Nanochem Res 4(2): 132-139, Summer and Autumn 2019

RESEARCH PAPER

Efficient Suzuki and Sonogashira coupling reactions catalyzed by Pd/DNA@MWCNTs in green solvents under mild conditions

Abdol R. Hajipour[1,2]*, Zahra Khorsandi[1]*

[1]Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

[2]Department of Pharmacology, University of Wisconsin, Medical School, 1300 University Avenue, Madison, WI, USA

ARTICLE INFO

Article History:
Received 18 May 2019
Accepted 21 June 2019
Published 15 October 2019

Keywords:
Suzuki
Sonogashira
DNA
Multi Walled Carbon Nanotubes
Heterogeneous Catalyst

ABSTRACT

The palladium nanoparticles were immobilized on DNA-modified multi walled carbon nanotubes as stable and powerful heterogeneous catalyst. The catalyst was characterized by FT-IR spectroscopy, UV-Vis spectroscopy, field emission scanning electron microscopy, X-ray diffraction, transmission electron microscopy, inductively coupled plasma and elemental analysis. DNA as a well-defined structure and biodegradable natural polymer was used to make the palladium catalyst which shows a high activity in Suzuki and Sonogashira cross-coupling reactions in excellent yields and good selectivity under ligand-free and mild reaction conditions. Moreover, the catalyst could be recovered and reused several times without any considerable loss of its catalytic activity. This air- and moisture-stable phosphine-free palladium catalyst was found to be highly active in aqueous ethanol with extremely small amount of palladium under mild conditions. To the best of our knowledge, this is the first report on using DNA base heterogonous catalyst for Suzuki and Sonogashira cross-coupling reactions.

How to cite this article
Hajipour AR, Khorsandi Z. Efficient Suzuki and Sonogashira coupling reactions catalyzed by Pd/DNA@MWCNTs in green solvents under mild conditions. Nanochem Res, 2019; 4(2): 132-139. DOI: 10.22036/ncr.2019.02.004

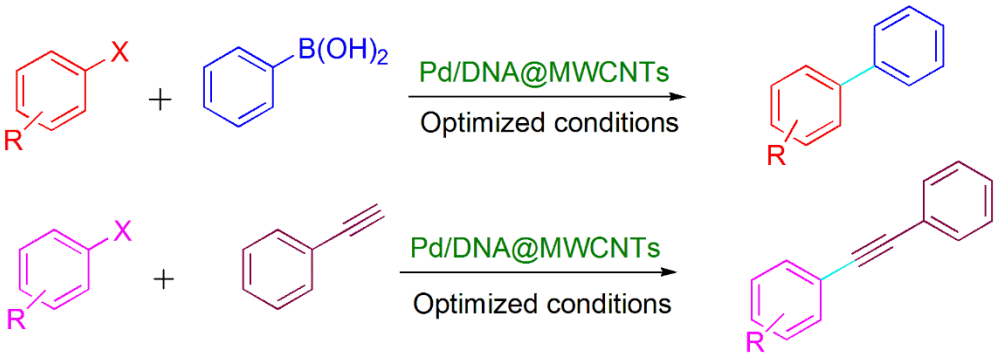
INTRODUCTION

The palladium-catalyzed cross-coupling reactions are efficient methods for carbon–carbon bond formation [1-7]. The biaryl derivatives generated in Suzuki cross-coupling reactions have been widely used in many natural products, pharmaceuticals and advanced materials; so, a large number of effective catalytic systems have been developed [8-11]. The standard Suzuki reaction using palladium salts and phosphine ligands suffers from limitations that have so far precluded many industrial applications. In spite of wide applications of Pd-catalysts in coupling reaction, the catalyst recovery and contamination of products by toxic palladium is a main problem; the acceptable limits of palladium pollution in pharmaceuticals were set as ppm level [12, 13]. Moreover, phosphine ligands are toxic and sensitive to air and moisture [14, 15]; so, heterogeneous phosphine-free catalysts are highly valuable.

In this regard, development of effective and practical catalytic approaches using an environmental friendly, low cost and safe ligands has been a topic of great interest during recent years [16-21]. Biomolecules such as DNA are highly favorable; their applications in various biomaterials and biocatalysts [22-27], their chemical stability, biodegradability, commercial availability, and also their low-cost make them attractive materials in catalyst field. Stabilization of metal nanoparticles such as Ag,[28] Au,[29] Co,[30, 31] Cu,[32] Pt[33] and Pd[34, 35] in DNA cavities by coordination and a large number of effective catalytic systems have been developed. [36, 37] However, solubility of DNA promoted us to fix it on a nano solid support to generate a recyclable heterogeneous catalyst.

