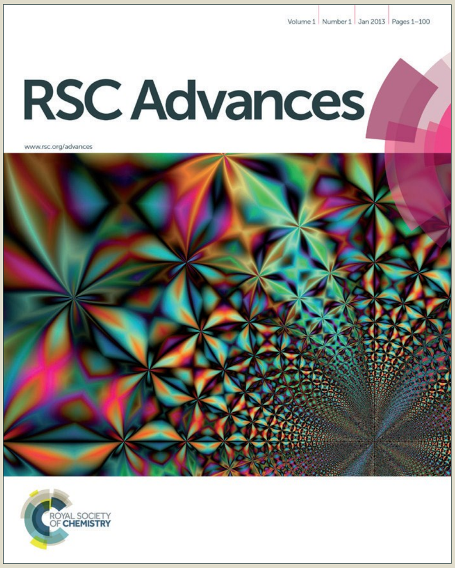
RSC Advances



Journal Name RSCPublishing

ARTICLE

Graphene oxide/carbon nanotubes-Fe_3O_4 support Pd nanoparticles for hydrogenation of nitroarenes and C-H activation

Cite this: DOI: 10.1039/x0xx00000x

Fan Yang,[a‡] Andong Feng,[a‡] Chunxia Wang,[b] Sen Dong,[a] Cheng Chi,[a] Xilai Jia,[a] Liqiang Zhang,[a] Yongfeng Li[a*]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Fe_3O_4 magnetic nanocomposites combined with graphene oxide (GO) and carbon nanotube (CNT) are synthesized by a hydrothermal method, followed by synthesis of GO/CNT-Fe_3O_4 support Pd nanoparticles using a gas-liquid interfacial plasma (GLIP) method with $Pd(OAc)_2$ as a precursor, and the Pd nanoparticles show uniform particles size distribution. The catalysts exhibit remarkable catalytic activity during the hydrogenation of nitroarenes under H_2 atmosphere at 60 ^{o}C in water by using small amount of catalysts, and the catalyst can be magnetically separated from the reaction mixture. The addition of Fe_3O_4 component in GO/CNT can be used to effectively prevent aggregation and restacking of GO and CNT, and the GO/CNT composite can adjust the hydrophilic-hydrophobic property of catalysts. Furthermore, the Pd catalyst can be readily recovered and reused for several times without significant decrease in activity. It is worth to mention that the Pd-3 catalysts show remarkable activity during C-H functionalization.

Introduction

Catalysis is becoming a strategic field of science because it represents a new way of meeting the challenges of energy and sustainability. Sustainable chemistry, also called green chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.[1-3] From the viewpoint of green chemistry, it is highly desirable to develop reusable heterogeneous catalysts which can be suitable to catalyze the reactions in aqueous media.[4,5]

As representatives of novel carbon nanomaterials, graphene and carbon nanotubes (CNT) have been used as an excellent catalyst support due to its large surface area and high thermal, chemical and mechanical stability.[6,7] However, two-dimensional graphene and one-dimensional CNT usually tend to aggregate and restack, which lead to the obvious reduction of available surface area.[8,9] In order to minimize the restacking-induced surface area loss, great efforts have been made to design and construct innovative composites. Most recently, three-dimensional (3D) interconnected network carbon nanomaterials composition of graphene and CNT are disclosed to enhance the availability of each surface area due to the combined structure can effectively avoid their aggregation and restacking.[10-12]

In the past several years, our group has focused on the development of carbon materials supported Pd and Au nanoparticles for organic molecule transformations in water.[13-17] Although, the GO/CNT support can be efficiently used as catalyst support for catalyzing the organic molecular transformation reactions in water due to its good hydrophilic-hydrophobic property,[15,18-21] the isolation and recovery of these tiny nanocatalysts from the reaction mixture is not easy. Therefore, the limitation of thus protocols is hard to recover these nanocatalysts from the reaction mixture.[22] To overcome this issue, the use of magnetic nanoparticles has emerged as a viable solution,[23] their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the

---

[a] State Key Laboratory of Heavy oil Processing, China University of Petroleum, Changping 102249, Beijing, China. Fax: +86-10-89739028; Tel: +86-10-89739028; E-mail: yfli@cup.edu.cn

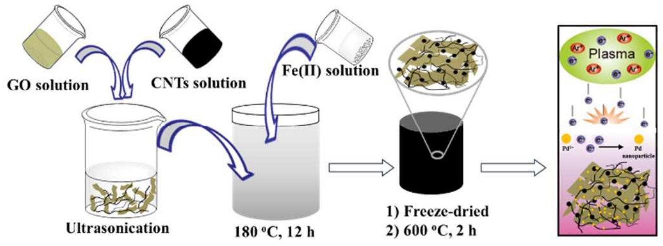
[b] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Analytical Chemistry for Living Biosystems, Institute of Chemistry, the Chinese Academy of Science, Beijing 100190, China

‡ These authors contributed equally.

