Journal of Molecular Catalysis A: Chemical 382 (2014) 106–113

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Synthesis of biguanide-functionalized single-walled carbon nanotubes (SWCNTs) hybrid materials to immobilized palladium as new recyclable heterogeneous nanocatalyst for Suzuki–Miyaura coupling reaction

Hojat Veisi[a,*], Ardeshir Khazaei[b,*], Maryam Safaei[a], Davood Kordestani[c]

[a] Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran
[b] Faculty of Chemistry, Bu-Ali Sina University, 6517838683 Hamedan, Iran
[c] Medical biology Research Center,Kermanshah University of Medical Sciences, Kermanshah-Iran; Faculty of Chemistry, Razi University, Kermanshah 67149, Iran

ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 30 October 2013
Accepted 31 October 2013
Available online 8 November 2013

Keywords:
Biguanide-functionalized SWCNTs
Metformine
Pd catalyst
Suzuki–Miyaura coupling

ABSTRACT

Pd supported on biguanide(metformine)-functionalized single-walled carbon nanotubes (SWCNT-Met/Pd^{2+}) hybrid materials was fabricated for the first time. The prepared heterogeneous nanocatalyst was characterized by XRD, FT-IR, SEM, TGA and TEM. The catalytic activity of the prepared catalyst was investigated by employing Suzuki–Miyaura coupling reaction as a model reaction. A series of biphenyl compounds were synthesized through the Suzuki–Miyaura reaction using SWCNT-Met/Pd^{2+} as catalyst. The yields of the products were in the range from 80% to 95%. The catalyst can be readily recovered and reused at least 5 consecutive cycles without significant loss its catalytic activity.

1. Introduction

Since their discovery by Iijima [1], carbon nanotubes (CNTs) have attracted great interest in the most fields of science and nanotechnology due to their fascinating and unique optical, electrical, mechanical, chemical and thermal properties [2,3]. The tubular structure of carbon nanotubes makes them unique among different forms of carbon, and they can thus be exploited as an alternative material for catalyst support in heterogeneous catalysis [4] and in fuel cells due to the large surface area to volume ratio, excellent electronic conductivity, and high chemical stability [5–14]. Consequently, the exceptional properties of CNTs made them as the ideal candidates for numerous applications in nanoelectronics [15,16], catalysis [17–19], diagnostics [20,21] and drug delivery [22,23]. Wildgoose et al. reviewed the recent developments in this area by exploring the various techniques to functionalize the carbon nanotubes with metals and other nanoparticles and the diverse applications of the resulting materials [24]. However, the applications of CNTs have been impeded by their poor solubility in solvents and polymers, which originated from strong van der Waals attractions among CNTs. Without the surface modification, most of CNTs lack sufficient binding sites for anchoring precursor metal ions or metal nanoparticles, which usually lead to poor dispersion and aggregation of metalnanoparticles, especially at high loading conditions. Therefore, functionalization of CNTs is generally prerequisite to further applications. According to the nature of the interaction between CNTs and functional groups, the functionalization of CNTs can be categorized into covalent and non-covalent functionalization.

The palladium-catalyzed carbon–carbon and carbon–heteroatom bond forming reactions plays a key role in the synthesis of many important chemicals including pharmaceuticals, herbicides, polymers and so on [25–33]. Recently, immobilization of Pd nanoparticles on solid supports have received considerable attention as a new generation of heterogeneous catalysts in various scientific fields and Suzuki reaction because of their superior catalytic performance, good stability, ease of separation and satisfactory reusability in comparison to the traditional homogeneous $Pd(OAc)_2$, $PdCl_2$ catalysts [34–59]. However, the catalytic activity of Pd^{2+}-CNTs a little decreased gradually when the catalyst was used repeatedly. This could be ascribed to the weak interaction between palladium and the support material, as well as the agglomeration and accumulation of Pd nanoparticles on the surface of the material [60,61]. Therefore, it is desirable to improve

* Corresponding author. Tel.: +98 831456768.
E-mail address: hojatveisi@yahoo.com (H. Veisi).

1381-1169/$ – see front matter.
http://dx.doi.org/10.1016/j.molcata.2013.10.028

the stability, recyclability, and catalytic activity of heterogeneous Pd nanocatalysts. Owing to these interests and also as a part of our ongoing research program on the application of catalysts for the development of useful new synthetic methodologies [62], herein, we report the synthesis of a heterogeneous palladium nanocatalyst supported on metformine-grafted-SWCNTs (SWCNT-Met/Pd(II)) and its catalytic activity of the prepared catalyst was investigated by employing Suzuki–Miyaura coupling reaction as a model reaction. The result showed that the new catalyst retains the reactivity characteristic of a homogeneous catalyst but at the same time it was easy to separate off and reuse.

2. Experimental

2.1. Materials

All the reagents were purchased from Aldrich and Merck used without any purification. The pure SWCNTs without functional groups were purchased from Petrol Co. (Tehran, Iran) (Fig. 1). $SOCl_2$, HCl, H_2SO_4, HNO_3, H_2O_2 (30 wt.%, aq), deionized water, NaH (80%), anhydrous dimethylformamide (DMF), CaH_2, and metformin hydrochloride were obtained from Sigma Aldrich and Merck.

2.2. Preparation of free metformin

1.65 g of metformin hydrochloride (10 mmol) and 0.40 g of NaOH (10 mmol) were added to 100 ml of ethanol and the resulting suspension was stirred for 5 h. Then, the suspension was filtered and ethanol was removed with rotary evaporation leading to free metformin in 99% yield. The obtained free metformin was freshly used in the next experiments.