Furthermore, use of robust reusable catalyst

* Corresponding Author Email: *haji@cc.iut.ac.ir*



Scheme 1. Reactions catalyzed by Pd/DNA@MWCNTs.

for cross-coupling reaction prepared from various solid supports such as microporous polymers, activated carbon, clays, magnetic nanoparticles and carbon nanotubes (CNTs) [9, 38-40] could be a suitable method for overcoming the disadvantages of palladium salts pollution. In recent years, carbon nanotubes (CNTs) due to their unique thermal, mechanical and chemical properties have attracted significant interests. They have unique features such as large surface, intrinsic low mass and easy surface modifications which might be favourable candidates as catalysts or supports [41-42]. Considering the fascinating structure of CNTs, such as large capability of loading organic molecules, they can be used as an efficient support for immobilization of DNA and palladium nanoparticles making a unique efficient and recoverable catalyst. The aromatic nucleobases of DNA interact through π–π stacking with carbon surface [43, 44] and stabilize palladium nanoparticles. Several reports in production and structure investigation of DNA-modified carbon materials and their uses in drug delivery, biosensors and high-performance modern materials are available [45].

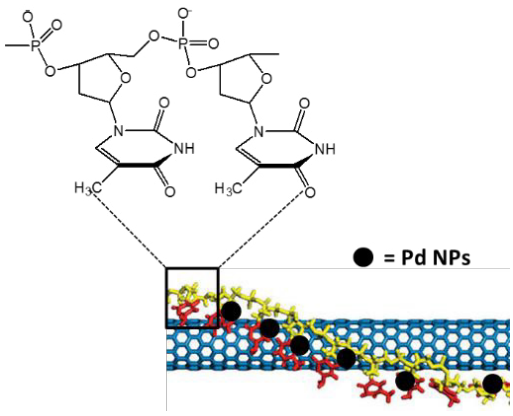
These observations motivated us to explore the potential of this catalyst for such cross-coupling reactions. Now, in continuation of our recent investigations on the application of heterogeneous catalytic systems in cross-coupling reactions [8, 46-48], we would like to report the application of Pd/DNA@MWCNTs in the Suzuki and Sonogashira coupling reactions (Scheme 1). Its catalytic applications are rare and, to the best of our knowledge, Suzuki and Sonogashira employing immobilized palladium on DNA-modified CNTs have not been reported previously.

One of the most valid metal catalyzed carbon–carbon cross-coupling reactions of aryl halides with a terminal acetylene is the Sonogashira reactionwhich is widely used in pharmaceuticals and advanced materials [49-56]. The original catalytic system for Sonogashira couplings include the use of a palladium catalyst and a co-catalyst of copper(I) salt. Many different synthetic methods based on copper-free palladium catalysts have been reported for this reaction [57]. However, from sustainability point of view, because of the high cost and toxicity of palladium, using effective heterogonous palladium catalytic systems is much more interesting.

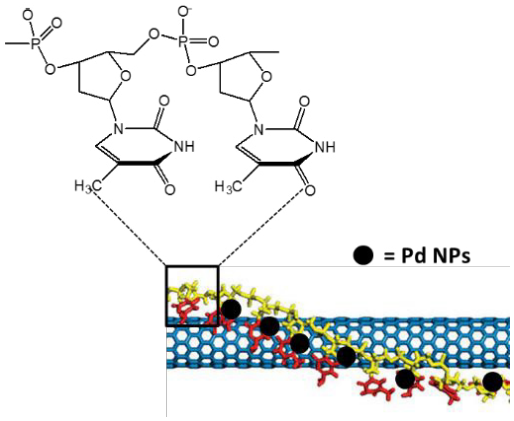
RESULTS AND DISCUSSION

The preparation of Pd/DNA@MWCNTs (Scheme 2) catalyst was performed as explained in experiment section.

Single-stranded salmon testes of DNA (ss-DNA) was loaded on MWCNTs via non-covalent and simple way by mixing them in an aqueous solution, DNA/MWCNTs was formed and then reacted with palladium to obtain Pd/DNA@MWCNTs. The produced catalyst was characterized by several instrumental methods; the results are given in supplemental data. The FT-IR spectrum



Scheme 2. Structure of Pd/DNA@MWCNTs



Scheme 2. Structure of Pd/DNA@MWCNTs

of the final catalyst was depicted presentation of aromatic nucleobases and phosphate group of DNA (Fig. S1). It can also be monitored by UV–Vis spectroscopy (Fig. S2). The structural properties of the synthesized catalyst was analyzed by XRD (Fig. S3). The palladium content of Pd/DNA@MWCNTs was found to be 0.12 mmolg^{-1} of the catalyst as measured by ICP-OES analysis. The morphology of the catalyst surface was studied by field emission scanning electron microscopy (FE-SEM) (Fig. 1). A transmission electron microscopy (TEM) image of catalyst revealed nanometer dimensions of the catalyst (Fig. S4). In the outset, for screening experiments, the model reaction was performed using bromobenzene and phenylboronic acid as substrates (Table 1).

