

Heterogeneous & Homogeneous & Bio- & Nano-

CHEM **CAT** CHEM

CATALYSIS

Accepted Article

Title: Graphene Quantum Dots Modified Fe₃O₄ Nanoparticles Supported PdCu with Enhanced Catalytic Activity for Sonogashira Reaction'

Authors: Carmen Nájera and Mohammad Gholinejad

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemCatChem* 10.1002/cctc.201601519

Link to VoR: <http://dx.doi.org/10.1002/cctc.201601519>

WILEY-VCH

www.chemcatchem.org



Graphene Quantum Dots Modified Fe₃O₄ Nanoparticles Supported PdCu with Enhanced Catalytic Activity for Sonogashira Reaction

Mohammad Gholinejad,^{*,[a]} Jahantab Ahmadi,^[a] Carmen Najera,^{*,[b]} Mohammad Seyedhamzeh,^[a] Fatemeh Zareh,^[a] Mohsen Kompany-Zareh^[a]

Abstract: In this report Fe₃O₄ nanoparticles are modified for the first time with graphene quantum dots (GQD) and used for the stabilization of PdCu bimetallic nanoparticles. The new magnetic compound PdCu@GQD@Fe₃O₄, is characterized by different methods such as SEM, HRTEM, EDS-map, XRD and XPS. This material is applied as an efficient catalyst for Sonogashira reaction of aryl iodides, bromides and chlorides in toluene or *N,N*-dimethylacetamide at 60-110 °C in very high yields with 0.3 mol% of Pd loading. According to different tests such PVP, hot filtration and kinetic studies this catalyst works under heterogeneous conditions. By magnetic separation of the catalyst can be recycled for 6 consecutive runs with small decrease in activity without appreciable structural modification of the reused catalyst which is characterized by TEM and XPS.

Introduction

Graphene quantum nanodots (GQD) with unique properties such as low-toxicity, excellent photostability, small size, biocompatibility, highly tunable photoluminescence properties, chemical inertness, exceptional multi-photon excitation property, electrochemiluminescence, and ease to be functionalized with biomolecules have recently been received great attention in materials science and engineering.^[1] However, despite the various applications of GQD, less attention has been paid for using GQD as catalyst or solid support for catalysis.^[2] It has been showed that the synergistic effect raised by GQD alone and in the metal supported GQD could dramatically improve the activity and stability of the catalysts by excellent electron transportation capability and good chemical/physical stabilities.^[3] For example Li and co-workers, showed high affinity between the metal nanoparticles (NPs) and the carbon surface in the GQD even in the absence of oxygen containing groups and confirmed stabilization of Pd NPs by covalent interactions with graphene.^[4] Pt/Cu nanoparticles supported on GQD showed enhanced catalytic activity for oxygen reduction reaction.^[5] Very

recently, GQD supported Pd NPs were synthesized and applied as an electrocatalyst towards oxygen reduction.^[6] Au/GQD composite was used for veratryl alcohol oxidation to veratryl aldehyde or veratric acid with excellent selectivity and efficient conversion.^[7] However, to the best of our knowledge there is no report on GQD supported Pd as a catalyst for cross-coupling reactions. In recent years, palladium-catalyzed carbon-carbon or carbon-heteroatom bond forming reactions are considered as powerful strategies in organic transformations.^[8] Because of high toxicity level and expensive price of Pd, nowadays different heterogeneous and recyclable palladium catalysts have been introduced for coupling reactions. However, despite advanced progress in this field, isolation of these Pd catalysts by usual methods such as centrifugation or filtration is time consuming and difficult to be performed. Especially important is the recovery of Pd in pharmaceutical synthetic processes in which <5 ppm content of Pd is allowable in the final products.^[9] On the other hand, magnetic nanoparticles having large ratio of surface area to volume, superparamagnetic behavior, low toxicity, and easy to separation from reaction mixture are excellent support for stabilization of Pd NPs.^[10] Pd-catalyzed Sonogashira reaction which is coupling of vinyl or aryl halides or triflates with terminal alkynes in the presence or absence of copper co-catalyst is a powerful method for the formation of arylalkynes and conjugated enynes.^[11] In spite of different reported copper-free Sonogashira reaction, it has been proved that presence of copper under oxygen-free reaction conditions can increase the efficiency of this alkynylation reaction.^[11] Along this line, in recent years different efforts have been made to prepare and apply bimetallic catalytic enhanced PdCu NPs in Sonogashira reaction.^[12] Now in this work, we report the preparation of PdCu bimetallic NPs supported on GQD modified Fe₃O₄ NPs and its application as an efficient recyclable catalyst for the Sonogashira reaction of aryl iodides, bromides and chlorides.

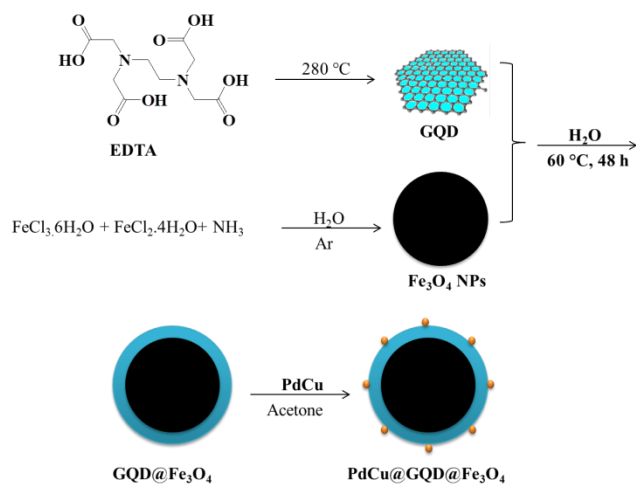
Results and Discussion

Preparation steps of catalyst are summarized in Scheme 1. Firstly, GQD were synthesized using ethylenediaminetetraacetic acid (EDTA) based on the direct carbonization of organic precursor in solid state.^[13] Normalized fluorescence spectrum of GQD in water (Figure 1, ESI) showed broad emission at 431 nm with excitation at 365 nm.^[13] Prepared GQD was treated with synthesized Fe₃O₄ NPs by heating at 60 °C in water for 2 d to produce GQD@Fe₃O₄. TEM image of GQD modified Fe₃O₄ NPs showed presence of uniform Fe₃O₄ NPs and very thin layer of GQD around the Fe₃O₄ NPs (Figure 1).