† Electronic supplementary information (ESI) available: materials, illustration of plasma system, SEM and TEM images, Pd nanoparticle size, high resolution XPS spectra, contact angle, XRD of reused catalyst, procedure for C-H functionalization, 1H NMR spectra data.

reaction mixture with an external magnet. They offer a promising option that can meet the requirements of high accessibility with improved reusability.[24,25]

In continuation of our previous work, we introduce Fe_3O_4 nanocomposite into the GO/CNT supports for further avoiding their aggregation and restacking.[26,27] Moreover, the insoluble and paramagnetic natures of magnetic nanoparticles enable easy and efficient separation of the catalysts from the reaction mixture with an external magnet.[28-32] In this work, we report a facile GLIP one-pot synthesis of GO/CNT-Fe_3O_4 support Pd nanoparticles (Scheme 1). The Pd catalysts exhibit high catalytic activity for hydrogenation of nitroarenes and C-H functionalization.



Scheme 1 The systhesis process of GO/CNT-Fe_3O_4 support Pd nanoparticles.

Experimental

General information

All chemicals and solvents were purchased from commercial suppliers. The morphology of the catalysts was characterized by transmission electron microscopy (TEM, Tecnai G2, F20) combined with a selected area electron diffraction (SAED) at an acceleration voltage of 200 kV. The crystalline phase of the catalysts was identified by X-ray diffraction (XRD) on a Rigaku D/Max 2500 X-ray diffractometer with Cu Kα radiation (18 kW). The elemental composition of samples was obtained by X-ray photoelectron spectroscopy (XPS) with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The water contact angle measurements were conducted on the contact angle meter (JC2000D3, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd.). The leaching of Pd in fourconsecutive cycles were determined by inductively coupled plasma optical emission spectrometer (ICP-OES). ^{1}H NMR spectra were recorded on JNM-LA300FT-NMR for checking the final product from the hydrogenation of nitroaromatics and C-H functionalization reactions.

Preparation of graphene oxide

GO was synthesized according to a modified Hummer's method.[33] A mixture of concentrated H_2SO_4-H_3PO_4 (60 mL/3.3 mL) was added to a flask containing a mixture of graphite powder (500 mg) and $KMnO_4$ (3 g). Then the mixture was heated to 50 °C and stirred for 12 h. After that, the flask was cooled to room temperature and the contents poured into an ice bath (40 mL). After that, 30% H_2O_2 (2.5 mL) was added dropwise with stirring. The mixture was centrifuged and cleaned with 100 mL HCl (0.04 $g \cdot mL^{-1}$) and then wet cleaned multiple times with deionized water to remove oxidizing agents. The remaining solution was dialyzed for one week to eliminate excess ions. Then, the obtained graphite oxide was dispersed in water and ultrasonicated for 3 h to form GO. Eventually, the final product was freeze-dried.

Preparation of GO/CNT-Fe_3O_4 composites

The GO/CNT-Fe_3O_4 composites were prepared by hydrothermal synthesis method.[34-36] GO (30 mg) and CNTs (15 mg) was dispersed in water (10 mL) by ultrasonication for 30 min, respectively. The above two solutions were mixed together, and the mixture was sonicated for another 30 min. Then, 45 mg iron (II) oxalate dihydrate dispersed in water (10 mL) was added and stirred for 10 min. The solution was transferred into an autoclave and aged at 180 °C for 12 h. After that, the obtained composites were freeze-dried and heated to 600 °C for 2 h. Several kinds of GO/CNT-Fe_3O_4 with different GO/CNT ratios (2:1, 1:1, 1:2, CNT, GO) were prepared, the weight ratio of GO/CNT and Fe_3O_4 for all samples were 7:3.