2.3. Covalent grafting of metformine to CNTs

Pristine CNTs (p-CNTs) were refluxed under stirring in the mixture of 1:3 (v/v) HNO_3 and H_2SO_4 at 70 °C for 30 h, which was followed by centrifugation and repeated washings with DI water [63]. The carboxylated CNTs (CNTs-COOH) thus obtained were dried at 60 °C for 1 day under reduced pressure and reacted with excess of $SOCl_2$ at room temperature for 24 h. The acylated CNTs (CNTs-COCl) were separated by centrifugation, subsequently washed with anhydrous THF to remove excess of $SOCl_2$, and dried in vacuum at 50 °C for 12 h. The final product was then subjected to functionalization with metformine. Free metformine (metformine-to-SWCNT weight ratio was 10:1) were mixed with 1 mL solution of DMF and NaH (80%) and then stirred for 1 h. The obtained acyl chloride SWCNTs in 20 mL DMF were then added to the suspension. The reaction mixture was kept at 120 °C for 3 days. The solid was then separated by filtration and washed with CH_2Cl_2 and deionized water for several times and dried in vacuum.

2.4. Preparation of SWCNT-Met/Pd^{2+} and SWCNT-Met/Pd^0 nanocatalysts

The SWCNT-Met (1 g) were dispersed in 30 mL acetonitrile by sonication for 10 min and a aqueous solution of $PdCl_2$ (10 mL, 0.6 mmol) was added to dispersion of SWCNT-Met. The mixture was stirred for 24 h in room temperature to complete attainment of coordination. Thus yielded SWCNT-Met/Pd^{2+} nanocatalyst was subjected to centrifugation, washed with acetonitrile and DI water and dried in vacuum at 40 °C for 12 h. The overall synthesis of SWCNT-Met/Pd^{2+} nanocatalyst is schematically demonstrated in Scheme 1.

The reduction of SWCNT-Met/Pd^{2+} by hydrazine hydrate was performed as follows: 30 mg of SWCNT-Met/Pd^{2+} was dispersed in 60 mL of water, and then 100 μL of hydrazine hydrate (80%) was added. The pH of the mixture was adjusted to 10 with 25% ammonium hydroxide and the reaction was carried out at 95 °C for 2 h. The final product SWCNT-Met/Pd^0 was washed with water and dried in vacuo at 50 °C. Scheme 1 depicted the synthetic procedure of SWCNT-Met/Pd^{2+} and SWCNT-Met/Pd^0. The concentration of palladium in SWCNT-Met/Pd^{2+} and SWCNT-Met/Pd^0 were 19 and 17 wt.%, respectively, which were determined by ICP-AES and TGA.

2.5. Catalytic activity

2.5.1. Suzuki–Miyaura coupling reaction

In a typical reaction, 10 mg of the catalyst (1 mol%) was placed in a 25 mL Schlenk tube, 1 mmol of the aryl halide in 5 mL of water/ethanol (1:1) was added 0.134 g (1.1 mmol) of phenyl boronic acid, 0.276 mg of K_2CO_3 (2 mmol). The mixture was then stirred for the desired time at 50 °C. The reaction was monitored by thin layer chromatography (TLC). After completion of reaction, the reaction mixture was cooled to room temperature and the catalyst was recovered by centrifuge and washed with ethyl acetate and ethanol. The combined organic layer was dried over anhydrous sodium sulfate and evaporated in a rotary evaporator under reduced pressure. The crude product was purified by column chromatography.

3. Results and discussion

3.1. Catalyst characterization

The synthesis of metformine-functionalized SWCNT anchored palladium catalyst consists in: (i) surface modification of carbon nanotubes with nitric acid and sulfuric acid to introduce carboxyl group (ii) conversion of the surface carboxylic acid groups into acid chloride groups by reaction with thionyl chloride, (iii) attachment of metformine to the SWCNTs surface through reaction with the acid chloride groups and (iv) complexation of the