[a] Mohammad Gholinejad, Jahantab Ahmadi, Mohammed Seyed Hamzeh, Mohsen Kompany
Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P. O. Box 45195-1159, Gavazang, Zanjan 45137-6731, Iran
E-mail: gholinejad@iasbs.ac.ir

[b] Carmen Najera
Departamento de Química Orgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Alicante, Apdo. 99, E-03080-Alicante, Spain
Email: cnajera@ua.es

Supporting information for this article is given via a link at the end of the document.



Scheme 1. Preparations steps of PdCu@GQD@ Fe_3O_4 .

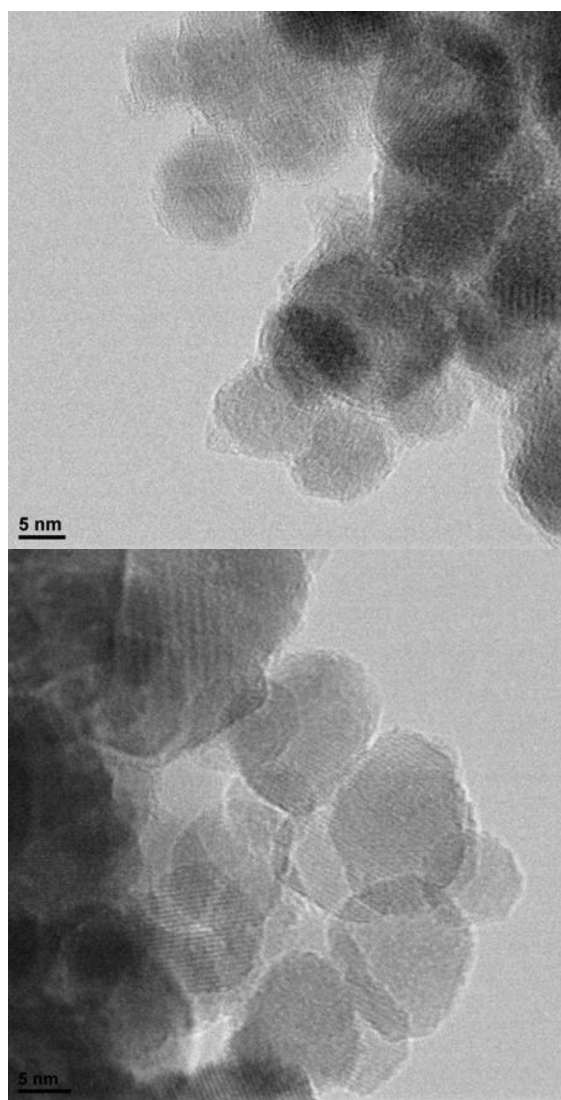


Figure 1. TEM images of GQD@ Fe_3O_4 NPs

In another flask bimetallic PdCu was prepared using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Pd}(\text{OAc})_2$ and the resulting mixture was allowed to react with GQD@ Fe_3O_4 in acetone. Final obtained PdCu@GQD@ Fe_3O_4 NPs had 0.12 and 0.14 mmol g^{-1} Pd and Cu, respectively, as has been determined by atomic absorption spectroscopy. TEM images of PdCu@GQD@ Fe_3O_4 NPs showed appearance of small nanoparticles in the structure (Figure 2). Particle size distribution plot obtained from TEM images of the catalyst showed that the major part of the particles are located in two ranges of 3–4 and 9–25 nm which are related to PdCu and GQD@ Fe_3O_4 nanoparticles respectively (Figure 2, ESI). Also, SEM image of PdCu@GQD@ Fe_3O_4 NPs showed morphology of structure and presence of uniform nanoparticles (Figure 3, ESI).

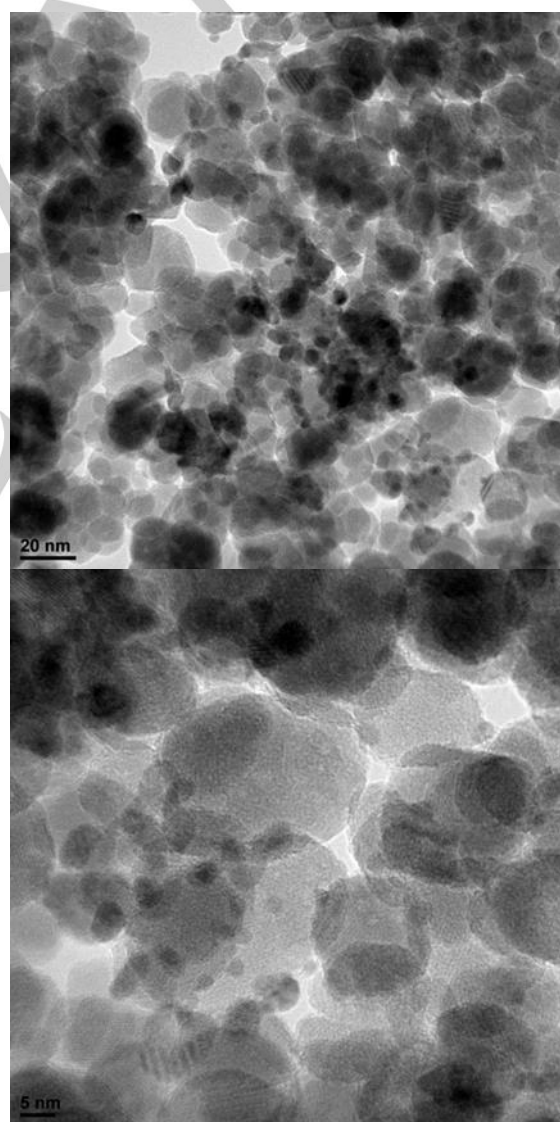


Figure 2. TEM images of PdCu@GQD@ Fe_3O_4

The corresponding EDS mapping images of PdCu@GQD@Fe₃O₄, showed that C, Pd, Cu, and Fe were dispersed uniformly in structure (Figure 3). The presence of these elements as well as nitrogen was further confirmed using EDX (Figure 4, ESI).

