</th>
<th>R[^b]</th>
<th>(\sigma^2(10^{-3} \text{Å}^2)^[^c]</th>
<th>(\Delta E_0) (eV)^[^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd@PdO-NDG</td>
<td>Pd-O</td>
<td>2.2±0.3</td>
<td>2.00±0.01</td>
<td>2.3±1.6</td>
</tr>
<tr>
<td></td>
<td>Pd-Pd</td>
<td>2.1±0.2</td>
<td>2.76±0.02</td>
<td>8.1±1.6</td>
</tr>
<tr>
<td>Pd foil</td>
<td>Pd-Pd</td>
<td>9.7±0.5</td>
<td>2.74±0.01</td>
<td>5.5±0.2</td>
</tr>
</tbody>
</table>

[^a] Coordination number; [^b] Distance between absorber and backscatterer atoms; [^c] Debye–Waller factor; [^d] Inner potential correction.

Generally, the coordination number \(N\) obtained from the fit of Pd K-edge EXAFS data is the mean of \(N\) for whole Pd atoms. The coordination number of Pd-O \(N_{\text{Pd-O}}\) and Pd-Pd \(N_{\text{Pd-Pd}}\) could be also calculated. Besides, by assuming that the shape of a Pd particle is spherical, we can calculate the ratio of surface atoms \(S\) to its whole atoms \(W\) with a given particle diameter \(d\), as shown as follows:

<table>
<thead>
<tr>
<th>(d) (nm)</th>
<th>1</th>
<th>1.2</th>
<th>1.5</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S/W)</td>
<td>84.5%</td>
<td>78.0%</td>
<td>68.8%</td>
<td>59.3%</td>
<td>42.4%</td>
<td>32.3%</td>
<td>26.5%</td>
</tr>
</tbody>
</table>

If one Pd atom is completely oxidated by O\(_2\), we assume that the \(N_{\text{Pd-O}}\) is equal to 6. Similarly, if one Pd atom is half oxidated by O\(_2\), we assume that the \(N_{\text{Pd-O}}\) is equal to 3. For a spherical Pd particle with oxidation only on the exterior surface, we can simply calculate the ratio \(x\) of Pd atoms on the surface to its whole Pd atoms according to equation (1) and (2).

\[
N_{\text{Pd-O}}=(1-x)\times0+x\times3=3x \quad (1)
\]

\[
N_{\text{Pd-Pd}}=(1-x)\times12+x\times0=12-12x \quad (2)
\]

According to the coordination number of Pd-O \(N_{\text{Pd-O}}=2.2\) for the Pd@PdO-NDG sample, we get the ratio \(x\) of Pd atoms on the surface to its whole Pd atoms as following:

\[ x = 0.73 \quad N_{\text{Pd-Pd}}=2.64 \quad d\approx1.5 \text{ nm} \]

According to serials of results, we find that the calculate result \(N_{\text{Pd-Pd}}=2.64\) of the model that a spherical Pd particle with oxidation only on the exterior surface is most consist with the experiment result \(N_{\text{Pd-Pd}}=2.1\). Therefore, we conclude the Pd@PdO clusters are about 1.5 nm with approximate surface single layer PdO structure.
Figure S4 After the Suzuki reaction, TEM image of the Pd@PdO-NDG catalyst (a) and the HRTEM images of Pd@PdO-NDG (b, c). The (b) and (c) correspond to the black square part and white square part, respectively.

Figure S5 The high-resolution XPS spectra of Pd 3d for Pd@PdO-NDG before and after Suzuki reaction.
Scheme S1. The structure schematic for Pd@PdO-NDG and Pd@PdO-Graphene, respectively.

Table S3. The Suzuki coupling reactions with the catalyst Pd@PdO-graphene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R1</th>
<th>X</th>
<th>Reaction time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>NO2</td>
<td>Br</td>
<td>60 min</td>
<td>83</td>
</tr>
<tr>
<td>No.2</td>
<td>CN</td>
<td>Br</td>
<td>60 min</td>
<td>79</td>
</tr>
<tr>
<td>No.3</td>
<td>OCH3</td>
<td>Br</td>
<td>60 min</td>
<td>66</td>
</tr>
</tbody>
</table>

The experiment condition is similar to the Suzuki coupling reactions by Pd@PdO-NDG catalyst. The yield is determined by high-performance liquid chromatography (HPLC).
Spectroscopic analysis of the Suzuki reaction products

![Diagram of compound 1](image1)

$^1$H NMR (TMS, CDCl$_3$, 400 M Hz): ppm $\delta = 7.741$ (dd, $J_1 = 6.8$ Hz, $J_2 = 1.5$ Hz, 2H); 7.695 (dd, $J_1 = 6.8$ Hz, $J_2 = 1.5$ Hz, 2H); 7.603 (dt, $J_1 = 7.2$ Hz, $J_2 = 2.2$ Hz, 2H); 7.505 (tt, $J_1 = 7.2$ Hz, $J_2 = 2.2$ Hz, 2H); 7.444 (tt, $J_1 = 7.2$ Hz, $J_2 = 2.4$ Hz, 1H).

![Diagram of compound 2](image2)

$^1$H NMR (TMS, CDCl$_3$, 400 M Hz): ppm $\delta = 8.318$ (dt, $J_1 = 9.2$ Hz, $J_2 = 2.2$ Hz, 2H); 7.756 (dt, $J_1 = 8.8$ Hz, $J_2 = 2.2$ Hz, 2H); 7.639 (dt, $J_1 = 8.4$ Hz, $J_2 = 1.5$ Hz, 2H); 7.522 (tt, $J_1 = 8.4$ Hz, $J_2 = 1.5$ Hz, 2H); 7.467 (tt, $J_1 = 6.8$ Hz, $J_2 = 1.4$ Hz, 1H).

![Diagram of compound 3](image3)

$^1$H NMR (TMS, CDCl$_3$, 400 M Hz): ppm $\delta = 7.561$ (dd, $J_1 = 9.2$ Hz, $J_2 = 8.8$ Hz, 4H); 7.639 (t, $J =7.6$ Hz, 2H); 7.315 (t, $J = 7.2$ Hz, 1H); 6.995 (dt, $J_1 = 8.4$ Hz, $J_2 = 2.8$ Hz, 2H); 3.848 (s, 3H).

References