Fabrication of GO/CNT-Fe_3O_4 support Pd nanoparticles

The GO/CNT-Fe_3O_4 support Pd nanoparticles were synthesized by the gas-liquid interfacial plasma. The glow discharge plasma (Fig. S1) was generated between the top flat stainless steel (SUS) and bottom ionic liquid electrode by CLASSMAN HIGH VOLTAGE INC. with the model as FJ1P120. Ar gas was introduced and used as the plasma-forming gas, the chamber was a stainless steel with inner diameter of 70 mm and four glass windows, and the gap between electrodes is 4 mm. A direct current (DC) power source with voltage V_{DC} = 220-250 V is applied to a stainless steel electrode in gas phase for the generation of an Ar plasma, where the discharge current I = 2 mA is fixed, and the Ar gas is introduced up to a pressure P_{gas} = 290 Pa. 4.9 mg $Pd(OAc)_2$ were dispersed in 1-butyl-3-methylimidazolium-tetrafluoro-borate ($[BMIM]BF_4$) by sonicating for 30 min. After that, 30 mg composites were added to the reactor, then the palladium solution was added to the reactor incubating 15 min. Electrons were irradiated toward the ionic liquid for 15 min, then the mixture were washed with ethanol several times to remove the excess impurities and extracted from the ionic liquid by a magnet. Pd nanoparticles decorated GO/CNT-Fe_3O_4 were prepared with the GO/CNT ratios (2:1, 1:1, 1:2, CNT, GO), and the respective materials were called Pd-n (n = 1, 2, 3, 4, 5).

The typical procedure for the hydrogenation of nitrobenzene in water

In a typical procedure for the hydrogenation of nitrobenzene in water, all hydrogenation reactions were carried out under standard conditions (60 °C, 1 atm of H_2). A micro-reaction vial, charged with the Pd-n (7.3 mg), corresponding to a percentage of Pd of 1 mmol% with respect to nitrobenzene was used, and 0.5 mmol nitrobenzene (51 μL) in 2 mL water with a magnetic stir was connected to a H_2 balloon. After consumption of nitrobenzene, which was monitored by Thin Layer Chromatography (TLC), the crude product was isolated by extracting with ethyl acetate for four times. The Pd-n catalysts in aqueous phase were recovered by a magnet and washed by both water and alcohol twice, respectively. Then, catalysts were dried at 50 °C for the next cycles. To the organic phase, the saturated hydrochloric ethyl acetate solution was added to induce the precipitation of the amine hydrochloride salt. The hydrochloride was removed by the filtration process, and washed with ether to give the yield.

Results and discussion

The GO/CNT-Fe_2O_3 hybrid was first synthesized by the hydrothermal reaction with ferrous oxalate dehydrate, GO and CNTs.[35] Then, the GO/CNT-Fe_3O_4 composites were synthesized by calcination of the synthesized GO/CNT-Fe_2O_3.[36] Finally, the GO/CNT-Fe_3O_4 supported Pd nanoparticles (Pd-n) catalysts were synthesized by a GLIP method. Fig. 1a displays optical photo of the GO/CNT-Fe_3O_4 porous aerogel, and the post-synthesized Pd-n catalysts can be attracted by a magnet easily as shown in Fig. 1b. The morphologies of different GO/CNT-Fe_3O_4 supported Pd nanoparticles are characterized by SEM and TEM images, as shown in Figs. 1c-f and Fig. S2. It can be observed that GO and CNTs are uniformly recombined in nanoscale dimension. The Fe_3O_4 nanoparticles are attached onto the surface of GO sheets and intercalated between the sheets with the interspersed CNTs which hinder the restacking of the sheets.[26,27] The Pd nanoparticles show monodisperse morphology on the surface of GO/CNT-Fe_3O_4, and the particle sizes of Pd-n are all around 4.0 nm (Table 1 and Fig. S3). These results illustrate that the GO/CNT-Fe_3O_4 porous aerogel structure can be efficiently synthesized by the hydrothermal method, and the GLIP method can decorate the Pd nanoparticles homogenously on the surface of the supports without destruction the GO/CNT-Fe_3O_4 microstructure.

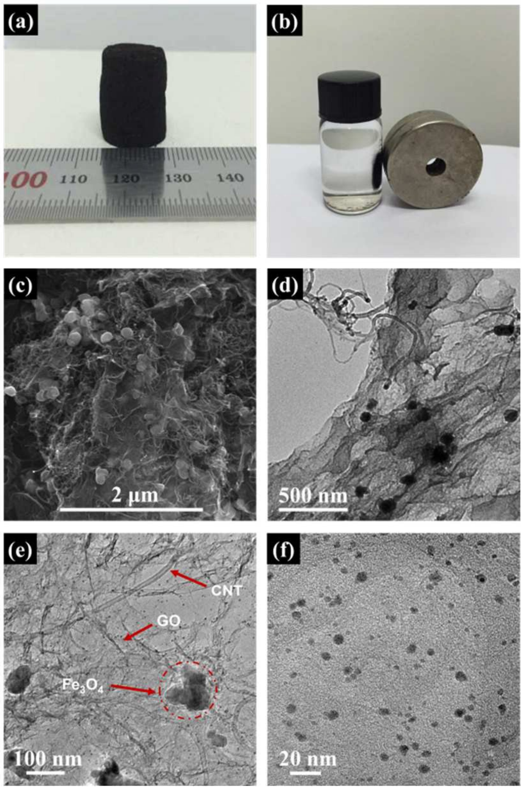


Fig. 1 Optical photo of the GO/CNT-Fe_3O_4 porous aerogel (a), and the GO/CNTs/Fe_3O_4 support Pd nanoparticles could be quickly separated from a dispersion of them by an external magnetic field (b), SEM and TEM images of Pd-3 (c-f).