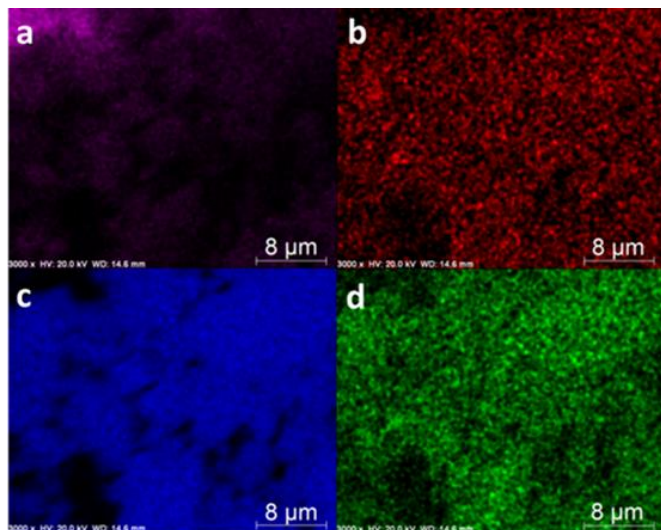


Figure 3. EDS mapping images of PdCu@GQD@Fe₃O₄, a) C, b) Cu, c) Fe, d) Pd

X-ray photoelectron spectrum (XPS) of the material confirmed the presence of carbon in the structure by appearing related peaks to C1s at 283.9 eV, 285.1, 286.8, and 287.4 eV assignable to C-C or C=C, C-N, C-O, and C=O forms of carbon (Figure 4a).^[13,14] XPS analysis was further confirmed presences of nitrogen by appearing related peak to N1s at 399 eV (Figure 4b).^[13, 15] Also, XPS study of Pd region showed two intense doublets at 335 and 340 eV related to Pd(0) and peaks at 337 and 342 eV related to Pd(II) corresponding to Pd 3d_{5/2} and Pd 3d_{3/2}, respectively (Figure 4c). Results of this study indicated that Pd was mostly existed in reduced Pd(0) oxidation state.^[12b,16]

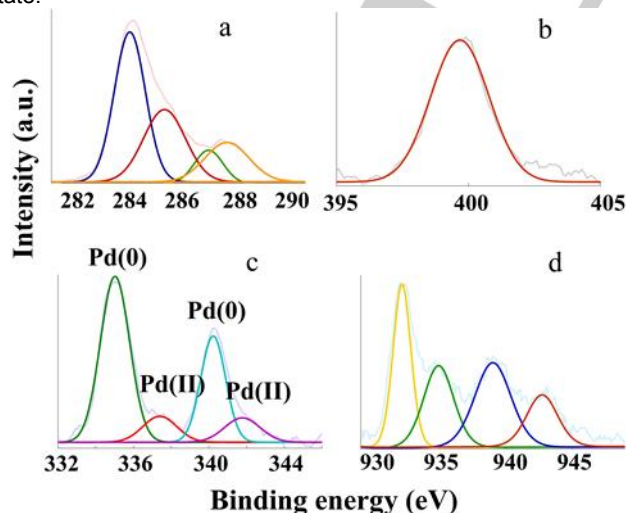


Figure 4. XPS spectra of PdCu@GQD@Fe₃O₄ in a) C 1s, b) N 1s, c) Pd 3d and d) Cu 2p regions.

In order to find information about oxidation state of copper, binding energy related to Cu 2p region was also studied. Results showed one main peak at 932.1 eV and the three satellite peaks. Three satellite peaks at 935.4, 939.4 and 943.1 eV are related to presence of CuO species in structure (Figure 4d). Peak at 932.1 is related to Cu(0) or Cu₂O species and since the binding energies of Cu(0) and Cu₂O are very close and are different by only 0.1 eV, detection of true species by binding energy of this region is very difficult.^[17] One way to distinguish them is using position of their LMM auger transition in XPS spectra which are 568 eV and 570 eV for Cu(0) and Cu₂O, respectively.^[17a,18] Results from our study showed the presence of a peak at 570 eV confirming that the peak in 932.1 eV is related to Cu₂O species (Figure 5, ESI).

X-ray powder diffraction (XRD) of PdCu@GQD@Fe₃O₄ showed diffracted peaks observed at 2theta value of 24°, 34° and 39°, which correspond to the lattice plane (101), (110) and (110), respectively of Cu₃Pd (JCPDS no.07-0138) and low intense peaks at 2theta value of 55°, 57.5° and 60° matches to the (207) planes of Cu₃Pd (JCPDS no. 07-0138) (Figure 5). Similarly, the crystalline peak occurring at 2theta value of 41.4° corresponds to the lattice plane (110) of CuPd (JCPDS no. 48-1551). Related peaks of Pd were observed at 2theta value of 40.3 and 68.7°, which corresponds to (220) plane.^[19] Furthermore, results showed that peaks at 2theta values of 36.3 and 61.4 correspond to (111) and (220) phases for Cu₂O^[20] and peaks at 32.5 and 38.5 are related to (111) and (220) phases for CuO.^[21] These data clearly confirmed the obtained results from XPS regarding presence of Cu₂O species instead of Cu(0). Also, peaks at 30.1°, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6° correspond to (210), (311), (400), (422), (511), and (440) planes of Fe₃O₄ observed in the XRD spectra (Figure 5).^[22]

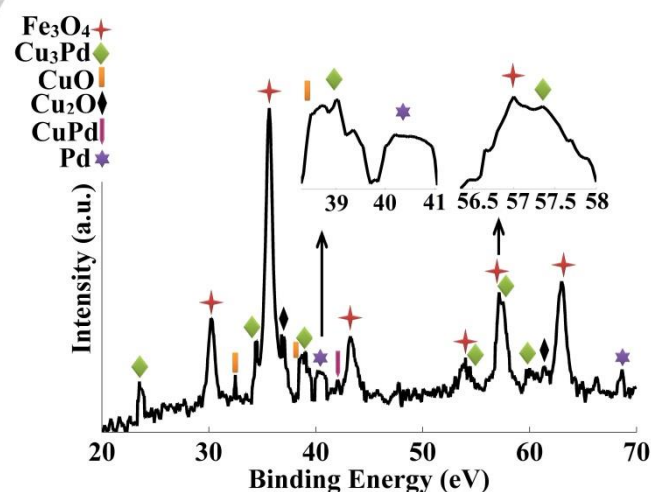
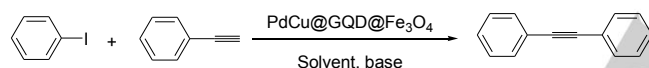


Figure 5. X-ray diagram of PdCu@GQD@Fe₃O₄.

