

# Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

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

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

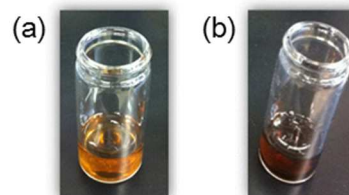
Shun-ichi Yamamoto,<sup>a</sup> Hiroshi Kinoshita,<sup>b</sup> Hideki Hashimoto,<sup>b</sup> and Yuta Nishina<sup>\*a,c</sup>

**Pd nanoparticles supported on single layer graphene oxide (Pd-slGO) was prepared by gentle heating of palladium (II) acetate (Pd(OAc)<sub>2</sub>) and GO in ethanol that served as a mild reductant of Pd precursor. Pd-slGO showed a high catalytic performance (TON and TOF = 237 000) in Suzuki–Miyaura cross-coupling reaction.**

In addition to graphene, graphene oxide (GO) has attracted much attention for application in the preparation of functional materials.<sup>1–5</sup> Flake graphite is typically employed as a source material for the synthesis of GO. Therefore, large-scale production of GO is possible even at the laboratory level (~100 g/day).<sup>†</sup> GO has oxygen functional groups at the edge (hydroxyl, carbonyl, and carboxyl groups) and on the plane (hydroxyl and epoxy groups) of the GO layer. Therefore, GO can form stable dispersions in water and polar organic solvents, which facilitates handling and functionalization using chemical techniques.<sup>1,6,7</sup> GO is an ideal precursor for mass production of graphene. However, because of the difficulty in completely removing oxygen from GO, it is impossible to fabricate perfectly structured graphene.<sup>8–11</sup> As such, one promising application of GO is to synthesize composites with novel functionalities. The surface oxygen functional groups and defects on GO can act as nucleation sites,<sup>12,13</sup> thus, GO can be used as a support material for metal nanoparticles (NPs).<sup>14–16</sup> Various graphene- and GO-supported metal NPs have been used as catalysts in organic reactions,<sup>17–23</sup> fuel cells, lithium-ion batteries, and supercapacitors.<sup>24–27</sup> Among these applications, we have focused on the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction that is a powerful tool to construct functional biaryl frameworks.<sup>28,29</sup> In 2009, Mülhaupt *et al.* reported a Pd(II)-graphite oxide-catalyzed Suzuki–Miyaura cross-coupling reaction with a turnover frequency (TOF) exceeding 39 000 h<sup>-1</sup> and a low Pd leaching in the reaction mixture.<sup>30</sup> Since then, many Pd-GO and Pd-graphene composites have been prepared and used as catalysts in cross-coupling reactions.<sup>31–40</sup> However, there are no reports on the preparation of Pd-single layer GO (slGO) composites—Pd NPs are usually deposited on GO under reductive and harsh conditions that leads to the undesired reduction of GO, which causes aggregation of

the GO sheets.<sup>41</sup> Herein, we focused on the preparation of Pd-slGO composites, with a high Pd NPs dispersibility, as a quasi-homogeneous/heterogeneous catalyst in liquid-phase organic reactions. A simple and practical preparation method for the synthesis of Pd-slGO composites using aqueous ethanol as solvent and reductant is demonstrated. The composite was characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). The prepared composite was then investigated as a catalyst in the Suzuki–Miyaura cross-coupling reaction.

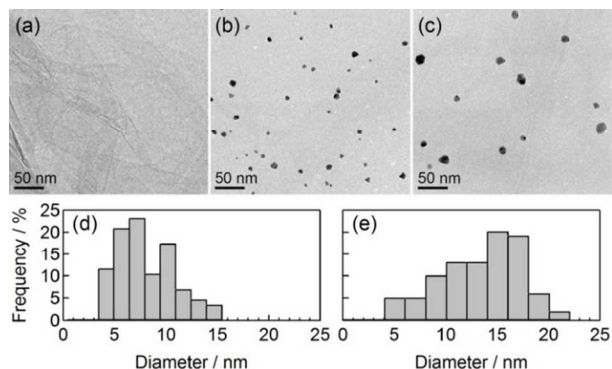
GO was prepared according to a modified Hummers method (Fig. 1a).<sup>42,43</sup> The Pd-slGO composites were prepared as follows: 20 mL of ethanol (EtOH) and 1.25 mg of Pd(OAc)<sub>2</sub> were added to 20 mL of 0.1 wt% GO dispersion in water. Then, the mixture was stirred for 1 h at room temperature, 60 °C or 100 °C; the resulting samples are denoted as Pd-slGO-rt, Pd-slGO-60, and Pd-slGO-100, respectively. The color of the solutions changed from yellowish brown to dark brown (Fig. 1b), and the smell of acetaldehyde was detected during the preparation of Pd-slGO-60 and Pd-slGO-100. The Pd-slGOs were washed by centrifugation with water (twice) and acetone to remove the byproducts (AcOH and acetaldehyde), then re-dispersed in water.<sup>†</sup>