Further insights of the structural properties of the Pd-n catalysts are obtained from XRD characterization, as shown in Fig. 2a. Several characteristic diffraction peaks at 30.1°, 35.5°, 40.1°, 43.1°, 57.0°, 62.6° and 68.1°, correspond to reflections of Fe_3O_4 (220), Fe_3O_4 (311), Pd (111), Fe_3O_4 (400), Fe_3O_4 (511), Fe_3O_4 (440) and Pd (220), respectively.[37,38] In addition, the lattice spacing measured from the diffraction rings are 0.35, 0.30, 0.25, 0.23, 0.21, 0.16, 0.15 and 0.13 nm as indicated in Fig.2b, which correspond to reflections C (002), Fe_3O_4 (220), Fe_3O_4 (311), Pd (111), Fe_3O_4 (400), Fe_3O_4 (511), Fe_3O_4 (440) and Pd (220), respectively. The SAED image of Pd-3 is consistent with the XRD results, which illustrates the Pd-n possess a face-centered crystalline structure.

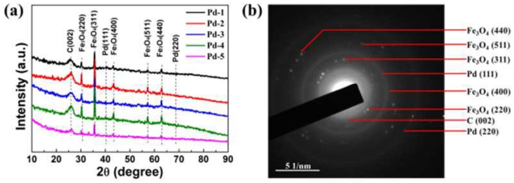


Fig. 2 XRD patterns (a) and SAED pattern (b) of Pd-n.

The XPS spectra of different samples are shown in Fig. 3a. The result indicates that the main chemical components of the materials are Pd, Fe, C and O. The peaks of the chemical components C1s and O1s are at 284.28 and 533.75 eV, respectively. The high-resolution XPS spectrum for Pd 3d of Pd-3 is shown in Fig. S4. Two peaks for Pd 3d centered at 335.98 and 341.38 eV can be assigned to Pd 3d5/2 and Pd 3d3/2, respectively. The Pd-3 catalyst shows two peaks for Pd 3d5/2 and Pd 3d3/2 which are split into two types of Pd electronic states (Pd0 and PdO) centred around 335.96, 338.54, 341.26 and 343.44 eV. The part of the Pd^0 nanoparticles was oxidized to PdO nanoparticles by the oxygen-containing functional groups in the graphene oxide, being in agreement with our previous work.[39] The Fe 2p XPS spectrum exhibits two peaks at 712.0 and 725.1 eV (Fig. 3b), corresponding to the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ spin-orbit peaks of Fe_3O_4.[40,41] The Pd and Fe_3O_4 loading contents of Pd-n are calculated by XPS, which is in agreement with the amount of Pd and Fe input, as shown in Table 1.

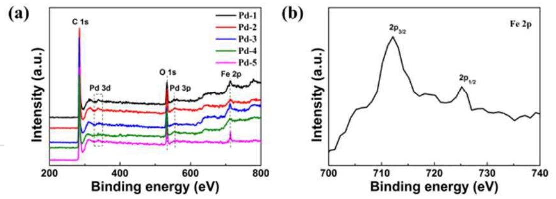


Fig. 3 XPS spectra of Pd-n: wide scan (a), and Fe 2p spectrum of Pd-3 (b).

Table 1 Pd nanoparticle size (nm)[a], and Pd and Fe_3O_4 loading content of Pd-n (wt.%)[b].

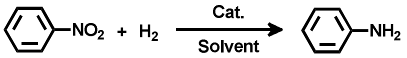
Sample	Pd-1	Pd-2	Pd-3	Pd-4	Pd-5
Pd-n size (nm)	4.1	4.1	4.7	4.5	3.6
Pd loading (wt.%)	11.8	10.4	10.1	11.4	10.0
Fe_3O_4 loading (wt.%)	27.9	24.6	28.9	25.9	26.3

[a] Average size obtained from the size distribution histogram.

[b] Calculated by XPS.