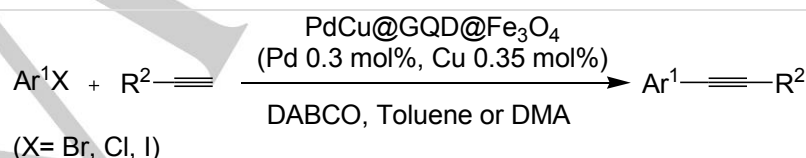
The catalytic activity of prepared PdCu@GQD@Fe₃O₄ was assessed in Sonogashira reaction. In order to find optimized reaction conditions, reaction of iodobenzene with phenylacetylene was selected as the model reaction and effect of different factors such as solvent, base, reaction temperature, and amount of Pd were studied. Results indicated that using different organic and inorganic bases in water as solvent reactions proceed well at 60 °C (Table 1, entries 1-9) and the best yield was obtained using DABCO (Table 1, entry 9). Selecting DABCO as base in other solvents such as toluene, 1,4-dioxane, CH₃CN, and DMA, gave 99%, 94%, 96%, and 97% yields, respectively. By lowering reaction temperature to 50 °C, yield of reaction in toluene was unchanged but for other solvents yields decreased lightly (Table 1, entries 15-19). However, by lowering temperature to 30-40 °C, lower yields were observed (Table 1, entries 20-26). According to the obtained results, we selected using 0.3 mol% of Pd and toluene as a solvent at 50 °C as the most efficient and optimized reaction conditions (Table 1, entry 16). It is worth mentioning that using 0.2 mol% of Pd yield of reaction was decreased to 81% under optimized conditions (Table 1, entry 27).

Table 1. Optimization of reaction condition for the coupling of iodobenzene and phenylacetylene catalyzed by PdCu@GQD@Fe₃O₄.^[a]



Entry	Base	Solvent	Temp (°C)	Time (h)	Yield (%) ^b
1	Et ₃ N	H ₂ O	60	24	88
2	K ₂ CO ₃	H ₂ O	60	24	73
3	NaOAc	H ₂ O	60	24	83
4	<i>t</i> -BuOK	H ₂ O	60	24	83
5	K ₃ PO ₄ ·3H ₂ O	H ₂ O	60	24	85
6	DABCO	H ₂ O	60	24	89
7	N(<i>i</i> -Pr) ₃	H ₂ O	60	24	72
8	K ₃ PO ₄ ·3H ₂ O	H ₂ O	60	24	78
9	Piperidine	H ₂ O	60	24	89
10	DABCO	Toluene	60	24	99
11	DABCO	Dioxane	60	24	94
12	DABCO	CH ₃ CN	60	24	96
13	DABCO	DMA	60	24	97
14	DABCO	PEG 200	60	24	53
15	DABCO	DMA	50	24	91
16	DABCO	Toluene	50	24	99

Table 2. Sonogashira-Hagihara reaction of terminal alkynes with aryl halides using PdCu@GQD@Fe₃O₄ as catalyst.^[a]

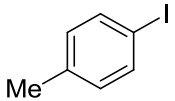
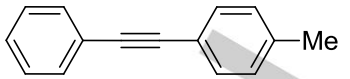
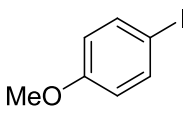
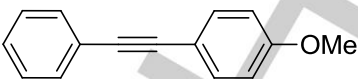
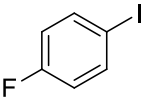
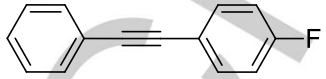
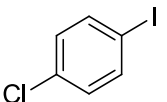
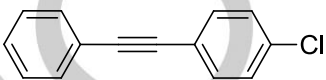
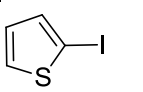

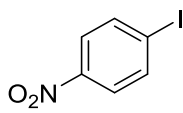
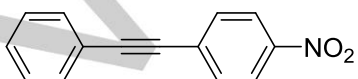
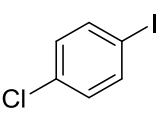
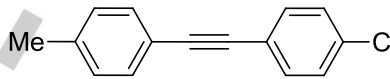
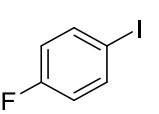
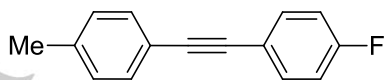
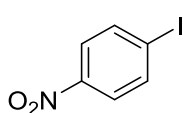
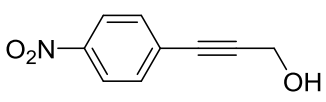
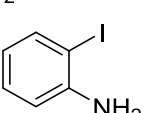
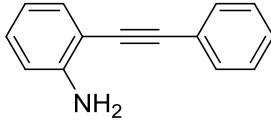
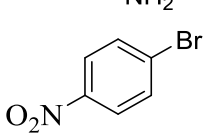
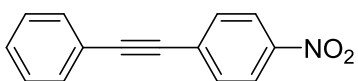
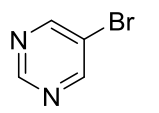
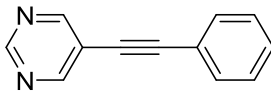
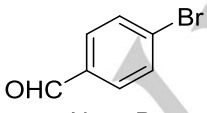
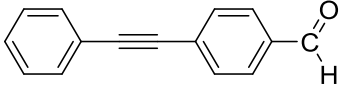
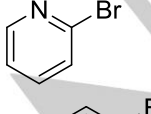
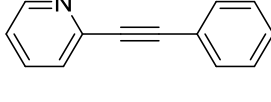
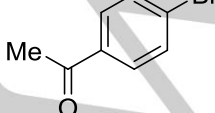
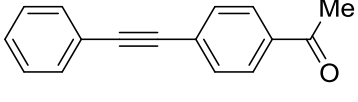