**Fig. 1** (a) GO and (b) Pd-slGO-60 in water.

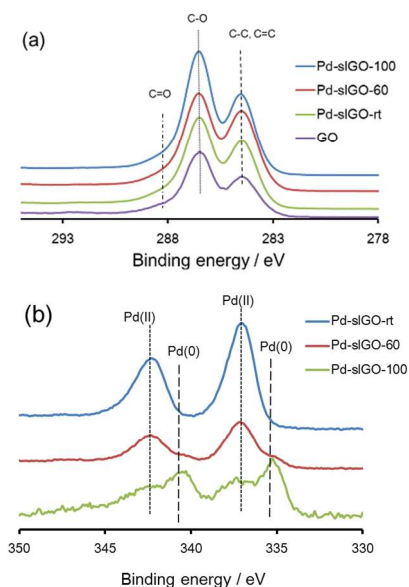
The particle size of Pd on GO was measured by TEM (Fig. 2). The nucleation and size of the Pd NPs were dependent on the preparation temperature. When Pd-slGO was prepared at room temperature, Pd NPs were rarely found (Fig. 2a). In contrast, increasing the preparation temperature to 60 and 100 °C led to the

observation of the Pd NPs (Fig. 2b and c). Pd-slGO-60 featured Pd NPs with a bimodal size of  $\sim 6$  nm and  $\sim 9$  nm with the average particle diameter of  $7.7 \pm 2.8$  nm (Figs. 2b and d). Pd-slGO-100 has one peak at  $\sim 15$  nm with the average particle diameter of  $13.5 \pm 2.8$  nm, which is nearly twice larger than that of Pd-slGO-60.



**Fig. 2** TEM images of Pd-slGO composites prepared at (a) room temperature, (b) 60 °C, and (c) 100 °C. Particle size distributions determined by TEM images of (d) 86 particles of Pd-slGO-60 °C and (e) 99 particles of Pd-slGO-100 °C.

Fig. 3 shows the XPS spectra of GO and Pd-slGOs. In general, the C 1s XPS spectrum of GO features peaks at 284.5, 285.6, 286.7, 287.7, and 289.0 eV that correspond to C=C, C-OH, C-O, C=O, and HO-C=O, respectively.<sup>44</sup> The GO and Pd-slGO composites prepared in this study also featured the same peaks (Fig. 3a). This finding indicates that the reduction of GOs is insignificant during the deposition of Pd. In contrast, the Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> XPS spectra displayed peaks at 335.3 and 340.5 eV, and 337 and 342.3 eV, which correspond to Pd(0) and Pd(II), respectively (Fig. 3b). The preparation temperature significantly influenced the oxidation state of Pd: Pd-slGO-rt was mainly composed of Pd(II), whereas half of the Pd(II) content was reduced to Pd(0) in Pd-slGO-100.



**Fig. 3** XPS spectra of GO and Pd-slGOs: (a) C 1s and (b) Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> regions.

The catalytic activity of the Pd-slGO composites in the Suzuki–Miyaura cross-coupling reaction was investigated using bromobenzene (**1a**) and phenylboronic acid (**2a**) in 50% aq. EtOH at room temperature for 1 h (Table 1). Pd-slGO-rt and Pd-slGO-60 catalysts produced biphenyl (**3a**) in 50% and 66% yields, respectively (Table 1, entries 1 and 2). In contrast, the yield significantly decreased when Pd-slGO-100 was used as the catalyst (Table 1, entry 3). Similarly, the catalytic activity was low when Pd and GO were reduced by hydrazine hydrate (Table 1, entry 4). These results suggest that the Pd NPs of  $>10$  nm are not active in the particular reaction.<sup>31,45</sup>