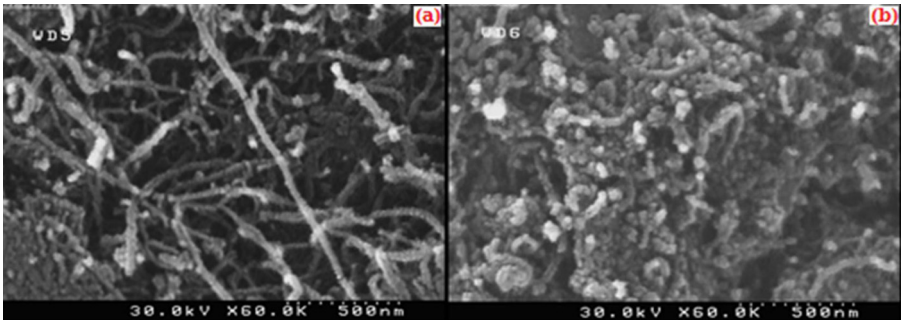
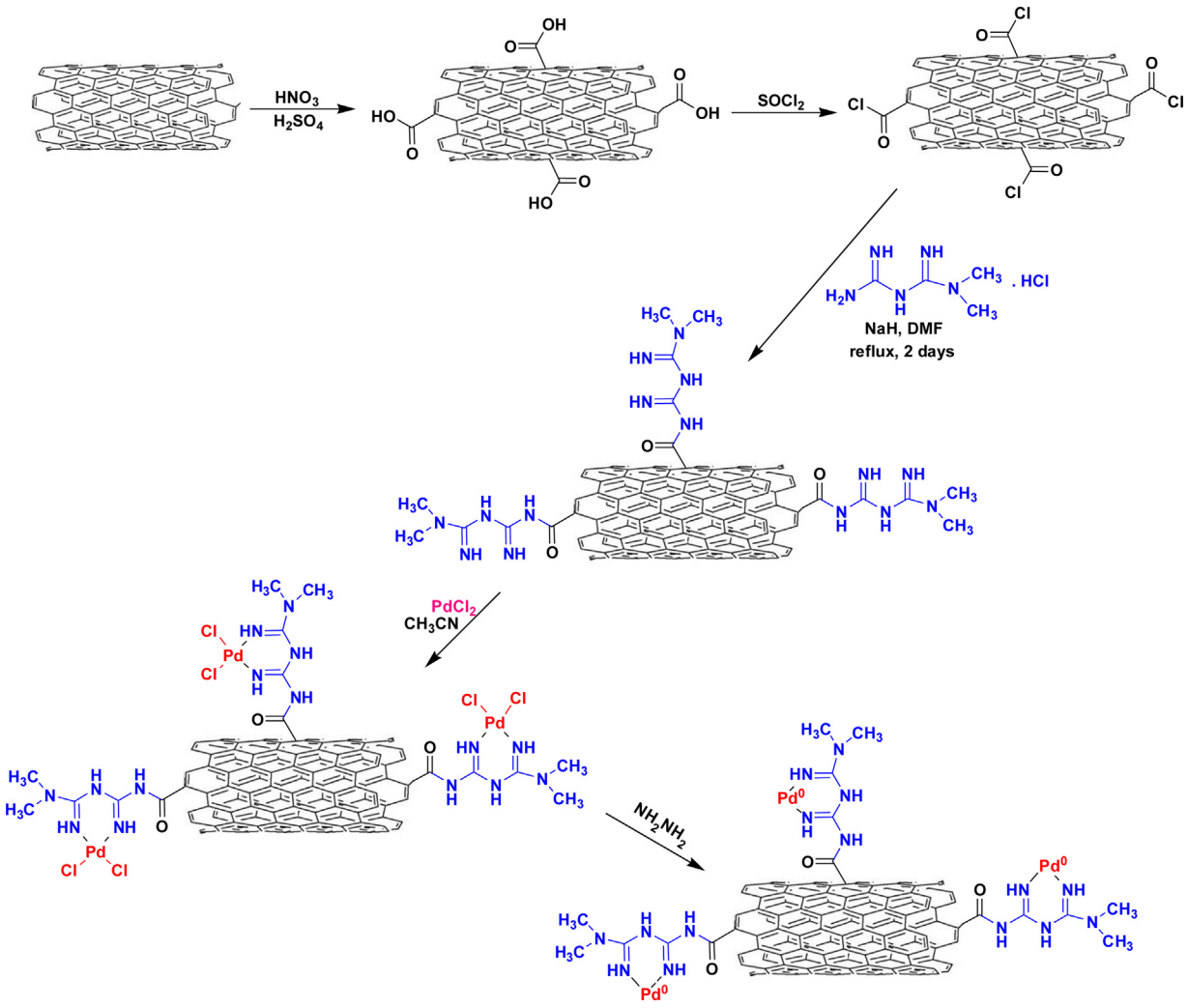


Fig. 1. SEM images of SWCNT before (a) and after (b) functionalization.



Scheme 1. Schematic diagram of SWCNT-CO-Met/Pd(II) fabrication.

metformine ligand to Pd by reaction with palladium chloride and then reduction with sodium borohydride (see Scheme 1). The metformine-functionalized single-walled carbon nanotubes anchored palladium (II) complex (SWCNT-Met/Pd^{2+}) was conveniently synthesized from commercially available and cheap materials via immobilization on SWCNTs. The pathways of SWCNT-Met/Pd^{2+} fabrication are shown in Scheme 1.

The surface structure of the materials was confirmed using Fourier transform infrared (FTIR) spectroscopy. Fig. 2 shows the FT-IR spectra obtained for (a) SWCNT, (b) SWCNT-COOH, (c) SWCNT-COCl, (d) SWCNT-CO-Met, (e) SWCNT-CO-Met/Pd(II). As it is seen in the curve b, the band at 1728 cm^{-1} is corresponding to carbonyl stretch of the carboxylic acid group. The converting of the carboxylic acid groups (SWCNT-COOH) into the acyl chloride intermediate (SWCNT-COCl) by treatment with thionyl chloride was confirmed by the appearance of peak near 1778 cm^{-1} streching in curve c. Curve d shows the spectrum of SWCNT-Met and the absorption band at 1658 cm^{-1} was attributed to the carbonyl stretching of the amide groups (—CONH—). Also, the band in the spectral region of 1671 cm^{-1} can be assigned to the imine (C=NH) bond of the attached metformine. These results indicated that the metformine was bonded to the surface of SWCNTs through amidation reaction. The signals appeared at 1671 and 1658 cm^{-1} in curve d for the metal-ligand co-ordination [43] presumably leads to a shift of these two peaks to lower frequencies (1671–1656 cm^{-1}). This shift can be observed comparing curve e. These peaks at curves d and e displayed the successful attachment of metformine organic ligands and subsequent coordination of Pd^{2+} ions within the hybride material. Also, the scanning electronic microscopy (SEM) analysis for SWCNT before (a) and after (b) functionalization with metformine to immobilize palladium ions (Fig. 1) was confirmed the successfully functionalization of single-walled carbon nanotubes.

Transmission electron microscopy (TEM) investigations are carried out to observe the morphology and distribution of palladium particles supported on SWCNT-Met/Pd. The existence of Pd nanoparticles, deposited on *f*-CNTs was clearly distinguishable as bright spots in Fig. 3. The density of Pd nanoparticles in *f*-CNTs-Pd nanocatalyst is abundant and these nanoparticles together formed some clusters. The formation of clusters might have originated by twinned or multiple twinned seeding of Pd nanoparticles, which is in accordance with previous reports [64,65]. The images of *f*-CNTs-Pd nanocatalyst (Fig. 3) exhibits that Pd nanoparticles are uniform dispersed on *f*-CNTs and some of them appeared twinned together. The large number of defect sites produced by the harsh treatment of acids, may be led to random distribution of Pd nanoparticles at some place of SWCNT. The mean diameter of Pd nanoparticles immobilized on *f*-CNTs was found to be around 5–10 nm.