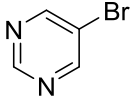
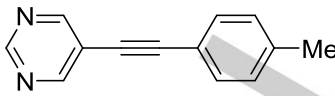
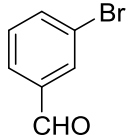
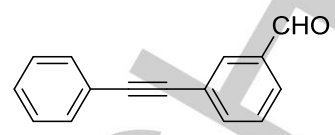
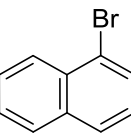
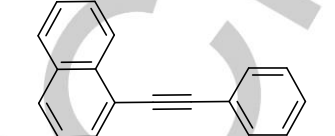
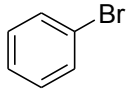
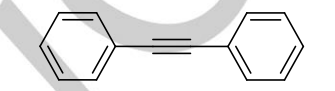
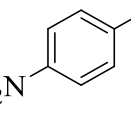
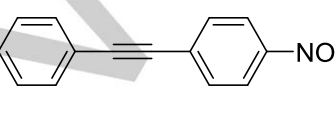
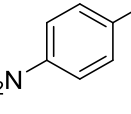
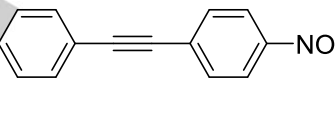
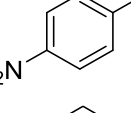
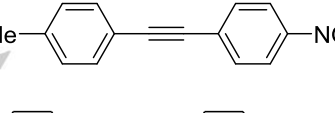
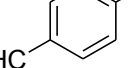
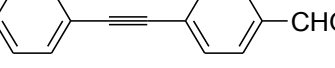
Entry	Ar ¹ X	R ²	T (°C)	t [h]	Product	Yield (%) ^[b]
1		C ₆ H ₅	50	24		99 ^c

17	DABCO	Dioxane	50	24	82
18	DABCO	CH ₃ CN	50	24	97
19	DABCO	H ₂ O	50	24	20
20	DABCO	CH ₃ CN	40	24	88
21	DABCO	Dioxane	40	24	77
22	DABCO	Toluene	40	24	85
23	DABCO	DMA	40	24	84
24	DABCO	CH ₃ CN	30	24	58
25	DABCO	Toluene	30	24	67
26	DABCO	H ₂ O	30	24	2
27	DABCO	Toluene	50	24	81 ^[c]

[a]Reaction conditions: iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol), base (0.75 mmol), solvent (1.5 mL), catalyst (12.5 mg containing 0.3 mol% Pd and 0.35 mol% Cu). [b]GC yields. [c] Using 0.2 mol% Pd and 0.23 mol% Cu

The scope of the reaction was studied using the optimized reaction conditions. Reactions of different aryl iodides containing electron-donating substituents such as -Me and -OMe and electron-withdrawing groups such as -F, -Cl, and -NO₂ as well as 2-iodothiophene with phenylacetylene afford the corresponding alkynes in very good 81-98% yields (Table 2, entries 1-7). Also, reactions of aryl iodides with other alkynes such as 4-ethynyltoluene and propargyl alcohol proceed with excellent yields (Table 2, entries 8-10). In the case of the reaction of 2-iodoaniline with phenyl acetylene resulted the acetylene without formation of the indol from a ring closing process (Table 2, entry 11). Reactions of less reactive aryl bromides under the established reaction conditions were sluggish. For instance reaction of 4-bromonitrobenzene with phenyl acetylene in toluene at 60, 80 and 100 °C gave 30%, 42% and 65% yields, respectively. Considering results of Table 1, we selected dimethylacetamide (DMA) as solvent for the reaction of aryl bromides. Using DMA at 60-80 °C, reactions of aryl bromides as well as challenging heterocyclic aryl bromides proceeded in high to excellent yields (Table 2, entries 12-20). To show the important effects of the both Cu and Pd in reaction efficiency, reaction of 4-bromonitrobenzene in the presence of similar catalyst without Cu, (Pd@GQD@Fe₃O₄) was studied. However, results indicated that reaction achieved only 52 % GC yield in 24 h (Table 2, entries 21). Reactions of less reactive activated aryl chlorides such as 4-nitrochlorobenzene, 4-chlorobenzaldehyde were performed at higher temperature (110 °C) in DMA and in the presence of TBAB (1 eq) affording the desired coupling products in high 86-91 yields (Table 2, entries 22-24).

2		C_6H_5	50	24		91
3		C_6H_5	50	24		81
4		C_6H_5	50	16		90
5		C_6H_5	50	21		82
6		C_6H_5	50	24		94
7		C_6H_5	50	8		92
8		4-MeC ₆ H ₄	50	24		91
9		4-MeC ₆ H ₄	50	24		99 ^[e]
10		CH ₂ OH	50	24		95
11		C_6H_5	50	24		78
12		C_6H_5	60	24		95
13		C_6H_5	60	24		94 ^[e]
14		C_6H_5	80	24		81
15		C_6H_5	80	24		94
16		C_6H_5	80	24		98 ^[c,d]

17		4-MeC ₆ H ₄	60	24		100 ^[c,d]
18		C ₆ H ₅	80	48		83
19		C ₆ H ₅	80	48		95
20		C ₆ H ₅	80	48		76
21		C ₆ H ₅	60	24		52 ^[c,e]
22		C ₆ H ₅	110	48		90 ^[d]
23		4-MeC ₆ H ₄	110	48		91 ^[d]
24		C ₆ H ₅	110	48		86 ^[d]

[a] Reaction conditions: ArX (1 mmol), alkyne (1.5 mmol), DABCO (168 mg, 1.5 mmol), catalyst (25 mg containing 0.3 mol% Pd, 0.35 mol% Cu), toluene (for ArI) or DMA (for ArCl and ArBr) (2 mL). [b] Isolated yields. ^c GC yields; ^d Reactions using 1 eq TBAB. [e] Reaction in the absence of Cu using Pd@GQD@Fe₃O₄.

Recycling ability of catalyst PdCu@GQD@Fe₃O₄ was studied for the reaction of iodobenzene and phenylacetylene. After completion of the reaction in first run (24 h), catalyst was separated by external magnet and after washing with diethyl ether was used in another reaction batch. Results showed that GC yield of the reaction was decreased from 99% to 90% in run 6 and from run 6 to 9 yield decreased to 77%. However in run 10 yield of the reaction was intensively decreased to 57%. Results of this study indicated that presented catalyst is recyclable at least for 6 consecutive runs with very small decrease in activity (Figure 6).

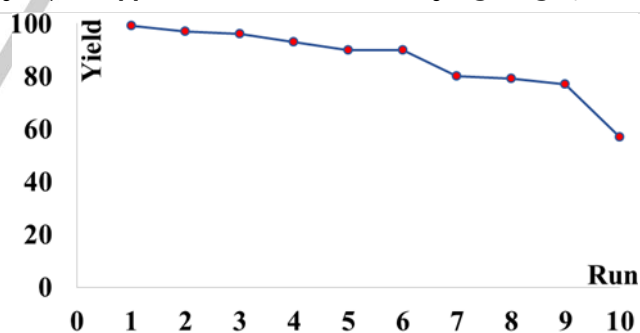


Figure 6. Recycling of catalyst PdCu@GQD@Fe₃O₄ for the reaction of iodobenzene with phenylacetylene.

