Electronic Supplementary Information

Facile preparation of Pd nanoparticles supported on singlelayer graphene oxide and application for Suzuki–Miyaura cross-coupling reaction

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Materials and Methods

The synthesis of GO was carried out in beaker under air. All Pd-slGO composites were prepared using screw glass bottle vessel under air. Suzuki-Miyaura reaction was carried out using test tube under air. Graphite powder was purchased from Bay Carbon, Inc. H_2SO_4 , NaNO₃, KMnO₄, 30% H_2O_2 , EtOH, Pd(OAc)₂, phenyl boronic acid, bromobenzene, iodobenzene, and sodium carbonate were purchased from Wako Pure Chemical Industries, Aldrich Chemical Co and Tokyo Chemical Industry Co. All reagents were used directly without further purification.

Transmission electron microscopy (TEM) images were obtained by using a JEOL JEM-2100F at an acceleration voltage of 200 kV. X-Ray photoelectron spectroscopy (XPS) measurements were performed on SHIMADZU Kratos AXIS-ULTRA DLD with pass energy of 20 eV. Gas chromatography (GC) analysis was performed on Shimazu GC-2014 equipped with FID detector. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measurement was performed by Agilent 7500c using stock solution of Pd(NO3)2 (0 ppb, 1 ppb, 10 ppb and 100 ppb) for calibration. Atomic force microscope (AFM) images were obtained by Bruker AXS, Multimode 8. Fourier transform infrared (FT-IR) was measured by JASCO ATR PRO450-S with Ge. Raman spectra were measured by JASCO NRS-1000. ICP-AES was measured by Vista Pro, SII using Pd(OAc)₂ treated with aq. HNO₃ as a standard sample.

Large-scale synthesis of GO

Graphite powder (100 g) was added into conc. H_2SO_4 (2.5 L), then the mixture was cooled with an ice bath, KMnO₄ (300 g) was added in portions to keep below 55 °C. The mixture was stirred at 35 °C for 2 h. The resulting suspension was cooled again, and deionized water (5 L) was added slowly to keep below 50 °C with stirring. 30% aq. H_2O_2 (250 mL) was added into the mixture. The resulting crude graphite oxide was moved into centrifuged vessel and purified by centrifugation for 10 times.

Preparation of Pd-slGO composites

20 mL of EtOH and 1.25 mg of $Pd(OAc)_2$ were added to 20 mL of 0.1 wt% GO dispersion in water. Then the mixtures were stirred for 1 h at room temperature (for Pd-slGO-rt), 60 °C (for Pd-slGO-60), or 100 °C (for Pd-slGO-100). The residual Pd in the solution was measured by ICP-AES, and found that 89% (1.11 mg, for Pd-slGO-rt), 89% (1.11 mg, for Pd-slGO-60), and 94% (1.18 mg, for Pd-slGO-100) of Pd(OAc)₂ was deposited on GO.

Other Pd(II) salts, such as Pd(NO)₃, PdCl₂ or PdCl₄NH₄, were used instead of Pd(OAc)₂,

however, reduction of Pd(II) did not occur or large size of Pd particles were formed. When other solvents (only H_2O or aq. *i*-PrOH) were used instead of aq. EtOH, reduction of Pd(II) did not occur and catalytic activity for Suzuki–Miyaura coupling reaction was low.



Charactalization of Pd-slGO composites

Figure S1. XRD spectra of Graphite, GO, and Pd-slGO-60.

Because Pd NPs are small enough, no significant peak of Pd(0) and PdO were observed. In addition, the peak of GO (2θ = 10.5) did not shift after deposition of Pd.



Figure S2. Raman spectra of (a) GO and (b) Pd-slGO60. The ratio of the peak intensity of the G and D bands was almost unchanged.

Representative procedure for Suzuki-Miyaura cross coupling reaction

For the synthesis of biphenyl (3a), bromobenzene (1a, 0.50 mmol), phenylboronic acid (2a, 0.55 mmol) and sodium carbonate (0.75 mmol) were added in 50% aq. EtOH (3 mL). Then, Pd-slGO suspension (containing 0.01 mol% of Pd) was added and stirred at room temperature for 1 h.

All products were already known. The structure of the products were determined by NMR comparing with the previous reports $(3a-c, 13d, 23e^3)$. The product yields were determined using dodecane as an internal standard, or isolation with silica gel column chromatography.

Comparing Pd-slGO with other previous catalysts

In comparison with previous Pd-Graphene and Pd-GO catalysts, our Pd-slGO has larger amount of oxygenated functional groups on GO sheets, which would increase dispersibility in polar solvents and prevent aggregation of both GO and Pd NPs. The Pd-slGO catalyst gave high catalytic activity for Suzuki–Miyaura cross coupling reaction with a remarkable TON and TOF of 237,000, compared with the previous reports (Table S1).

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Catalyst	Oxidation state of Pd	Pd particle diamater (nm)	TOF and TON	Reuse	Reference
Pd-GO	(II)	4±1	39,000 and 6,700	-	4
Pd-G	(0)	7–9	108,000 and 9,000	5 times	5
Pd-partially reduced GO (PRGO)	(0)	7.8±3.5	230,000 and 7,800	3 times	6
Our work (Pd-sIGO)	(II) and (0)	7.7±2.8	237,000	2 times	

Table S1. Comparison of the catalytic activity

Recycling experiment with Pd-slGO-60



Table S2. Recycling experiment with Pd-slGO-60

After each reaction, the resulting mixture was centrifuged with water and THF (3 times) to remove inorganic salt, starting materials, product, and byproducts. The product yield was significantly dropped after 3rd cycle. The reason of the decreased yield after the second recycling is not clear. We think one of the possible reasons is additional Pd-rGO (used Pd-slGO) reduction and aggregation occurred during second recycling reaction.



Figure S3. TEM images of fresh Pd-slGO-60 (a, b) and used Pd-slGO-60 for 4 times (c, d). The large thin GO sheet was observed in a. While, aggregated GO sheets were observed in

c. Well-dispersed nanoparticles were supported on the GO sheet as shown in b. While, aggregated nanoparticles were observed in d, although keeping a small primary particle size. (e) Particle size distribution derived from TEM images of Pd-slGO-60 after reaction. The mean diameter $(4.9 \pm 1.5 \text{ nm})$ was smaller than that of Pd-slGO-60 before reaction $(7.7 \pm 2.8 \text{ nm})$, suggesting the partial leaching and re-deposition of Pd during the catalytic process. The inset image in b is an electron diffraction pattern with the [001] zone axis of the fresh Pd-slGO-60. The well-defined diffraction spots show the highly crystalline feature of GO. GO was found to be unstable under electron beam irradiation. During the TEM observation, after a few minutes exposure of electron beam irradiation, the 100 and 110 spots became ring-like pattern indicating amorphousness, which was presumably caused by the elimination of the oxygen-containing functionalized groups and damaging of the graphene sheet.

References

- 1. Spectral Database for Organic Compounds, http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology)
- 2. M. -T. Chen, D. A. Vicic, M. L. Turner, O. Navarro, Organometallics, 2011, 30, 5052.
- 3. M. Giannerini, M. Fañanás-Mastral, B. L. Feringa, Nature Chem. 2013, 5, 667.
- 4. G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, J. Am. Chem. Soc., 2009, 131, 8262.
- 5. A. R. Siamaki, A. E. R. Khder, V. Abdelsayed, M. S. El-Shall, B. F. Gupton, J. Catal., 2011, 279.
- 6. S. Moussa, A. R. Siamaki, B. F. Gupton, M. S. El-Shall, ACS Catal., 2012, 2, 145.