It was first carried out without any catalyst, and no product was formed (Table 1, entry 1). In the presence of Pd@MWCNTs (with 5 mol% Pd), as ligand-free systems, appeared to be less active, and produced only trace amounts of product after 4 h (Table 1, entries 2). However, surprisingly, 0.002 g of Pd/DNA@MWCNTs containing 0.024 mol% of Pd showed the highest activity, and afforded the product in 96% yield. The critical effect of ligand on reaction performance was indicated. The effect of bases on the model reaction was investigated. As shown in Table 1, $NaHCO_3$, K_2CO_3, K_3PO_4, Na_2CO_3 and NaOH were tested and NaOH was found as the most effective agent (Table 1, entries 3-7).

Further investigations revealed that the reaction is also affected by the other parameters including the amount of catalyst, substrate and base ratio, solvent and temperature which upon them the optimal reaction conditions should be EtOH: H_2O in 1:1 ratio, bromobenzene : phenylbroronic acid in 1:1.2,

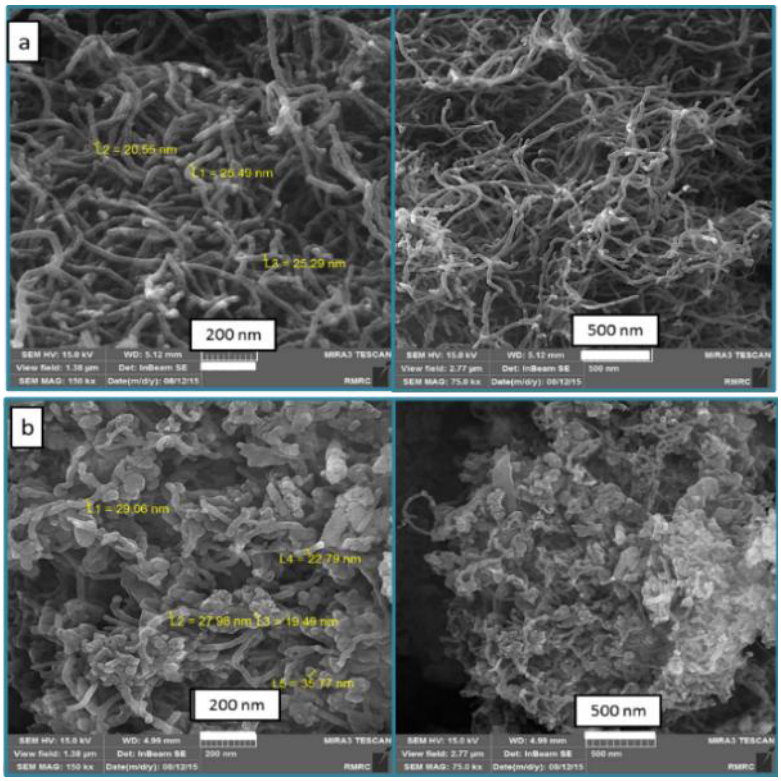
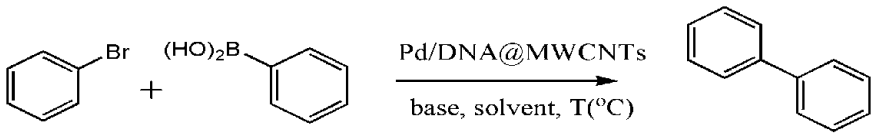


Fig. 1. FE-SEM images of (a) MWCNTs and (b) Pd/DNA@MWCNTs

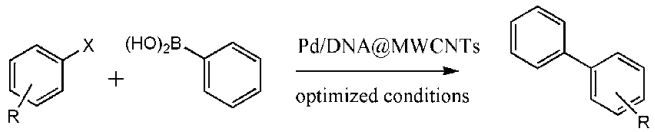
Table 1. Optimization of Suzuki Reaction Conditions[a]