Leaching of Pd and Cu to reaction mixture after second run in recycling process was determined by ICP to be 1.1 and 1.6%, respectively. TEM image of reused catalyst after 3rd run showed preserve of the catalyst structure with small aggregation of nanoparticles (Figure 7). Also, XPS study of reused catalyst showed that all Pd species are in reduced Pd(0) state. However, Cu species preserve Cu(I) and Cu(II) oxidation states (Figure 8).

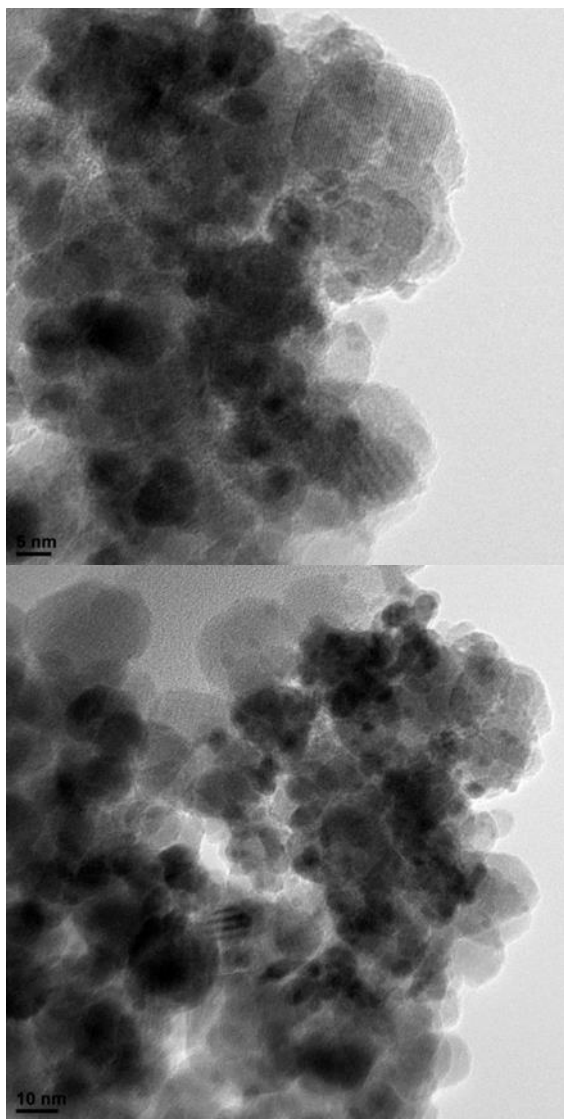


Figure 7. TEM images of reused catalyst after 3rd run

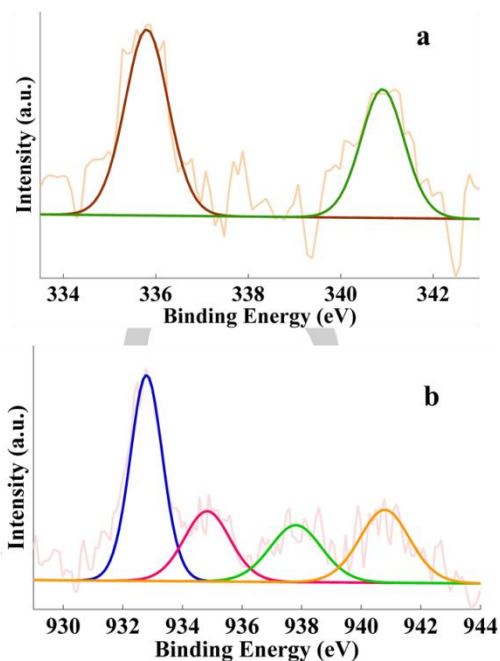


Figure 8. XPS spectra of reused catalyst PdCu@GQD@Fe₃O₄ in Pd and Cu regions.

In order to find information about the homogeneous or heterogeneous nature of the catalysis, different experiments were performed using the model reaction of iodobenzene with phenylacetylene under optimized conditions: a) hot filtration test was carried out after 2 h with 27% progress of the reaction. Then, the reaction mixture was filtered off and the filtrate was allowed to react at 50 °C. Analysis of the reaction after 24 h showed very sluggish progress of the reaction with formation of desired product in 40% GC yields. It is worth mentioning that a positive hot filtration test explained as a proof for homogeneous catalysis, however a negative hot filtration test does not necessarily indicate the emergence of heterogeneous catalysis due to possibility of fast deactivation or redeposition of soluble active species.²³ Therefore, further experiments are required for proving that heterogeneous catalysis is operating. b) Excess of polyvinylpyridine (PVP),^[23] which is a strong poison for homogeneous Pd species, was added to the reaction of iodobenzene with phenylacetylene under optimized reaction conditions (molar ratio to [Pd] ~400). GC analysis of the reaction in different times showed small decrease in reactivity confirming absence of leached Pd nanoparticles in solution (Figure 9).

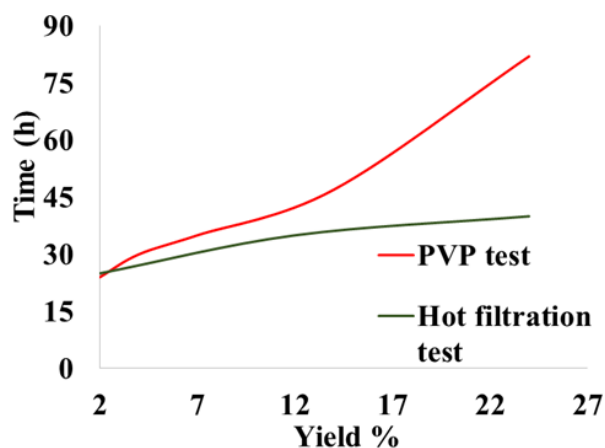


Figure 9. PVP poisoning and hot filtration tests for the reaction of iodobenzene with phenylacetylene catalyzed by PdCu@GQD@Fe₃O₄.