Table 1. Catalyst optimization<sup>a</sup>

Entry	Catalyst	Yield (%) <sup>b</sup>
1	Pd-slGO-rt	50
2	Pd-slGO-60	66
3	Pd-slGO-100	4
4	Pd-rGO <sup>c</sup>	16

<sup>a</sup>Bromobenzene (**1a**, 0.50 mmol), phenylboronic acid (**2a**, 0.55 mmol), K<sub>2</sub>CO<sub>3</sub> (0.75 mmol), and Pd-GO (0.01 mol% Pd) were mixed in 50% aq. EtOH (3 mL) at room temperature for 1 h. <sup>b</sup>Yields were determined by GC using dodecane as an internal standard. <sup>c</sup>Pd-rGO composite was prepared by reduction with hydrazine at 90 °C for 2 h.

The performance of the reaction was then investigated under optimal reaction conditions using Pd-slGO-60 as the catalyst (Table 2). The reaction between **1a** and **2a** was performed for 2 h at room temperature to give **3a** in quantitative yield (Table 2, entry 1). The leaching of Pd following completion of the reaction was monitored by ICP-MS; only 0.10 ppm of Pd was detected. Although an aryl bromide possessing an electron donating group (**1b**) was less reactive than that with an electron withdrawing group (**1c**), both substrates could generate products **3b** and **3c** quantitatively by changing the reaction time (Table 2, entries 2 and 3). The tendency was altered by changing the electronic state of the arylboronic acids; the reaction proceeded smoothly when an electron donating group was substituted (Table 2, entry 4), and the product yield decreased when electron withdrawing group was substituted (Table 2, entry 5). Heterocyclic bromides, such as thienyl bromide (**1d**) and indolyl bromide (**1e**), were also examined in the present catalyst system (Table 2, entries 6 and 7). The reaction between iodobenzene (**1f**) and **2a** displayed the highest catalytic activity with a turnover number (TON) and TOF (h<sup>-1</sup>) of 237 000 (Table 2, entry 8). Catalyst activity with both TON and TOF (h<sup>-1</sup>) exceeding 100 000 at room temperature is rarely reported. The single-layer hydrophilic sheet structure onto which polarized substrates, especially arylboronic acids, can easily adsorb and from which the less polarized biphenyl products can readily dissociate is one of the main factors contributing to the high activity of the Pd-slGOs.

The surface areas of the Pd-slGOs were measured via nitrogen sorption studies (Macrosorb Model 1201, Mountech); the Brunauer–Emmett–Teller (BET) method was applied on the nitrogen gas adsorption branch. The measured surface areas were less than 30 m<sup>2</sup> g<sup>-1</sup> that are significantly lower than the theoretical surface area limit

of graphene ( $2630 \text{ m}^2 \text{ g}^{-1}$ ). This result suggests that the BET surface area of the composite in the dry state was affected by the stacking of the GO sheets. Despite the dispersibility property of Pd-slGO in

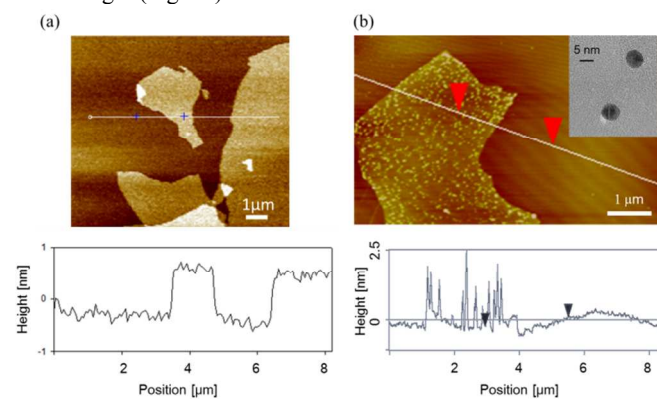
Table 2. Investigation of substrates<sup>a</sup>

Entry	1	R' 2	Product	Time (h)	Yield (%) <sup>b</sup>
1		H		2	99
	1a	2a	3a		
2		H		3	99
	1b	2a	3b		
3		H		1	99
	1c	2a	3c		
4		OMe		3	99
	1a	2b	3d		
5		Ac		24	83
	1a	2c	3e		
6		H		3	99 <sup>c</sup>
	1d	2a	3f		
7		H		24	76
	1e	2a	3g		
8		H		1	44 <sup>d</sup>
	1f	2a	3a		

<sup>a</sup>Aryl halide (**1**, 0.50 mmol), aryl boronic acid (**2**, 0.55 mmol),  $\text{K}_2\text{CO}_3$  (0.75 mmol), and Pd-slGO-60 (0.01 mol% Pd) were mixed in 50% aq. EtOH (3 mL) at room temperature. <sup>b</sup>Yields were determined by GC using dodecane as an internal standard. <sup>c</sup>The reaction was performed under reflux condition. <sup>d</sup>0.00016 mol% of Pd was used.