Entry	Cat. (mg/mol%)	Base (eq)	Solvent	T (°C)	Yield[b] (%)
1[c]	-	K_2CO_3 (3)	DMF	100	-
2[c]	0.02 (5) of (Pd @MWCNTs)	K_2CO_3 (3)	DMF	100	30
3	0.002 (0.024)	K_2CO_3 (3)	DMF	100	96
4	0.002 (0.024)	$NaHCO_3$ (3)	DMF	100	67
5	0.002 (0.024)	K_3PO_4 (3)	DMF	100	93
6	0.002 (0.024)	Na_2CO_3 (3)	DMF	100	74
7	0.002 (0.024)	NaOH (3)	DMF	100	97
8	0.002 (0.024)	NaOH (3)	H_2O	100	90
9	0.002 (0.024)	NaOH (3)	PEG(200)	100	95
10	0.002 (0.024)	NaOH (3)	EtOH	80	91
11	0.002 (0.024)	NaOH (3)	H_2O:EtOH[d]	80	98
12	0.002 (0.024)	NaOH (3)	H_2O:EtOH	65	97
13	0.002 (0.024)	NaOH (3)	H_2O:EtOH	r.t.	42
14	0.001 (0.012)	NaOH (3)	H_2O:EtOH	65	72
15	0.005 (0.06))	NaOH (3)	H_2O:EtOH	65	98
16	0.002 (0.024)	NaOH (1)	H_2O:EtOH	65	88
17	0.002 (0.024)	NaOH (2)	H_2O:EtOH	65	94
18	0.002 (0.024)	NaOH (4)	H_2O:EtOH	65	96

[a]Reaction conditions: 1 mmol 4-bromobenzen, 1.2 mmol phenylboronic acid in 3 mL of solvent for 1 h. [b]GC and isolated yield. [C]24 h, [d] 1:1 ratio

Table 2. Suzuki cross-coupling of various aryl halides in the presence of the catalyst.[a]

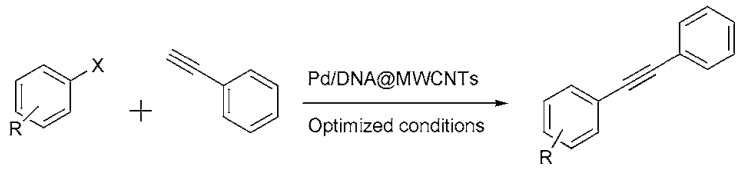


Entry	X	R	Yeild[b](%)
1	I	H	98
2	I	4-NH_2	79
3	I	3-NO_2	94
4	Br	H	96
5	Br	2-NH_2	73
6	Br	4-NH_2	81
7	Br	4-CN	96
8	Br	4-CHO	98
9	Br	3-CHO-4-OH	73
10	Cl	H	86
11	Cl	4-NH_2	68
12	Cl	4-COH	87

[a]The reaction was carried out with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (3.0 equiv.) in 3.0 mL H_2O:EtOH (1:1), 0.002 mg of catalyst (0.024 mol% of Pd) at 65 °C for 1h.
[b]Isolated yield.

at 65 °C, and 60 min (Table 1, entries 8-18). Under the optimized conditions, the scope of the reaction regarding to the kind of aryl halides was probed. The results are summarized in Table 2. Various substituents of aryl iodides, aryl bromides and aryl chlorides are transformed into the corresponding products in high to excellent yields. However, no significant different was observed among aryl iodides and aryl bromides substrate. The results show that aryl halides with electron-withdrawing substituents in comparison to electron-donating groups give more yields. Under the optimized

Table 3. Sonogashira cross-coupling of various aryl halides in the presence of the catalyst.[a]



Entry	X	R	Yeild[b](%)
1	I	H	98
2	I	4-NH_2	89
3	Br	H	97
5	Br	2-NH_2	76
6	Br	4-CHO	95
7	Br	3-CHO-4-OH	90
6	Cl	H	81
7	Cl	4-NH_2	64
8	Cl	4-COH	88
9	Cl	4-NO_2	86

[a]The reaction was carried out with aryl halide (1.0 mmol), phenylacetylene (1.2 mmol), NaOH (3.0 equiv.) in 3.0 mL H_2O:EtOH (1:1), 0.002 mg of catalyst (0.024 mol% of Pd) at 65 °C for 1h. [b]Isolated yield.

reaction conditions assigned; application of this catalyst was also studied in the Sonogashira reaction. Aryl halides with various living groups and substituents converted to their corresponding products in high to excellent yields (Table 3). All of the products are known and characterized by comparing their physical data with those reported in the literature.

Generally, the catalyst was compatible with a wide range of functional groups and exhibited good activity in cross-coupling reactions for the construction of C–C bonds to synthesize derivatives of biphenyl and diphenylethyne using low amounts of palladium and green solvent (ethanol and water) under mild reaction conditions.