The phase structure of the nanocatalyst was revealed through powder X-ray diffraction spectroscopy (XRD). The XRD patterns acquired for pristine CNTs (*p*-CNTs), *f*-CNTs and *f*-CNTs-Pd

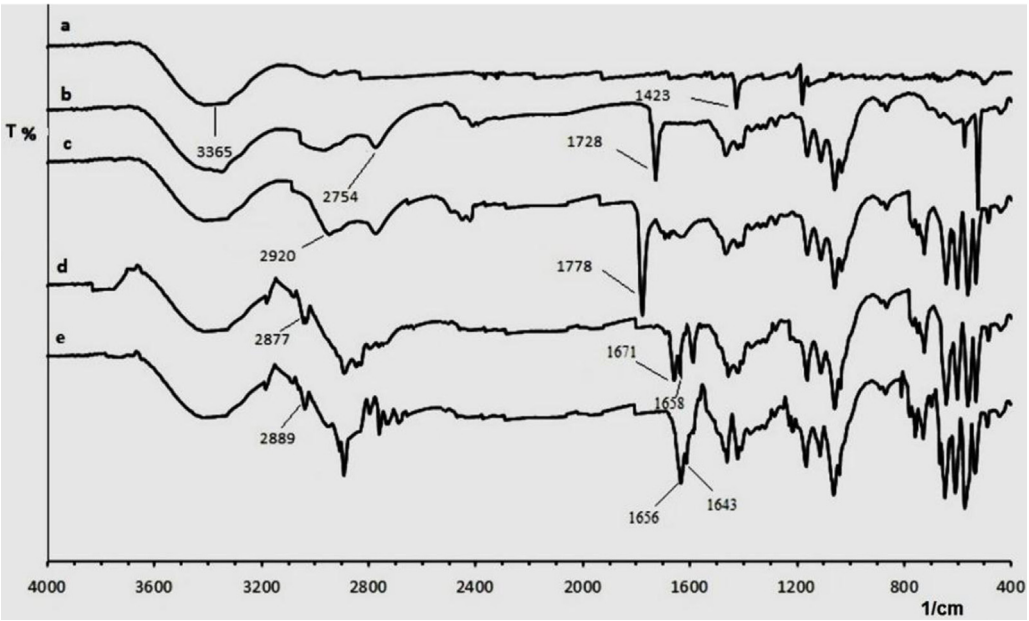


Fig. 2. FTIR spectra of (a) SWCNT, (b) SWCNT-COOH, (c) SWCNT-COCl, (d) SWCNT-CO-Met, (e) SWCNT-CO-Met/Pd(II).

nanocatalyst is shown in Fig. 4. The diffraction peaks at 26.3° and 42.6° for *p*-CNTs (Fig. 4a) are attributed to (0 0 2) and (1 0 0) planes of hexagonal graphite and appearance of these peaks with high intensity suggests that *p*-CNTs have a high graphitic structure [63]. After functionalization, the diffraction peaks corresponding to (0 0 2) and (1 0 0) planes of CNTs were appeared at 26° and 42.5° for *f*-CNTs (Fig. 4b). A minute blue shift in the bands was observed for *f*-CNTs, which signifies that functionalization of CNTs with metformine did not destroy or alter the original structure of *p*-CNTs. The *f*-CNTs-Pd nanocatalyst (Fig. 4c) clearly exhibited (1 1 1), (2 0 0) and (2 2 0) crystallographic planes of face-centered cubic (fcc) palladium at 39.8°, 46° and 67.2°, respectively (JCPDS No. 89–4897). The additional two peaks in Fig. 4c at 26.3° and 46° were from CNTs. Thus the XRD results indicate efficient immobilization of fcc structured Pd nanoparticles on *f*-CNTs.

The thermogravimetric analysis (TGA) in inert atmosphere (N_2) was used for the quantification of the metformine on the surface Fig. 5. These curves are related to SWCNT (curve "a" in Fig. 5) and SWCNT-Met/Pd(II) (curve "b" in Fig. 5). Two main mass loss regions are observed for SWCNT. The first weight loss occurred at a temperature range of 100–650 °C and was moderate. Another weight loss was observed the temperature range of 660–780 °C. The results showed that solvent loss such as water start at 100 °C and carbon tubes and amorphous carbon decompose start at 650 °C. Curve "b" shows that several weight losses were observed for SWCNT-Met/Pd(II). The first mass loss occurs at temperature range of 100–310 °C that is related to the loss of solvent trap in complex. The second mass loss occurs at temperature range of 310–450 °C that is related to the loss of ligand (metformine) in complex and third mass losses occur at 600–800 °C and that related to the decomposition of CNT. The mass loss at 600–800 °C (Fig. 5b) is due to the decomposition of carbon nanotubes shown that the rate of mass loss is slower and the shape is not similar with the (a) curve at

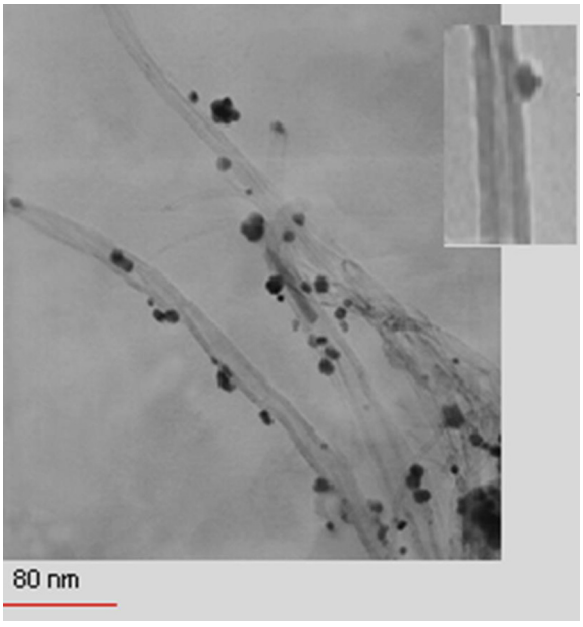


Fig. 3. TEM images of SWCNT-Met/Pd.