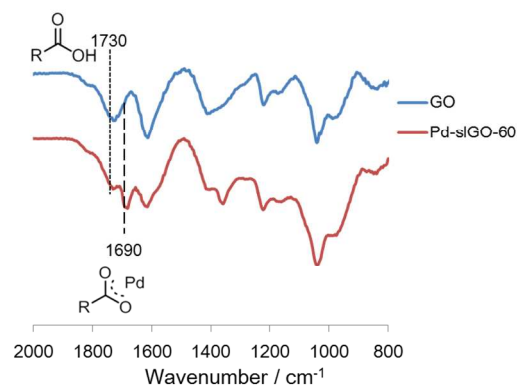
polar solvents, nitrogen gas does not penetrate the GO layers. Hence, to re-evaluate the BET data of the samples, the samples were suspended in a methylene blue (MB) dye aqueous suspension. MB has been previously used as a probe to estimate the surface area of graphitic materials; 1 mg of adsorbed MB can be assigned to a surface area of  $2.45 \text{ m}^2$ .<sup>46,47</sup> A known amount of MB solution was added to the GO or Pd-slGO suspensions, stirred, allowed to settle, and centrifuged to remove the suspended material. Based on the concentration of MB in the supernatant, as determined by UV-vis spectroscopy, the surface areas were estimated as  $1170 \text{ m}^2 \text{ g}^{-1}$  (GO),

$1145 \text{ m}^2 \text{ g}^{-1}$  (Pd-slGO-rt),  $1097 \text{ m}^2 \text{ g}^{-1}$  (Pd-slGO-60), and  $1001 \text{ m}^2 \text{ g}^{-1}$  (Pd-slGO-100). However, these values remain smaller than the theoretical value. Although the surface area of the dispersed GO (as opposed to the solid state GO) is more likely to reflect the actual surface area, the adsorption of MB molecule is likely influenced by the oxygen functional groups and Pd NPs present on the GO surface. The discrepancies in the surface areas determined by the BET and MB methods prompted the use of AFM to assess the presence of slGO (Fig. 4a). The prepared GO featured a thickness of 0.8 nm, which is comparable with that reported for slGO.<sup>48</sup> It is important to note that the height of GO remained smaller than 1 nm after deposition of the Pd NPs, and the NPs were clearly observed at ~2 nm in height (Fig. 4b).



**Fig. 4** AFM images of (a) GO and (b) Pd-slGO. The inset image is a corresponding TEM image of the Pd NPs on GO.

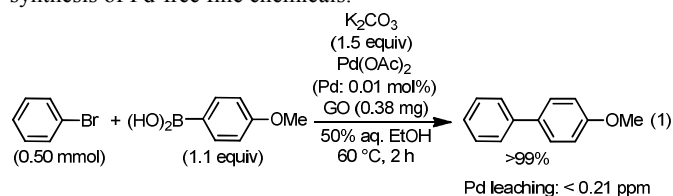
FT-IR spectroscopy was employed to analyze the environment of the oxygen functional groups on GO that would interact with Pd. As depicted in Fig. 5, characteristic absorption bands corresponding to the C–O stretching, O–H bend vibration, and C=O carbonyl stretching were observed at  $1050 \text{ cm}^{-1}$ ,  $1380 \text{ cm}^{-1}$ , and  $1730 \text{ cm}^{-1}$ , respectively. Compared with the prepared GO, the C=O stretching of Pd-GO was slightly shifted to a shorter wavenumber, *i.e.*  $1690 \text{ cm}^{-1}$ , suggesting the formation of Pd carboxylates on GO.