Moreover, combination of advantages of heterogeneous catalysts, such as a reasonable catalytic activity, stability and reusability, make this catalyst sufficient for cross-coupling reactions on efficiency, environmental and economic grounds. The template reaction of Suzuki was selected for studying the leaching of catalyst. After 30 minutes, the catalyst was separated and the remaining solution was stirred for 1 h, without catalyst, and no increase in conversion was detected. Moreover, ICP analysis of the remaining solution indicates no Pd in the reaction mixture. These results clearly confirm that this catalyst is heterogeneous in nature and Pd is not leached out from the solid surface of the catalyst during the coupling reaction.

Catalyst reusing is important from economic, environmental and industrial points of view. So, the recyclability of catalyst was checked in model reaction of Suzuki. At the end of reaction, the catalyst was separated, washed with ethanol and acetone and reused. As reported in Table 4, the catalyst was reused seven times with no significant loss of activity. Great recyclability of CNTs supported heterogonous catalyst was also reported previously [58]. All these results demonstrate that the Pd/DNA@MWCNTs give high catalytic activity in cross-coupling reactions with more environmental and economic benefits compared to the wide range of homogenous catalysts reported previously.

Table 4. Reusability of the catalyst in the Suzuki reaction of 4-bromobenzen with phenylboronic acid

Run	Yield[a] (%)	Run	Yield[a] (%)
1	98	5	89
2	95	6	90
3	92	7	86
4	90		

[a]Isolated yield

CONCLUSION

This work provides a green and economical method for efficient Suzuki and Sonogashira under mild and aerobic conditions by DNA-modified MWCNTs-based Pd hybrid catalyst. In addition, our catalytic system has significantly low amount of palladium loading and could be reused for seven consecutive cycles without any marked loss of its activity.

EXPERIMENT

General procedure for catalyst preparation

The catalyst (Pd/DNA@MWCNTs) was synthesized through the method which is described: 0.3 g of the as-received MWCNTs was dispersed in 25 mL of piranha (mixture of sulphuric acid 96 wt% and hydrogen peroxide 30 wt% in ratio 70:30) in a 100 mL round bottom flask equipped with a condenser, and dispersion was kept for 5 h.

Next, the dispersion was diluted in water and filtered. Then, the resulting solid was washed up to neutral pH and dried in vacuum at 40°C overnight. The DNA-functionalized MWCNTs were synthesized using Qu's strategy [37]. The ss-DNA was heated at 95°C for 1 h to obtain the single-stranded DNA. The CO_2H-MWCNTs dispersion was mixed with single-stranded DNA (10 ml, 2 mg mL^{-1}), $NaBH_4$ was added (8 µL, 75 wt %; $NaBH_4$/MWCNTs-O) and the mixture refluxed at 100°C for 1 h. Then, the solution was centrifuged and washed several times with water and dried.

General procedure for Suzuki reaction

In a round-bottomed flask equipped with a mechanical stirring, aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (4.0 equiv.) and 0.002 mg of catalyst (0.024 mol % of Pd) in 3.0 mL H_2O : EtOH were stirred for 1 h under air atmosphere at 65. The progress of the reaction was monitored by TLC and GC. After completion of the reaction, the mixture was diluted with dichloromethane and water. The organic layer was washed, dried, concentrated and isolated by chromatography to afford the corresponding products. The products were characterized by comparing their properties, such as m.p, IR, ^{1}H, and ^{13}C NMR spectra with those reported in literature.

General procedure for Sonogashira reaction

In a round-bottom flask equipped with a mechanical stirrer, phenyl acetylene (1.2 mmol), aryl halide (1.0 mmol), catalyst (0.002 mg, 0.024 mol%), and NaOH (4.0 eq.) in H_2O:EtOH (3 mL) were stirred under an air atmosphere at 65. The progress of the reaction was monitored by TLC and GC. After the end of the reaction, the mixture was diluted with dichloromethane and water. The organic layer was washed with brine and concentrated under reduced pressure. The product was isolated by column chromatography to give the corresponding products. The products were characterized by comparing their properties, such as m.p, IR, ^{1}H, and ^{13}C NMR spectra with those reported in the literature.

ACKNOWLEDGEMENTS

Financial support from the Isfahan University of Technology (IUT), Iran is appreciated. Additional financial support from the Center of Excellence in Sensor and Green Chemistry Research (IUT) is gratefully acknowledged.

CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Zarei A, Khazdooz L, Hajipour AR, Rafiee F, Azizi G, Abrishami F. Suzuki–Miyaura cross-coupling of aryldiazonium silica sulfates under mild and heterogeneous conditions. Tetrahedron Letters. 2012;53(4):406-8.
2. Aghahosseini H, Tabatabaei Rezaei SJ, Maleki M, Abdolahnjadian D, Ramazani A, Shahroosvand H. Pt(II)-Based Artificial Nitroreductase: An Efficient and Highly Stable Nanozyme. ChemistrySelect. 2019;4(4):1387-93.
3. Kalantari F, Ramazani A, Heravi MRP. Recent Advances in the Applications of Hybrid Magnetic Nanomaterials as Magnetically Retrievable Nanocatalysts. Current Organic Chemistry. 2019;23(2):136-63.
4. Yaghoubi A, Ramazani A. Synthesis of Amino-functionalized Carbon Nanotubes and their Applications. Current Organic Chemistry. 2018;22(15):1505-22.
5. Aghahosseini H, Tabatabaei Rezaei SJ, Tadayyon M, Ramazani A, Amani V, Ahmadi R, et al. Highly Efficient Aqueous Synthesis of Propargylamines through C–H Activation Catalyzed by Magnetic Organosilica-Supported Gold Nanoparticles as an Artificial Metalloenzyme. European Journal of Inorganic Chemistry. 2018;2018(22):2589-98.
6. Motevalizadeh SF, Alipour M, Ashori F, Samzadeh-Kermani A, Hamadi H, Ganjali MR, et al. Heck and oxidative boron Heck reactions employing Pd(II) supported amphiphilized polyethyleneimine-functionalized MCM-41 (MCM-41@aPEI-Pd) as an efficient and recyclable nanocatalyst. Applied Organometallic Chemistry. 2018;32(3):e4123.
7. Ramazani A, Khoobi M, Sadri F, Tarasi R, Shafiee A, Aghahosseini H, et al. Efficient and selective oxidation of alcohols in water employing palladium supported nanomagnetic Fe3O4@hyperbranched polyethylenimine (Fe3O4@HPEI.Pd) as a new organic–inorganic hybrid nanocatalyst. Applied Organometallic Chemistry. 2018;32(1):e3908.
8. Hajipour AR, Boostani E, Mohammadsaleh F. Proline-functionalized chitosan–palladium(ii) complex, a novel nanocatalyst for C–C bond formation in water. RSC Advances. 2015;5(31):24742-8.
9. Hajipour AR, Khorsandi Z. Immobilized Pd on (S)-methyl histidinate-modified multi-walled carbon nanotubes: a powerful and recyclable catalyst for Mizoroki–Heck and Suzuki–Miyaura C–C cross-coupling reactions in green solvents and under mild conditions. Applied Organometallic Chemistry. 2016;30(5):256-61.
10. Hajipour AR, Tadayoni NS, Khorsandi Z. Magnetic iron