Another method for detection of homogeneous toward heterogeneous catalysis is a inverse the relationship between the concentration of active Pd and amount of products in homogeneous systems because of aggregation and deactivation of Pd species at higher concentrations.^[24] For this purpose reaction of iodobenzene with phenylacetylene was studied using different mol% of the catalyst within 12 h. Results of this study showed smooth increase of reaction rate by increasing the Pd concentration. From all these results, it seems that PdCu@GQD@Fe₃O₄ catalyzed these reactions under heterogeneous conditions (Figure 10).

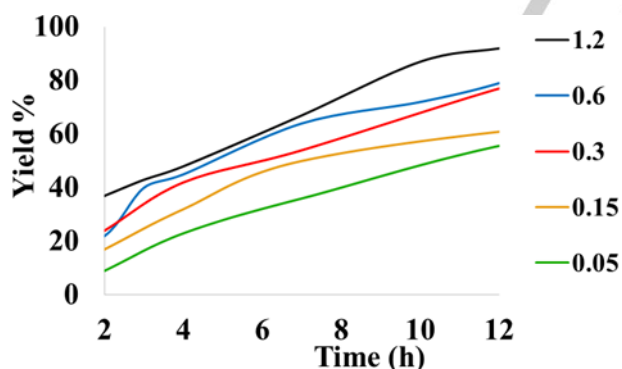


Figure 10. Influence of the catalyst loading PdCu@GQD@Fe₃O₄ on the yield of the Sonogashira reaction of iodobenzene with phenylacetylene.

Conclusions

The new supported PdCu catalyst PdCu@GQD@Fe₃O₄, prepared by a very simple method and characterized by different techniques, have shown good catalytic efficiency to perform the Sonogashira reaction at 60 °C of aryl iodides in toluene and with aryl bromides in DMA at 60 to 80 °C with different terminal acetylenes. In the case of activated aryl chlorides higher temperature (110 °C) and TBAB have to be used for completion of the reaction. The presence of Cu was demonstrated to be crucial to obtain good yields. This catalyst can be easily recovered by separation with a magnet and reused at least for 6 cycles without detriment of its catalytic activity. Different tests such as addition of PVP, hot filtration, and kinetic studies support the heterogeneous nature of this catalysis.

Experimental Section

Synthesis of GQD^[13]

0.5 g (1.7 mmol) EDTA was loaded into a crucible and then heated in the furnace at 280 °C for 5 min. After cooling to room temperature, the dark brown solid was dispersed in water and undissolved residue was removed by centrifugation at 8000 rpm for 5 min. The mixture was further purified by centrifugation and filtration using Ultra filter (Millipore, Billerica MA) with a molecular mass cut off of 10 kDa to remove large sheets.

Synthesis of GQDs@Fe₃O₄

Fe₃O₄ nanoparticles^[24] (1 g) were sonicated in water (5 mL) for 15 min. Then, the GQDs suspension (20 mL) was added to the flask containing the magnetic NPs and this mixture was mechanically stirred for 48 h at 60 °C. The resulting GQDs modified Fe₃O₄ was subjected to magnetic separation and the obtained material was washed with deionized water (3×10 mL) and ethanol (3×10 mL) and dried under vacuum.

Synthesis of PdCu bimetallic nanoparticles

Pd(OAc)₂ (22.5 mg, 0.1 mmol) and polyvinylpyrrolidone (200 mg) were dissolved in dioxane (5 mL) and stirred at room temperature under argon atmosphere. In another flask, CuSO₄·5H₂O (25 mg, 0.1 mmol) was dissolved in a solution of ethylene glycol (5 mL) and polyvinylpyrrolidone (200 mg) and the mixture was stirred for 2 h at 80 °C under argon atmosphere. The obtained solution was mixed with the Pd(OAc)₂ solution and mechanically stirred under argon atmosphere. During the stirring, a solution of NaOH (1 mol·L⁻¹) was added upon reaching pH to 9-10 and the mixture was stirred for 2 h at 100 °C. Then, reaction was cooled to room temperature and the resulting suspension was concentrated to 5 mL by centrifugation (10000 rpm, 10 min). The obtained mixture was diluted by acetone (5 mL) for *in situ* using in next step.

Synthesis of PdCu@GQD@Fe₃O₄

GQDs@Fe₃O₄ (0.5 g) was sonicated in acetone (20 mL) for 30 min at room temperature. Then, prepared PdCu suspension was added slowly to the flask containing CQDs@Fe₃O₄ composite. The resulting mixture was mechanically stirred for 48 h under argon atmosphere at room temperature. Then, the solid was separated magnetically, washed with water (3×20 mL) and ethanol (3×20 mL) and dried in an oven at 60 °C.

General procedure for Sonogashira reaction

The catalyst (25 mg containing 0.3 mol% Pd and 0.35 mol% Cu), aryl halides (1 mmol), alkyne (1.5 mmol), DABCO (168 mg, 1.5 mmol) and toluene or DMA (2 mL) were added to flask equipped with a stir bar under argon atmosphere. The reaction mixture was stirred for the appropriate reaction time at 50-110 °C. The progress of the reactions was monitored using gas chromatography. After completion of reaction, pure products were obtained using column chromatography using hexane and ethyl acetate as eluents.

Typical procedure for recycling of the catalyst for the reaction of iodobenzene and phenylacetylen:

After stirring of reaction mixture under optimized conditions for 24 h, the catalyst was separated from reaction mixture by an external magnetic field and washed with diethyl ether and after drying was used in another batch of the reaction. This process was repeated for 10 consecutive runs.

Acknowledgements

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Iran National Science Foundation (INSF-Grant number of 94010666) for support of this work. C. Nájera is also thankful to the Spanish Ministerio de Economía y Competitividad (MINECO) (projects CTQ2013-43446-P and CTQ2014-51912-REDC), FEDER, the Generalitat Valenciana (PROMETEOII/2014/017) and the University of Alicante for financial support.