In current stage, there are some reports for the hydrogenation of nitroarenes using Pd catalysts. Sodium borohydride, hydrazine and silanes are commonly used as reducing agents. Compared with these methods, catalytic hydrogenation using H_2 as reduction reagent is of particular interest owing to its environmental friendliness, atomic efficiency and compatibility with industrial process. However, the hydrogenation of nitroarenes is usually carried out under hydrogen at high pressure and high temperature, leading to high energy input and difficulties in H_2 handling.[42-44] On the other hand, chemical reactions using water as solvent are expected to receive much more attention in organic synthesis from both a practical and an economic standpoints. However, the hydrogenation of nitroarenes carried out by the Pd catalyst at atmospheric pressure in water is seldom reported.[45] The results of the hydrogenation of nitroarenes catalyzed by our synthesized catalysts are shown in Table 2. To our delight, when using 1 mol% Pd-n catalyst to catalyze 0.5 mmol of nitrobenzene with H_2 in H_2O, the aniline is obtained in good yield. The Pd-1, Pd-2, Pd-3 catalysts show better catalytic activity than Pd-4 and Pd-5, indicating that the GO and CNT combined composite support are indispensable for enhancing the hydrogenation of nitroarenes react activity in water (entries 1-5). The Pd-3 catalyst with GO/CNT ratio as 1/2 shows the best activity, probable due to the suitable hydrophilic-hydrophobic property of Pd-3 produced by GO/CNT for the hydrogenation of nitroarenes in water.[15] In order to prove our prediction, the measurements for water contact angles of Pd-n experiment are taken, as shown in Fig. S5. The water contact angles show an increase by decreasing the GO component with hydrophilic property. The water contact angle results are in good agreement with our prediction, which is caused by hydrophilic property of GO and hydrophobic property of CNT. Moreover, the reaction is performed at 40 °C, 60 °C, and 80 °C, respectively (entries 3, 6 and 7). The optimal reaction temperature for the hydrogenation of nitroarenes reaction is 60 °C. The result illustrate that the H_2 can become active by Pd-3 catalyst at least at 60 °C, and continuous enhanced temperature produced the lower yield of nitrobenzene due to the hydrogenation reaction is exothermic type reaction.[46] We have further identified several reactions with various solvents including EtOH, THF, EtOAc, being carried out in the benchmark conditions. It is found that the Pd-3 catalyst shows great compatibility for these three solvents in the current catalytic system (entries 8-10).

Table 2 Hydrogenation of nitrobenzene under different conditions[a].



Entry	Cat.	Solvent	T (°C)	Time (h)	Yield[b] (%)
1	Pd-1	H_2O	60	3	85
2	Pd-2	H_2O	60	3	87
3	Pd-3	H_2O	60	3	90
4	Pd-4	H_2O	60	3	82
5	Pd-5	H_2O	60	3	76
6	Pd-3	H_2O	40	3	85
7	Pd-3	H_2O	80	3	67
8	Pd-3	EtOH	60	3	98
9	Pd-3	THF	60	3	96
10	Pd-3	EtOAc	60	3	99

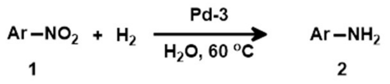
[a] Reaction conditions: nitrobenzene (0.5 mmol), Cat. Pd (1 mol%), H_2 (1 atm) in 2 ml H_2O.

[b] Isolated yield.

In the view of sustainable development, we have further explored the generality of the reduction reaction in water by using Pd-3 as catalyst (Table 3). To our surprise, in all cases, the hydrogenation of nitroarenes proceeds completely, yielding aniline with high selectivity. Both electron-donating and electron-withdrawing groups on the nitroarenes have little effect on the reaction yield or selectivity. However, nitroarenes substituted by $-NO_2$, -OH, -CN, -COOH, $-COOCH_3$ and $-COCH_3$ need long time to obtain the high yield (entries 3-10). The reason for the low reaction rate is due to that these substrates are solid, and the reaction products are also water-insoluble. The slower reaction rate is rationalized by the lattice energy of solid substrates, which increases the activation energy of the reaction.[45] For compounds with two nitro groups, 1,3-dinitrobenzene (1j), both nitro groups can be reduced (entry 10). Heterocycle nitroarene 8-nitroquinoline (1k) is converted to 8-aminoquinoline in quantitative yields (entry 11).