oxide nanoparticles–N-heterocyclic carbene–palladium(II): a new, efficient and robust recyclable catalyst for Mizoroki–Heck and Suzuki–Miyaura coupling reactions. Applied Organometallic Chemistry. 2016;30(7):590-5.
11. Hajipour AR, Rafiee F. Synthesis of substituted biaryls via Suzuki, Stille and Hiyama cross-coupling and homo-coupling reactions by CN-dimeric and monomeric ortho-palladated catalysts. Applied Organometallic Chemistry. 2013;27(7):412-8.
12. Paul S, Clark JH. A highly active and reusable heterogeneous catalyst for the Suzuki reaction: synthesis of biaryls and polyaryls. Green Chemistry. 2003;5(5):635-8.
13. Yin, Liebscher J. Carbon−Carbon Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts. Chemical Reviews. 2007;107(1):133-73.
14. Das P, Bora U, Tairai A, Sharma C. Triphenylphosphine chalcogenides as efficient ligands for room temperature palladium(II)-catalyzed Suzuki–Miyaura reaction. Tetrahedron Letters. 2010;51(11):1479-82.
15. Marziale AN, Jantke D, Faul SH, Reiner T, Herdtweck E, Eppinger J. An efficient protocol for the palladium-catalysed Suzuki–Miyaura cross-coupling. Green Chemistry. 2011;13(1):169-77.
16. Breuer M, Hauer B. Carbon–carbon coupling in biotransformation. Current Opinion in Biotechnology. 2003;14(6):570-6.
17. Sukumaran J, Hanefeld U. Enantioselective C–C bond synthesis catalysed by enzymes. Chemical Society Reviews. 2005;34(6):530-42.
18. Brovetto M, Gamenara D, Saenz Méndez P, Seoane GA. C−C Bond-Forming Lyases in Organic Synthesis. Chemical Reviews. 2011;111(7):4346-403.
19. Fesko K, Gruber-Khadjawi M. Biocatalytic Methods for C-C Bond Formation. ChemCatChem. 2013;5(6):1248-72.
20. Schoemaker HE, Mink D, Wubbolts MG. Dispelling the Myths--Biocatalysis in Industrial Synthesis. Science. 2003; 299(5613): 1694-7.
21. Tufvesson P, Lima-Ramos J, Nordblad M, Woodley JM. Guidelines and Cost Analysis for Catalyst Production in Biocatalytic Processes. Organic Process Research & Development. 2011;15(1):266-74.
22. Wang C, Jia G, Zhou J, Li Y, Liu Y, Lu S, et al. Enantioselective Diels–Alder Reactions with G-Quadruplex DNA-Based Catalysts. Angewandte Chemie International Edition. 2012;51(37):9352-5.
23. Wang C, Li Y, Jia G, Liu Y, Lu S, Li C. Enantioselective Friedel–Crafts reactions in water catalyzed by a human telomeric G-quadruplex DNA metalloenzyme. Chemical Communications. 2012;48(50):6232-4.
24. Rafique MMA. A Smart Way of Synthesis and Characterization of New DNA Based Hybrid Catalysts. Current Smart Materials. 2018;3(1):40-8.
25. Li Y, Wang C, Jia G, Lu S, Li C. Enantioselective Michael addition reactions in water using a DNA-based catalyst. Tetrahedron. 2013;69(32):6585-90.
26. Park S, Sugiyama H. DNA-Based Hybrid Catalysts for Asymmetric Organic Synthesis. Angewandte Chemie International Edition. 2010;49(23):3870-8.
27. Silverman SK. DNA – eine vielseitige chemische Verbindung für die Katalyse, zur Kodierung und zur Stereokontrolle. Angewandte Chemie. 2010;122(40):7336-59.
28. Braun E, Eichen Y, Sivan U, Ben-Yoseph G. DNA-templated assembly and electrode attachment of a conducting silver wire. Nature. 1998;391(6669):775-8.
29. Wang Y, Ouyang G, Zhang J, Wang Z. A DNA-templated catalyst: the preparation of metal-DNA nanohybrids and their application in organic reactions. Chemical Communications. 2010;46(42):7912-4.
30. Gu Q, Cheng C, Haynie DT. Cobalt metallization of DNA: toward magnetic nanowires. Nanotechnology. 2005;16(8):1358-63.
31. Kinsella JM, Ivanisevic A. DNA-Templated Magnetic Nanowires with Different Compositions: Fabrication and Analysis. Langmuir. 2007;23(7):3886-90.
32. Dittmer WU, Simmel FC. Chains of semiconductor nanoparticles templated on DNA. Applied Physics Letters. 2004;85(4):633-5.
33. Mertig M, Colombi Ciacchi L, Seidel R, Pompe W, De Vita A. DNA as a Selective Metallization Template. Nano Letters. 2002;2(8):841-4.
34. Nguyen K, Monteverde M, Filoramo A, Goux-Capes L, Lyonnais S, Jegou P, et al. Synthesis of Thin and Highly Conductive DNA-Based Palladium Nanowires. Advanced Materials. 2008;20(6):1099-104.
35. Hatakeyama Y, Umetsu M, Ohara S, Kawadai F, Takami S, Naka T, et al. Homogenous Spherical Mosslike Assembly of Pd Nanoparticles by using DNA Compaction: Application of Pd–DNA Hybrid Materials to Volume-Expansion Hydrogen Switches. Advanced Materials. 2008;20(6):1122-8.
36. Rioz-Martínez A, Roelfes G. DNA-based hybrid catalysis. Current Opinion in Chemical Biology. 2015;25:80-7.
37. Qu K, Wu L, Ren J, Qu X. Natural DNA-Modified Graphene/Pd Nanoparticles as Highly Active Catalyst for Formic Acid Electro-Oxidation and for the Suzuki Reaction. ACS Applied Materials & Interfaces. 2012;4(9):5001-9.
38. Dai H, Hafner J. A. G, Rinzler, DT Colbert, RE Smalley. Nature. 1996;384:147.
39. Hajipour AR, Khorsandi Z. Immobilized Pd on (S)-methyl histidinate-modified multi-walled carbon nanotubes: a powerful and recyclable catalyst for Mizoroki–Heck and Suzuki–Miyaura C–C cross-coupling reactions in green solvents and under mild conditions. Applied Organometallic Chemistry. 2016;30(5):256-61.
40. Hajipour AR, Khorsandi Z, Farrokhpour H. Regioselective Heck reaction catalyzed by Pd nanoparticles immobilized on DNA-modified MWCNTs. RSC Advances. 2016;6(64):59124-30.
41. Sun Q, Zorin NA, Chen D, Chen M, Liu T-X, Miyake J, et al. Langmuir−Blodgett Films of Pyridyldithio-Modified Multiwalled Carbon Nanotubes as a Support to Immobilize Hydrogenase. Langmuir. 2010;26(12):10259-65.
42. Rajarao R, Kim TH, Bhat BR. Multi-walled carbon nanotube bound nickel Schiff-base complexes as reusable catalysts for oxidation of alcohols. Journal of Coordination Chemistry. 2012;65(15):2671-82.
43. Rodrigues EG, Carabineiro SAC, Delgado JJ, Chen X, Pereira MFR, Órfão JJM. Gold supported on carbon nanotubes for the selective oxidation of glycerol. Journal of Catalysis. 2012;285(1):83-91.
44. Li X, Peng Y, Qu X. Carbon nanotubes selective destabilization of duplex and triplex DNA and inducing B–A transition in solution. Nucleic Acids Research. 2006; 34(13): 3670-6.
45. Li X, Peng Y, Qu X. Carbon nanotubes selective destabilization of duplex and triplex DNA and inducing