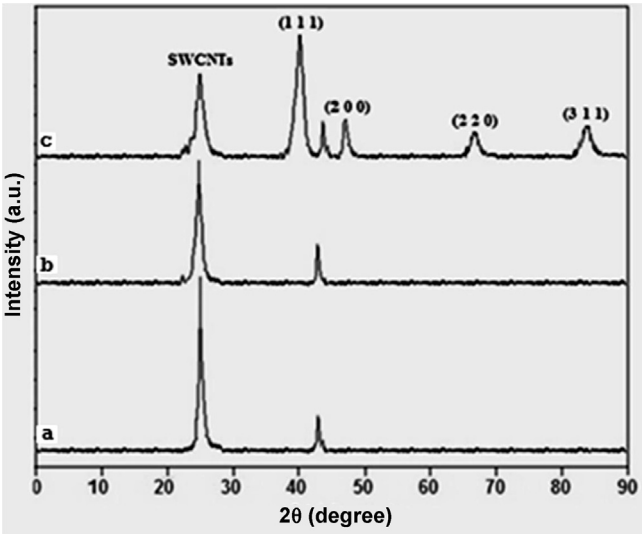


Fig. 4. The XRD patterns for (a) SWCNT, (b) SWCNT-Met, (c) SWCNT-Met/Pd(0).

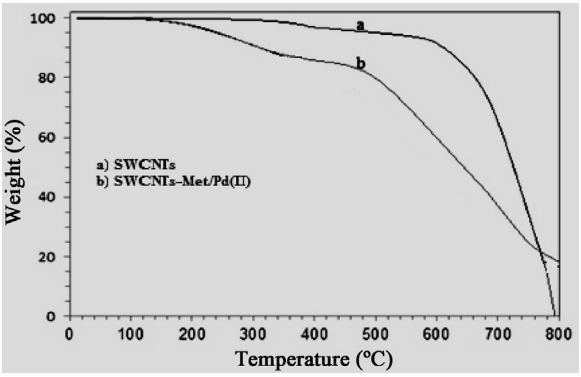


Fig. 5. Weight loss as measured by TGA for (a) SWCNT, (b) SWCNT-Met/Pd(II).

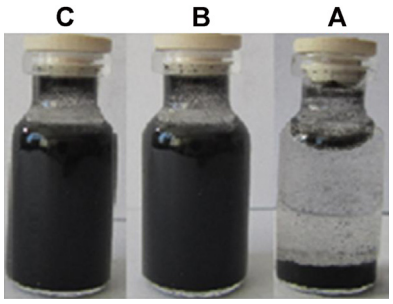


Fig. 6. Photographs of the solubility of (a) the pristine SWCNTs, in H_2O (b) grafted-SWCNTs-metformin (SWCNT-Met), in H_2O (c) and SWCNT-Met/Pd(II), in H_2O.

this temperature range. This indicates there is a strong interaction between Pd particles and CNT that slow down the CNT decomposition rate. The remaining weight percent up to the temperature of 800 °C is equal to 0 and 19.1 are related to curves "a" and "b", respectively. The remaining weight of SWCNT is zero because all carbons, at a temperature of 800 °C, burned and converted to carbon dioxide. The remaining weights percent of complexes (19.1), due to the presence of metal palladium installed on the SWCNT-Met.

3.2. Dispersion

Unsurprisingly, the functionalized SWCNTs could easily disperse in water. Fig. 6 depicts the appreciably higher dispersibility of grafted-SWCNTs-metformin (SWCNT-Met) and it's Pd catalyst SWCNT-Met/Pd(II) in water, as compared with the pristine sample. The easily-miscible di-imine functionalities may explain the higher dispersion of the functionalized SWCNTs.

3.3. Catalytic testing

3.3.1. Suzuki–Miyaura coupling reaction

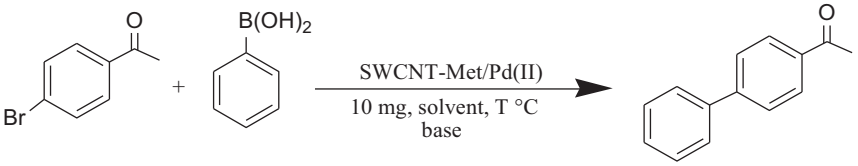
Catalytic activity of the SWCNT-Met/Pd(II) was evaluated in the Suzuki–Miyaura reaction. Initially, we explored the catalyst ability for mentioned reaction and the optimized conditions of coupling reaction between bromoacetophenone and phenylboronic acid as a model reaction with different amounts of the catalyst, solvents, bases and at different temperatures (25, 50, 80 and 100 °C) (Table 1).

The influences of various reaction parameters such as base (Et_3N, AcONa and K_2CO_3), solvent (nonpolar, protic and aprotic), and catalyst amount on the reaction were tested (Table 1). Among the bases evaluated, K_2CO_3 was found to be the most effective and other bases were substantially less effective. We also investigated the effect of solvents on the Suzuki–Miyaura cross-coupling reaction and found that H_2O/EtOH (1:1) was the best choice. It was found that SWCNT-Met/Pd^{+2} (10 mg, 1 mol% Pd) gave the optimum results using H_2O/EtOH (1:1) as solvent and 50 °C as the reaction temperature. Thus, the optimum conditions selected are: bromoacetophenone (1 mmol), phenylboronic acid (1.1 mmol), SWCNT-Met/Pd^{+2} (10 mg, 1 mol% Pd), H_2O/EtOH (2 mL, 1:1), K_2CO_3 (2 mmol) and 50 °C as the reaction temperature.

To generalize the application of the SWCNT-Met/Pd^{+2}catalyst, the coupling reactions of various substituted aryl halides and phenylboronic acids were carried out using 1 mol% SWCNT-Met/Pd^{+2} as catalyst at 50 °C (Table 2). The reactions proceeded well with a wide range of aryl halides. For most of the substrates, the reaction could be completed in 0.25–3 h with moderate or excellent yields, with the substrates having either electron-donating groups or electron-withdrawing groups.