**Fig. 5** FT-IR spectra of GO and Pd-slGO-60.

TEM and XPS analyses of the used Pd-slGO-60 catalyst were performed after the reaction. As a result, the oxygen functional groups on GO were partially removed.<sup>49</sup> GO nanosheets and Pd NPs were aggregated, and the average particle size slightly decreased (See Figures S3c and d).† The activity of the catalyst gradually decreased after 3 cycles. These results suggest that dispersibility of Pd NPs and GO nanosheets derived from their surface functional groups are primarily responsible for the high catalytic activity.

Nevertheless, formation of large Pd particles and leaching into solution of Pd were rarely observed. Pd leaching was only 0.21 ppm when Pd(OAc)<sub>2</sub> and GO were separately added to the reaction mixture containing bromobenzene (**1a**) and phenylboronic acid (**2a**) (Eq. 1). The adsorbing characteristic of GO would be suitable for the synthesis of Pd-free fine chemicals.<sup>50</sup>



In summary, we have developed a facile method for the preparation of Pd NPs on sLGO using EtOH as solvent and reductant. It was demonstrated that the oxidation state and particle formation of Pd can be controlled with inhibiting aggregation of GO. Pd-sLGO-60 shows the highest catalytic activity for the Suzuki–Miyaura cross-coupling reaction. Moreover, we have demonstrated that GO can be used as a scavenger to prevent Pd contamination of the product.

### Notes and references

<sup>a</sup> Research Core for Interdisciplinary Sciences, Okayama University, 3-1-1, Tsushimanaka, Kita-ku, Okayama 700-8530, Japan. Fax: +81-86-251-8718; Tel: +81-86-251-8718; E-mail: nisina-y@cc.okayama-u.ac.jp

<sup>b</sup> Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-Ku, Okayama 700-8530, Japan

<sup>c</sup> Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

† Electronic Supplementary Information (ESI) available: Synthesis details, peak separation of XPS spectra of GO and Pd-sLGO composites, TEM and XPS analyses of the spent composite catalysts. See DOI: 10.1039/c000000x/