Moreover, the recyclability of the catalyst is further examined in the hydrogenation of nitrobenzene. The reaction is carried out under atmospheric H_2 pressure in water at 60 °C for 3 h. After completion of the reaction, the catalyst is separated from the reaction mixture by using a magnet, and washed by EtOH for the next run. The isolated yield obtained from each run after the reaction is shown in Fig. 4a. No leaching of Pd in the reaction mixture was detected by ICP-OES examination. This result illustrates that the reaction is fully catalyzed by heterogeneous Pd catalyst. The above results indicate that

Table 3 Pd-3 catalyzed hydrogenation of nitroarenes in water[a].



$$\underset{\mathbf{1}}{Ar{-}NO_2} + H_2 \xrightarrow[H_2O,\ 60\ ^{o}C]{Pd\text{-}3} \underset{\mathbf{2}}{Ar{-}NH_2}$$

Entry	Ar-NO$_2$ (1)	Ar-NH$_2$ (2)	Time (h)	Yield[b] (%)
1	4-$MeC_6H_4NO_2$ (1a)	4-$MeC_6H_4NH_2$ (2a)	3	88
2	4-$MeOC_6H_4NO_2$ (1b)	4-$MeOC_6H_4NH_2$ (2b)	3	99
3	4-$NO_2C_6H_4COOCH_3$ (1c)	4-$NH_2C_6H_4COOCH_3$ (2c)	12	93
4	4-$NO_2C_6H_4OH$ (1d)	4-$NH_2C_6H_4OH$ (2d)	24	91
5	2-$NO_2C_6H_4OH$ (1e)	2-$NH_2C_6H_4OH$ (2e)	24	87
6	4-$NO_2C_6H_4COOH$ (1f)	4-$NH_2C_6H_4COOH$ (2f)	12	92
7	2-$NO_2C_6H_4COOH$ (1g)	2-$NH_2C_6H_4COOH$ (2g)	12	90
8	4-$NO_2C_6H_4CN$ (1h)	4-$NH_2C_6H_4CN$ (2h)	12	90
9	4-$NO_2C_6H_4COCH_3$ (1i)	4-$NH_2C_6H_4COCH_3$ (2i)	12	94
10	3-$NO_2C_6H_4NO_2$ (1j)	3-$NH_2C_6H_4NH_2$ (2j)	12	99
11	8-Nitroquinoline (1k)	8-Aminoquinoline (2k)	3	99

[a] Reaction conditions: nitroarenes (0.5 mmol), Cat. Pd-3 (1 mol%), H_2 (1 atm) in 2 ml H_2O.

[b] Isolated yield.

the synthesized hybrid materials exhibit good reactivity and recyclability without prolonging the reaction time. After the reaction for 4 cycles, the catalyst has been examined by TEM, and it is found that particle size shows a little bit increase as shown in Fig. 4b. Moreover, the structural property of the recovered catalyst is again detected by XRD, as shown in Fig. S6. The Fe_2O_3 crystal peak is detected with the peak at 33.2°. The result indicates that the property of support is changed after four consecutive cycles, which is possibly used to explain the reason why the catalysts lose their activity.

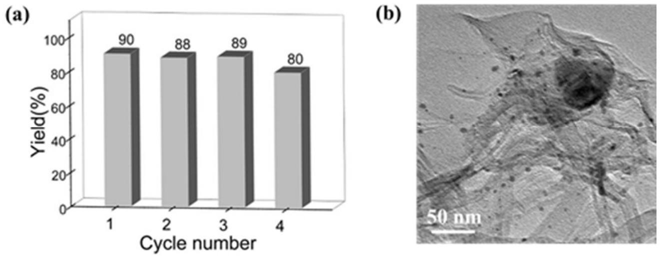


Fig. 4 The yields for 4 cycles of Pd-3 catalyzed nitrobenzene hydrogenation reaction (a), and TEM image of Pd-3 catalyst after 4 cycles.

Eventually, to extend the Pd-3 applications, we further use the Pd-3 catalyst for C-H bond functionalization reactions, the results are shown in Fig. 5. The reaction of benzoxazole (3a) with iodobenzene (4a) has been carried out with Pd-3, CsF and CuI in DMF. The result shows that the reaction gives 2-phenylbenzoxazole (5a) with 76% yield. Moreover, we have examined the Glaser reaction of phenylacetylene (6a) performed with Pd-3 and Ag_2O in THF, and the 1,4-diphenylbutadiyne (7a) is obtained in good yield.

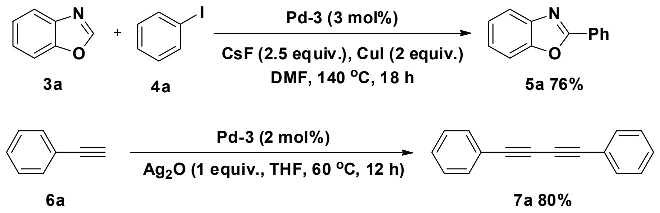


Fig. 5 C-H bond functionalization reaction and Glaser coupling reaction.