As it is seen, under optimized conditions, phenyl iodide, bromide and chloride was reacted efficiently with phenylboronic acid (Table 2, entries 1–3). Both electron-withdrawing and releasing groups with phenylboronic acid afforded the corresponding products in high yields (Table 2, entries 4–10). It was found that the

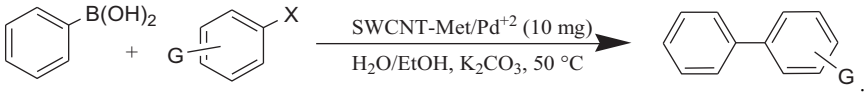
Table 1
Optimization of the conditions for the Suzuki–Miyaura reaction of bromoacetophenone with phenylboronic acid[a]

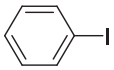
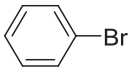
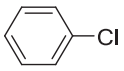
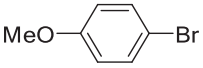
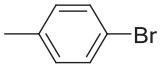
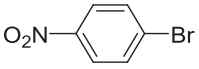
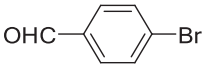
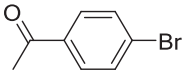
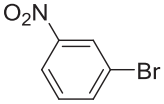
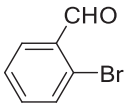


Entry	Solvent	Pd catalyst (mg)	Base	T °C	Time (min)	Yield (%)[b]
1	DMF	10	K_2CO_3	50	50	89
2	Toluene	10	K_2CO_3	50	50	66
3	EtOH	10	K_2CO_3	50	50	75
4	H_2O	10	K_2CO_3	50	50	60
5	EtOH/H_2O[c]	10	K_2CO_3	50	30	98
6	EtOH/H_2O[c]	10	NaOAc	50	60	67
7	EtOH/H_2O[c]	10	Et_3N	50	60	88
8	EtOH/H_2O[c]	5	K_2CO_3	50	30	85
9	EtOH/H_2O[c]	15	K_2CO_3	50	30	98
10	EtOH/H_2O[c]	10	K_2CO_3	25	300	70
11	EtOH/H_2O[c]	10	K_2CO_3	80	30	98
12	EtOH/H_2O[c]	10	K_2CO_3	100	30	98

[a] Reaction conditions: bromoacetophenone (1 mmol), $PhB(OH)_2$ (1.1 mmol), SWCNT-Met/Pd(II) (10 mg, 1 mol%), solvent (4 ml).
[b] Isolated yield.
[c] EtOH/H_2O = 1:1.

Table 2
Suzuki cross-coupling reaction of aryl halides with phenylboronic acid



Entry	Aryl halide	Time (min)	Yield (%)[a]
1		15	98
2		50	95
3		240	65
4		60	90
5		60	93
6		30	92
7		40	95
8		30	98
9		30	90
10		240	72
11		60	93

[a] Isolated yield.

yield of reaction ortho-position aryl bromide is lower (Table 2, entry 10) than those of para- or meta-substituted aryl bromides (Table 2, entries 4–9). Notably, when 2-iodothiophene was used as coupling partner, the desired product was obtained and no poisoning of palladium catalyst occurred (Table 2, entry 11).

Finally, to assess the present protocol with respect to other reported methods for the preparation of biaryls, the catalytic performance of the SWCNT-Met/Pd^{+2} was compared with some of the reported catalysts. From Table 3, it can be seen that present catalyst exhibited higher conversions and yields compared to the other reported system [38,66–69].

3.4. Recycling of the catalyst

In order to investigate the recycling of the catalyst, the Suzuki–Miyaura cross-coupling reaction between iodobenzene and phenylboronic acid catalyzed by 1 mol% of SWCNT-Met/Pd^{+2} was chosen as a model reaction. The results indicated that SWCNT-Met/Pd^{+2} can be reused 5 times without significant loss of catalytic activity (Fig. 7). The result indicated that the palladium leaching of the catalyst was low. The results demonstrated that metformine play a key role to improve the stability of the SWCNT-Met/Pd^{+2} catalyst. Also, it is notably, after using SWCNT-Met/Pd^{+2}, no palladium ion could be detected in the liquid reaction mixtures by atomic absorption spectroscopy.

3.5. Leaching test

In order to investigate the leaching of Pd during the reaction in our catalytic system, we conducted a filtration test for the Suzuki reaction between iodobenzene and phenylboronic acid using SWCNT-Met/Pd^{+2} as catalyst. After 5 min (the reaction was completed in 15 min), the reaction was stopped and the reaction

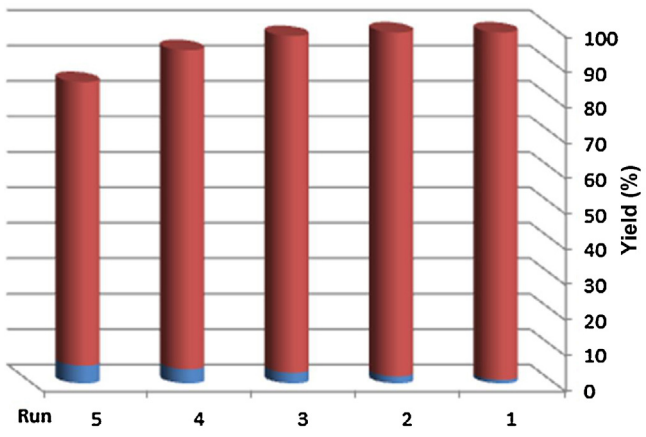


Fig. 7. The recycling of the SWCNT-Met/Pd^{+2} for the Suzuki coupling reaction.

Table 3
Comparison of the activity of different catalysts in the Suzuki cross-coupling reaction.