- 1 C. Su, K. P. Loh, *Acc. Chem. Res.*, 2013, **46**, 3523.
- 2 D. Chen, H. Feng, J. Li, *Chem. Rev.*, 2012, **112**, 6027.
- 3 Y. Zhu, D. K. James, J. Tours, *Adv. Mater.* 2012, **24**, 4924.
- 4 C. Huang, C. Li, G. Shi, *Energy Environ. Sci.* 2012, **5**, 8848.
- 5 R. Ruoff, *Nature Nanotechnol.*, 2008, **3**, 10.
- 6 D. R. Dreuer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228.
- 7 M. J. McAllister, J. -L. Li, D. H. Adamson, H. C. Sehniapp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme, I. A. Aksay, *Chem. Mater.*, 2007, **19**, 4396.
- 8 S. Obata, H. Tanaka, K. Saiki, *Carbon*, 2013, **55**, 126.
- 9 S. F. Pei, H. M. Cheng, *Carbon*, 2012, **50**, 3210.
- 10 R. S. Dey, S. Hajra, R. K. Sahu, C. R. Raj, M. K. Panigrahi, *Chem. Commun.*, 2012, **48**, 1787.
- 11 R. Larciprete, S. Fabris, T. Sun, P. Lacovig, A. Baraldi, S. Lizzit, *J. Am. Chem. Soc.*, 2011, **133**, 17315.
- 12 G. Goncalves, P. A. A. P. Marques, C. M. Granadeiro, H. I. S. Nogueira, M. K. Singh, J. Gracio, *Chem. Mater.*, 2009, **21**, 4796.
- 13 S. J. Ding, D. Y. Luan, F. Y. C. Boey, J. S. Chen, X. W. Lou, *Chem. Commun.*, 2011, **47**, 7155.
- 14 S. Bai, X. Shen, *RSC Adv.*, 2012, **2**, 64.
- 15 V. Georgakilas, M. Otyepka, A. B. Boulinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156.
- 16 X. Huang, X. Qi, F. Boey, H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 666.
- 17 C. Huang, C. Li, G. Shi, *Energy Environ. Sci.*, 2012, **5**, 8848.
- 18 B. F. Machado, P. Serp, *Catal. Sci. Technol.*, 2012, **2**, 54.
- 19 S. K. Movahed, M. Fakharian, M. Dabiri, A. Bazgir, *RSC Adv.* 2014, **4**, 5243.
- 20 D. Verma, S. Verma, A. K. Sinha, S. L. Jain, *Chempluschem*, 2013, **78**, 860.
- 21 G. Fan, W. Huang, C. Wang, *Nanoscale*, 2013, **5**, 6819.
- 22 N. Morimoto, S. -I. Yamamoto, Y. Takeuchi, Y. Nishina, *RSC Adv.*, 2013, **3**, 15608.
- 23 Q. -Y. Meng, Q. Liu, J. -J. Zhong, H. -H. Zhang, Z. -J. Li, *Org. Lett.*, 2012, **14**, 5992.
- 24 H. Chang, H. Wu, *Energy Environ. Sci.* 2013, **6**, 3483.
- 25 I. V. Lightcap, P. V. Kamat, *Acc. Chem. Res.*, 2013, **46**, 2235.
- 26 B. Luo, S. M. Liu, L. J. Zhi, *Small*, 2012, **8**, 630.
- 27 Z. -S. Wu, G. Zhou, L. -C. Yin, W. Ren, F. Li, H. -M. Cheng, *Nano Energy*, 2012, **1**, 107.
- 28 N. Miyaura, A. Suzuki, *Chem. Rev.* 1995, **95**, 2457.
- 29 C. C. C. Johansson Seechurn, M. O. Kiching, T. J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.*, 2012, **51**, 5062.
- 30 G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262.
- 31 Y. Li, X. Fan, J. Qi, S. Wang, G. Zhang, F. Zhang, *Nano Res.*, 2010, **3**, 429.
- 32 A. R. Siamaki, A. E. R. Khder, V. Abdelsayed, M. S. El-Shall, B. F. Gupton, *J. Catal.*, 2011, **279**, 1.
- 33 L. Rumi, G. M. Scheuermann, R. Mülhaupt, W. Bannwarth, *Helv. Chim. Acta.*, 2011, **94**, 966.
- 34 S. Moussa, A. R. Siamaki, B. F. Gupton, M. S. El-Shall, *ACS Catal.* 2012, **2**, 145.
- 35 J. Hu, Y. Wang, M. Han, Y. Zhou, X. Jiang, P. Sun, *Catal. Sci. Technol.*, 2012, **2**, 2332.
- 36 Y. Nishina, J. Miyata, R. Kawai, K. Gotoh, *RSC Adv.* 2012, **2**, 9380.
- 37 N. Shang, C. Feng, H. Zhang, S. Gao, R. Tang, C. Wang, Z. Wang, *Catal. Commun.*, 2013, **40**, 111.
- 38 S. Santra, P. K. Hota, R. Bhattacharyya, P. Ghosh, S. K. Mandal, *ACS Catal.* 2013, **3**, 2776.
- 39 R. N. Juanjuan, W. Shi, D. Z. Hou, *Appl. Catal. A: Gen.* 2014, **473**, 1.
- 40 K. Qu, L. Wu, J. Ren, X. Qu, *ACS Appl. Mater. Interfaces* 2012, **4**, 5001.
- 41 D. R. Dreyer, S. Murali, Y. Zhu, R. S. Ruoff, C. W. Bielawski, *J. Mater. Chem.*, 2011, **21**, 3443.
- 42 W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- 43 Y. Xu, H. Bao, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 5856.
- 44 S. D. Gardner, C. S. K. Singamsetty, G. L. Booth, *Carbon*, 1995, **3**, 587.
- 45 A. K. Diallo, C. Omelas, L. Salmon, J. R. Aranzaes, D. Astruc, *Angew. Chem. Int. Ed.*, 2007, **46**, 8644.
- 46 H. P. Boehm, A. Clauss, G. O. Fisher, U. Hofmann, *Z. Anorg. Allg. Chem.*, 1962, **316**, 119.

Journal Name

- 47 H. C. Schniepp, J. -L. L. M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville, I. A. Aksay, *J. Phys. Chem. B*, 2006, **110**, 8535.
- 48 D. Pandey, R. Reifengerger, R. Piner, *Surf. Sci.* 2008, **602**, 1607.
- 49 Y. Li, H. Chen, L. Y. Voo, J. Ji, G. Zhang, G. Zhang, F. Zhang, X. Fan, *J. Mater. Chem.* 2012, **22**, 15021.
- 50 I. De'ka'ny, R. Krüger-Grasser, A. Weiss, *Colloid. Polym. Sci.*, 1998, **271**, 570.