Conclusions

In conclusion, we have developed an efficient hydrothermal approach for the synthesis of GO/CNT-Fe_3O_4 supports. The synthesis of Pd nanoparticles decorate GO/CNT-Fe_3O_4 is performed by using a GLIP method. The Pd nanoparticles on the surface of GO/CNTs-Fe_3O_4 show uniform size distribution, and the size distributions of the Pd-n are around 4 nm. It is found that GO and CNT combined composite support are indispensable for enhancing the hydrogenation of nitroarenes react activity in water. Our results reveal that the catalyst with GO/CNT ratio as 1/2 shows best reactivity. Moreover, the current catalyst can be easily separated from the reaction mixture by using external magnetic field. The catalyst can be used for four consecutive runs without significant decrease in activity. It is worth to mention that the Pd-3 catalyst shows remarkable activity during C-H functionalization. Further work is in progress to extend other applications by using such kind of catalyst.

Acknowledgements

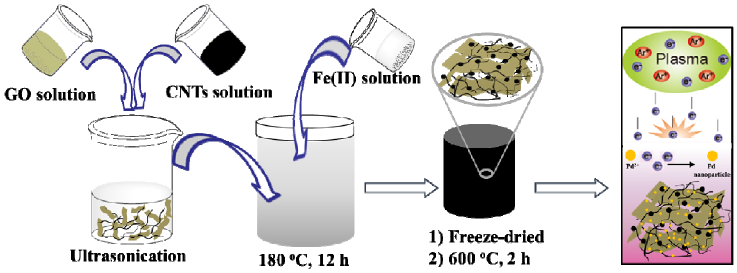
This work was supported by National High-tech R&D Program of China (863 Program, No. 2015AA034603), National Natural Science Foundation of China (Nos. 21202203, 21576289 and 21322609), Science Foundation Research Funds Provided to New Recruitments of China University of Petroleum, Beijing (No. YJRC-2013-31), Science Foundation of China University of Petroleum, Beijing (Nos. 2462015YQ0306 and 2462014QZDX01).

References

1. V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.M. Basset, *Chem. Rev.*, 2011, **111**, 3036-3075.
2. V. Polshettiwar, R.S. Varma, *Chem. Sov. Rev.*, 2008, **37**, 1546-1557.
3. M. Poliakoff, J.M. Fitzpatrick, T.R. Farren, P.T. Anastas, *Science*, 2002, **297**, 807-810.
4. V. Polshettiwar, R.S. Varma, *Green Chem.*, 2010, **12**, 743-754.
5. R.N. Baig, R.S Varma, *Chem. Commu.*, 2013, **49**, 752-770.
6. E. Lam, J.H. Luong, *ACS Catal.*, 2014, **4**, 3393-3410.
7. P. Trogadas, T.F. Fuller, P. Strasser, *Carbon*, 2014, **75**, 5-42.
8. W.L. Yang, Z. Gao, J. Wang, J. Ma, M.L. Zhang, L.H. Liu, *ACS Appl. Mater. Inter.*, 2013, **5**, 5443-5454.