Reaction	Catalyst	Reaction conditions	Yield (%)	Ref.
Iodobenzene + phenylboronic acid	SWCNT-Met/Pd^{+2}	K_2CO_3, H_2O/EtOH, 50 °C, 15 min	98	This study
	GO-NH_2-Pd^{2+}	K_2CO_3, H_2O/EtOH, 60 °C, 30 min	87	66
	Cell-$OPPh_2$-Pd^0	K_2CO_3, EtOH, 78 °C, 20 min	85	68
	Pd-$ZnFe_2O_4$	K_2CO_3, EtOH, 78 °C, 4 h	92	69
	Chitosan-Schiff base-Pd(II)	K_2CO_3, Xylene, 130 °C, 6 h	34	38
p-nitrobromobenzene + phenylboronic acid	SWCNT-Met/Pd^{+2}	K_2CO_3, H_2O/EtOH, 50 °C, 30 min	92	This study
	GO-NH_2-Pd^{2+}	K_2CO_3, H_2O/EtOH, 60 °C, 4 h	80	66
	PS-dtz-Pd(II)	K_2CO_3, H_2O, 70 °C, 5 h.	80	67
	Chitosan-Schiff base-Pd(II)	K_2CO_3, Xylene, 130 °C, 6 h.	76	38

mixture was centrifuged at 10,000 rpm for 10 min. Then the mixture without the solid catalyst was allowed to continue under the same conditions for another 10 min, and the conversation did not proceed significantly. This suggests that the leaching of Pd species from the solid support is low and the prepared catalyst is stable. On the other hand, atomic absorption spectroscopy of the filtrate also confirmed that the Pd content in the solution was below the detection limit (0.1 ppm).

4. Conclusion

In conclusion, a novel and recyclable palladium catalyst supported on metformine modified SWCNT was fabricated for the first time. The results indicated that the stability of the catalyst was much improved and SWCNT-Met/Pd^{+2} was an efficient and recyclable catalyst for the Suzuki–Miyaura cross-coupling reactions. The catalyst can be readily recovered and reused without significant loss of its catalytic activity. The proposed method can be a promising alternative approach for the preparation of biphenyl compounds.