B–A transition in solution. Nucleic Acids Research. 2006;34(13):3670-6.
46. Liu X, Diao H, Nishi N. Applied chemistry of natural DNA. Chemical Society Reviews. 2008;37(12):2745-57.
47. Hajipour AR, Khorsandi Z. Multi walled carbon nanotubes supported N-heterocyclic carbene–cobalt (II) as a novel, efficient and inexpensive catalyst for the Mizoroki–Heck reaction. Catalysis Communications. 2016;77:1-4.
48. Hajipour AR, Khorsandi Z, Karimi H. Cobalt nanoparticles supported on ionic liquid-functionalized multiwall carbon nanotubes as an efficient and recyclable catalyst for Heck reaction. Applied Organometallic Chemistry. 2015;29(12):805-8.
49. Hajipour AR, Khorsandi Z, Mortazavi M, Farrokhpour H. Green, efficient and large-scale synthesis of benzimidazoles, benzoxazoles and benzothiazoles derivatives using ligand-free cobalt-nanoparticles: as potential anti-estrogen breast cancer agents, and study of their interactions with estrogen receptor by molecular docking. RSC Advances. 2015;5(130):107822-8.
50. Hajipour AR, Boostani E, Mohammadsaleh F. Proline-functionalized chitosan–palladium(ii) complex, a novel nanocatalyst for C–C bond formation in water. RSC Advances. 2015;5(31):24742-8.
51. Sonogashira K. Development of Pd–Cu catalyzed cross-coupling of terminal acetylenes with sp2-carbon halides. Journal of Organometallic Chemistry. 2002;653(1):46-9.
52. Molnár Á. Efficient, Selective, and Recyclable Palladium Catalysts in Carbon−Carbon Coupling Reactions. Chemical Reviews. 2011;111(3):2251-320.
53. Tamami B, Allahyari H, Ghasemi S, Farjadian F. Palladium nanoparticles supported on poly (N-vinylpyrrolidone)-grafted silica as new recyclable catalyst for Heck cross-coupling reactions. Journal of Organometallic Chemistry. 2011;696(2):594-9.
54. Climent MJ, Corma A, Iborra S, Mifsud M. Heterogeneous Palladium Catalysts for a New One-Pot Chemical Route in the Synthesis of Fragrances Based on the Heck Reaction. Advanced Synthesis & Catalysis. 2007;349(11-12):1949-54.
55. Yinghuai Z, Peng SC, Emi A, Zhenshun S, Monalisa, Kemp RA. Supported Ultra Small Palladium on Magnetic Nanoparticles Used as Catalysts for Suzuki Cross-Coupling and Heck Reactions. Advanced Synthesis & Catalysis. 2007;349(11-12):1917-22.
56. Sonogashira K, Diedrich F, Meijere A. Modern Arylation Method. Wiley-VCH, Weinheim; 2004.
57. Khalafi-Nezhad A, Panahi F. Immobilized palladium nanoparticles on a silica–starch substrate (PNP–SSS): as an efficient heterogeneous catalyst for Heck and copper-free Sonogashira reactions in water. Green Chemistry. 2011;13(9):2408-15.
58. Sonogashira K, Diedrich F, Meijere A. Modern Arylation Method. Wiley-VCH, Weinheim; 2004.
59. Astruc D. Palladium Nanoparticles as Efficient Green Homogeneous and Heterogeneous Carbon−Carbon Coupling Precatalysts: A Unifying View. Inorganic Chemistry. 2007;46(6):1884-94.
60. Chun YS, Shin JY, Song CE, Lee S-g. Palladium nanoparticles supported onto ionic carbon nanotubes as robust recyclable catalysts in an ionic liquid. Chemical Communications. 2008(8):942-4.