9. H.C. Gao, F. Xiao, C.B. Ching, H.W. Duan, *ACS Appl. Mater. Inter.*, 2012, **4**, 7020–7026.
10. S.H. Lee, V. Sridhar, J.H. Jung, Karthikeyan K, Y.S. Lee, R. Mukherjee, *ACS Nano*, 2013, **7**, 4242-4251.
11. G.K. Dimitrakakis, E. Tylianakis, G.E. Froudakis, *Nano Lett*., 2008, **8**, 3166-3170.
12. V. Sridhar, H.J. Kim, J.H. Jung, C. Lee, S. Park, I.K. Oh, *ACS Nano*, 2012, **6**, 10562-10570.
13. C. Wang, F. Yang, W. Yang, L. Ren, *RSC Adv.*, 2015, **5**, 27526-27532.
14. F. Yang, C. Chi, S. Dong, C. Wang, *Catal. Today*, 2015, **256**, 186–192.
15. F. Yang, C. Wang, L. Wang, *RSC Adv*. 2015, **5**, 37710-37715.
16. L. Ren, F. Yang, Y. Li, T. Liu, *RSC Adv.*, 2014, **4**, 26804-26809.
17. T. Liu, F. Yang, Y. Li, L. Ren, *J. Mater. Chem. A*, 2014, **2**, 245-250.
18. T. Sun, Z. Zhang, J. Xiao, C. Chen, F. Xiao, *Sci. Rep.*, 2013, **3**, 1-6.
19. I.V. Pavlidis, T. Vorhaben, T. Tsoufis, P. Rudolf, U.T. Bornscheuer, D. Gournis, H. Stamatis, *Bioresource Technol.*, 2012, **115**, 164-171.
20. S. Kabiri, D.N.H. Tran, T. Altalhi, D. Losic, *Carbon*, 2014, **80**, 523-533.
21. S. Chen, W. Yeoh, Q. Liu, G. Wang, *Carbon*, 2012, 50, 4557-4565.
22. Á. Molnár, *Chem. Rev.*, 2011, **111**, 2251-2320.
23. S. Shylesh, V. Schünemann, W.R. Thiel, *Angew. Chem. Int. Ed.*, 2010, **49**, 3428-3459.
24. V. Polshettiwar, R.S. Varma, *Green Chem.*, 2010, **12**, 743-754.
25. A.H. Lu, E.L. Salabas, F. Schüth, *Angew. Chem. Int. Ed.*, 2007, **46**, 1222-1244.
26. J. Su, M. Cao, L. Ren, *J. Phys. Chem. C*, 2011, **115**, 14469–14477.
27. J. Liang, Y. Huang, J. Oh, *Adv. Funct. Mater*., 2011, **21**, 3778-3784.
28. H.A. Elazab, A.R. Siamaki, S. Moussa, B.F. Gupton, M.S. El-Shall, *Appl. Catal. A: Gen.*, 2015, **491**, 58-69.
29. S.J. Hoseini, V. Heidari, H. Nasrabadi, *J. Mol. Catal. A: Chem.*, 2015, **396**, 90-95.
30. S. Shylesh, V. Schünemann, W.R. Thiel, *Angew. Chem. Int. Edit.*, 2010, **49**, 3428-3459.
31. A.H. Lu, E.E. Salabas, F. Schüth, *Angew. Chem. Int. Edit.*, 2007, **46**, 1222-1244.
32. W. Li, B.Zhang, X. Li, H. Zhang, Q. Zhang, *Appl. Catal. A: Gen.*, 2013, **459**, 65-72.
33. D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J. M. Tour, *ACS Nano*, 2010, **4**, 4806-4814.
34. S. Yang, L. Chen, L. Mu, P.C. Ma, *J. Colloid Interf. Sci.*, 2014, **430**, 337-344.
35. L. Li, G. Zhou, Z. Weng, X.Y. Shan, *Carbon*, 2014, **67**, 500-507.
36. M. Zhang, M.Q. Jia, Y.H. Jin, *Appl. Surf. Sci.*, 2012, **261**, 298-305.
37. A. Fukuoka, H. Araki, Y. Sakamoto, S. Inagaki, Y. Fukushima, M. Ichikawa, *Inorg. Chim. Acta.*, 2003, **350**, 371-378.
38. Z.S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Müllen, *J. Am. Chem. Soc.*, 2012, **134**, 9082-9085.
39. L. Ren, F. Yang, C. Wang, *RSC Adv*., 2014, **4**, 63048–63054
40. L. Wang, X. Jia, Y. Li, F. Yang, L. Zhang, L. Liu, *J. Mater. Chem. A*, 2014, **2**, 14940-14946.
41. V. Chandra, J. Park, Y. Chun, J.W. Lee, I.C. Hwang, K.S. Kim, *ACS Nano*, 2010, **4**, 3979-3986.
42. R.F. Nie, J.H. Wang, L.N. Wang, *Carbon*, 2012, **50**, 586-596.
43. J.J. Shi, Y.Y. Wang, W.C. Du, *Carbon*, 2016, **99**, 330-337.
44. M. Turáková, M. Králik, P. Lehocký, *Appl. Catal. A: Gen*, 2014, **476**, 103-112.
45. J. Li, X.Y. Shi, Y.Y.Bi, J. F. Wei, *ACS Catal.*, 2011, **1**, 657-664.
46. P. Sangeetha, P. Seetharamulu, K. Shanthi, S. Narayanan, K.R. Rao, *J. Mol. Catal. A: Chem.*, 2007, **273**, 244-249.

Graphic abstract



The Fe_3O_4 magnetic nanocomposites with graphene oxide (GO) and carbon nanotube (CNT) support Pd nanoparticles are synthesized by gas-liquid interfacial plasma (GLIP) method. The catalysts exhibit remarkable catalytic activity during the hydrogenation of nitroarenes. Furthermore, the Pd catalyst can be readily recovered and reused for four times without significant decrease in activity. It is worth to mention that the as-prepared catalysts show remarkable activity during C-H functionalization.