Acknowledgement

We are thankful to Iran National Science Foundation (INSF) and Payame Noor University (PNU) for partial support of this work.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Science 297 (2002) 787.
[3] J. Gooding, J. Electochim. Acta 50 (2005) 3049.
[4] D.J. Guo, H.L. Li, J. Power Sources 160 (2006) 44.
[5] G. Che, B.B. Lakshmi, E.R. Fisher, C.R. Martin, Nature 393 (1998) 346.
[6] G. Che, B.B. Lakshmi, C.R. Martin, E.R. Fisher, Langmuir 15 (1999) 750.
[7] B. Rajesh, V. Karthik, S. Karthikeyan, K.R. Thampi, J.M. Bonard, B. Viswanathan, Fuel 81 (2002) 2177.
[8] Z.L. Liu, X.H. Lin, J.Y. Lee, W.D. Zhang, M. Han, L.M. Gan, Langmuir 18 (2002) 4054.
[9] W.Z. Li, C.H. Liang, W.J. Zhou, J.S. Qiu, Z.H. Zhou, G.Q. Sun, J. Phys. Chem. B 107 (2003) 6292.
[10] T. Matsumoto, T. Komatsu, H. Nakano, K. Arai, Y. Nagashima, E. Yoo, T. Yamazaki, M. Kijima, H. Shimizu, Y. Takasawa, J. Nakamura, Catal. Today 90 (2004) 277.
[11] C. Kim, Y.J. Kim, Y.A. Kim, T. Yanagisawa, K.C. Park, M. Endo, M.S. Dresselhaus, J. Appl. Phys. 96 (2004) 5903.
[12] Y.C. Xing, J. Phys. Chem. B 108 (2004) 19255–19259.
[13] C. Wang, M. Waje, X. Wang, J.M. Tang, C.R. Haddon, Y. Yan, Nano Lett. 4 (2004) 345.
[14] M. Carmo, V.A. Paganin, J.M. Rosolen, E.R. Gonzalez, J. Power Sources 142 (2005) 169.
[15] Y. Saito, S. Uemura, Carbon 38 (2000) 169.
[16] A. Javey, H. Kim, M. Brink, Q. Wang, A. Ural, J. Guo, P. Mcintyre, P. Mceuen, M. Lundstrom, H. Dai, Nat. Mater. 1 (2002) 241.
[17] S. Wang, E. Humphreys, S. Chung, D. Delduco, S. Lustig, H. Wang, K. Parker, N. Rizzo, S. Subramoney, Y. Chiang, A. Jagota, Nat. Mater. 2 (2003) 196.
[18] G. Dieckmann, A. Dalton, P. Johnson, J. Razal, J. Chen, G. Giordano, E. Munoz, I. Musselman, R. Baughman, R. Draper, J. Am. Chem. Soc. 125 (2003) 1770.
[19] G.G. Samsonidze, E.D. Semke, M. Usrey, D.J. Walls, Science 302 (2003) 1545.
[20] Y. Wang, X. Wang, B. Wu, Z. Zhao, F. Yin, S. Li, X. Qin, Q. Chen, Sens. Actuat. B 130 (2008) 809.
[21] H. Zhao, H. Ju, Anal. Biochem. 350 (2006) 138.
[22] E. Miyako, H. Nagata, K. Hirano, Y. Makita, K. Nakayama, T. Hirotsu, Nanotechnology 18 (2007) 475103.
[23] M.J. O'Connell, S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J. Ma, R.H. Hauge, R.B. Weisman, R.E. Smalley, Science 297 (2002) 593.
[24] G.G. Wildgoose, C.E. Banks, R.G. Compton, Small 2 (2006) 182–193.
[25] N.R. Shiju, V.V. Guliants, Appl. Catal. A: Gen. 356 (2009) 1.
[26] R. Narayanan, Molecules 15 (2010) 2124.
[27] S. Cheong, J.D. Watt, R.D. Tilley, Nanoscale 2 (2010) 2045.
[28] L. Xue, Z. Lin, Chem. Soc. Rev. 39 (2010) 1692.
[29] G.A. Molander, B. Canturk, Angew. Chem. Int. Ed. 48 (2009) 9240.
[30] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[31] C. Amatore, A. Jutand, Acc. Chem. Res. 33 (2000) 314.
[32] K.C. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 44 (2005) 4442.
[33] B. Schlummer, U. Scholz, Adv. Synth. Catal. 346 (2004) 1599.
[34] M. Lamblin, L. Nassar-Hardy, J.C. Hierso, E. Fouquet, F.X. Felpin, Adv. Synth. Catal. 352 (2010) 33.
[35] L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133.
[36] J.Y. Kim, Y. Jo, S.K. Kook, S. Lee, H.C. Choi, J. Mol. Catal. A: Chem. 323 (2010) 28.
[37] S.A. Patel, K.N. Patel, S. Sinha, B.V. Kamath, A.V. Bedekar, J. Mol. Catal. A: Chem. 332 (2010) 70.
[38] B.C.E. Makhubela, A. Jardine, G.S. Smith, Appl. Catal. A: Gen. 393 (2011) 231.
[39] B. Tamami, H. Allahyari, S. Ghasemi, F. Farjadian, J. Organomet. Chem. 696 (2011) 594.
[40] Y. Zhao, X. Yang, J. Tian, F. Wang, L. Zhan, Mater. Sci. Eng. B 171 (2010) 109.
[41] N. Karousis, G.E. Tsotsou, F. Evangelista, P. Rudolf, N. Ragoussis, N. Tagmatarchis, J. Phys. Chem. C 112 (2008) 13463.
[42] S. Bhunia, R. Sen, S. Koner, Inorg. Chim. Acta 363 (2010) 3993.
[43] J. Guerra, M.A. Herrero, Nanoscale 2 (2010) 1390.
[44] T. Borkowski, A.M. Trzeciak, W. Bukowski, A. Bukowska, W. Tylus, L. Kepinski, Appl. Catal. A: Gen. 378 (2010) 83.
[45] F. Durap, M. Rakap, M. Aydemir, S. Ozkar, Appl. Catal. A: Gen. 382 (2010) 339.
[46] Y. He, C. Cai, Catal. Commun. 12 (2011) 678.
[47] A. Villa, D. Wang, N. Dimitratos, D. Su, V. Trevisan, L. Prati, Catal. Today 150 (2010) 8.
[48] Y.S. Chun, J.Y. Shin, C.E. Song, S. Lee, Chem. Commun. (2008) 942.
[49] S. Ungureanua, H. Deleuzeb, O. Babotb, M.F. Acharda, C. Sanchezc, M.I. Popad, R. Backov, Appl. Catal. A: Gen. 390 (2010) 51.
[50] S.M. Islam, P. Mondal, K. Tuhina, A.S. Roy, S. Mondal, D. Hossain, J. Inorg. Organomet. Polym. 20 (2010) 264.
[51] Z. Gaoa, Y. Fengb, F. Cuia, Z. Huaa, J. Zhoua, Y. Zhua, J. Shi, J. Mol. Catal. A: Chem. 336 (2011) 51.
[52] S.M. Islam, P. Mondal, K. Tuhina, A.S. Roy, S. Mondal, D. Hossain, J. Organomet. Chem. 695 (2010) 2284.
[53] R.U. Islam, M.J. Witcomb, E. Lingen, M.S. Scurrell, W.V. Otterlo, K. Mallick, J. Organomet. Chem. 696 (2011) 2206.
[54] D.H. Lee, J.Y. Jung, M.J. Jin, Green Chem. 12 (2010) 2024.
[55] C.M. Cirtiu, A.F. Dunlop-Briere, A. Moores, Green Chem. 13 (2011) 288.
[56] X. Chen, Y. Hou, H. Wang, Y. Cao, J. He, J. Phys. Chem. C 112 (2008) 8172.
[57] J. Zhu, J. Zhou, T. Zhao, X. Zhou, D. Chen, W. Yuan, Appl. Catal. A: Gen. 352 (2009) 243.
[58] S. Wu, H. Ma, X. Jia, Y. Zhong, Z. Lei, Tetrahedron 67 (2011) 250.
[59] S.M. Islam, P. Mondal, K. Tuhina, A.S. Roy, J. Chem. Technol. Biotechnol. 85 (2010) 999.
[60] G.M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, J. Am. Chem. Soc. 131 (2009) 8262.
[61] L. Rumi, G.M. Scheuermann, R. Mülhaupt, W. Bannwarth, Helv. Chim. Acta 94 (2011) 966.

[62] (a) H. Veisi, Synthesis 2631 (2010);
(b) H. Veisi, Tetrahedron Lett. 51 (2010) 2109;
(c) H. Veisi, Curr. Org. Chem. 15 (2011) 2438.
[63] G.M. Neelgund, A. Oki, J. Nanosci. Nanotechnol. 11 (2011) 3621.
[64] Y. Xiong, Y. Xia, Adv. Mater. 19 (2007) 3385.
[65] O. Winjobi, Z. Zhang, C. Liang, W. Li, Electrochim. Acta 55 (2010) 4217.
[66] N. Shang, C. Feng, H. Zhang, S. Gao, R. Tang, C. Wang, Z. Wang. Catal. Commun. 40 (2013) 111.
[67] M. Bazherad, S. Jajarmi, J. Mol. Catal. A: Chem. 370 (2013) 152.
[68] Q. Du, Y. Li. Beilstein J. Org. Chem. 7 (2011) 378.
[69] A.S. Singh, U.B. Patil, J.M. Nagarkar, Catal. Commun. 35 (2013) 11.