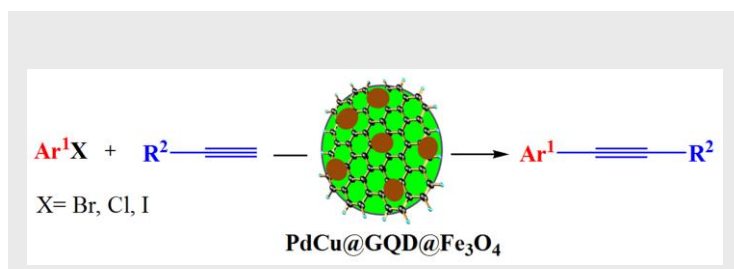
Keywords: GQD • Magnetic • Sonogashira • PdCu • Heterogeneous

- [1] a) H. Sun, L. Wu, W. Wei and X. Qu, *Mater. Today* **2013**, *16*, 433-442; b) J. Shen, Y. Zhu, X. Yang and C. Li, *Chem. Commun.* **2012**, *48*, 3686-3699; c) S. Zhu, S. Tang, J. Zhang and B. Yang, *Chem. Commun.* **2012**, *48*, 4527-4539; d) Z. Zhang, J. Zhang, N. Chen and L. Qu, *Energy Environ. Sci.* **2012**, *5*, 8869-8890; e) L. Li, G. Wu, G. Yang, J. Peng, J. Zhao and J. J. Zhu, *Nanoscale* **2013**, *5*, 4015-4039; f) D. Qu, M. Zheng, L. Zhang, H. Zhao, Z. Xie, X. Jing, R. E. Haddad, H. Fan and Z. Sun, *Sci. Rep.* **2014**, *4*, 5294-5302.
- [2] a) Y. Du, and S. Guo, *Nanoscale* **2016**, *8*, 2532-2543; b) L. Zhang, D. Peng, R. P. Liang and J. D. Qiu, *Anal. Chem.* **2015**, *87*, 10894-10901; c) H. Jin, H. Huang, Y. He, X. Feng, S. Wang, L. Dai and J. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 7588-7591; d) Y. Liu and P. Wu, *ACS Appl. Mater. Interfaces* **2013**, *5*, 3362-3369; e) X. Zhou, Z. Tian, J. Li, H. Ruan, Y. Ma, Z. Yang and Y. Qu, *Nanoscale* **2014**, *6*, 2603-2607.
- [3] a) C. P. Deming, R. Mercado, V. Gadiraju, S. W. Sweeney, M. Khan and S. Chen, *ACS Sustain. Chem. Eng.* **2015**, *3*, 3315-3323; b) P. Luo, L. Jiang, W. Zhang, X. Guan, *Chem. Phys. Lett.* **2015**, *641*, 29-32; c) L. Wang, C. Hu, Y. Zhao, Y. Hu, F. Zhao, N. Chen, L. Qu, *Carbon* **2014**, *74*, 170-179.
- [4] X. Yan, Q. Li and L. S. Li, *J. Am. Chem. Soc.* **2012**, *134*, 16095-16098.
- [5] X. Du, S. Luo, H. Du, M. Tang, X. Huang, P. K. Shen, *J. Mater. Chem. A* **2016**, *4*, 1579-1585.
- [6] C. P. Deming, R. Mercado, V. Gadiraju, S. W. Sweeney, M. Khan and S. Chen, *ACS Sustain. Chem. Eng.* **2015**, *12*, 3315-3323.
- [7] X. Wu, S. Guo and J. Zhang, *Chem. Commun.* **2015**, *51*, 6318-6321.
- [8] a) A. Molnár, *Palladium-Catalyzed Coupling Reactions: Practical Aspects, Future Developments*, Wiley-VCH, V. Weinheim, **2013**; b) M. Lamblin, L. Nassar-Hardy, J. C. Hierso, E. Fouquet, F. X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33-79; c) A. Molnár, *Chem. Rev.* **2011**, *111*, 2251-2320; d) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417-1492; e) A. Fihri, M. Bouhrara, B. Nekoueshahraki, J. M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* **2011**, *40*, 5181-5203.
- [9] C. E. Garrett, K. Prasad, *Adv. Synth. Catal.* **2004**, *346*, 889-900.
- [10] a) J. Kim, J. E. Lee, J. Lee, Y. Jang, S. W. Kim, K. An, J. H. Yu, T. Hyeon, *Angew. Chem. Int. Ed.* **2006**, *45*, 4789-4793; b) S. Shylesh, L. Wang, W. R. Thiel, *Adv. Synth. Catal.* **2010**, *352*, 425-432; c) R. Cano, D. J. Ramón, M. Yus, *Tetrahedron* **2011**, *67*, 5432-5436; d) X. Jin, K. Zhang, J. Sun, J. Wang, Z. Dong, R. Li, *Catal. Commun.* **2012**, *26*, 199-203; e) D. Rosario-Amorin, M. Gaboyard, R. Clerac, L. Vellutini, S. Nlate, K. Heuze, *Chem. Eur. J.* **2012**, *18*, 3305-3315; f) R. Cano, M. Yus, D. J. Ramón, *Tetrahedron* **2012**, *68*, 1393-1400; g) B. R. Vaddula, A. Saha, J. Leazer, R. S. Varma, *Green Chem.* **2012**, *14*, 2133-2136; h) D. Wang, C. Deraedt, L. Salmon, C. Labrugere, L. Etienne, J. Ruiz, D. Astruc, *Chem. Eur. J.* **2014**, *21*, 1508-1519; i) F. P. da Silva, L. M. Rossi, *Tetrahedron* **2014**, *70*, 3314-3318; j) B. Karimi, F. Mansouri, H. Vali, *Green Chem.* **2014**, *16*, 2587-2596; k) B. Karimi, F. Mansouri, H. Mirzaei, *ChemCatChem* **2015**, *7*, 1736-1789; l) S. Verma, D. Verma, A. K. Sinha, S. L. Jain, *Appl. Catal., A* **2015**, *489*, 17-23; m) Z. Wang, Y. Yu, Y. X. Zhang, S. Z. Li, H. Qian, Z. Y. Lin, *Green Chem.* **2015**, *17*, 413-420; n) H. Veisi, J. Gholami, H. Ueda, P. Mohammadi, M. Noroozi, *J. Mol. Catal. A: Chem.* **2015**, *396*, 216-223; o) T. H. Rehm, A. Bogdan, C. Hofmann, P. Lob, Z. B. Shifrina, D. G. Morgan, L. M. Bronstein, *ACS Appl. Mater. Interfaces* **2015**, *7*, 27254-27261; p) P. Heidaria, R. Cheraghiala, H. Veisi, *Appl. Organomet. Chem.* **2016**, *28*, 868-873; q) M. Hajjghorbani, M. Hekmati, *RSC Adv.* **2016**, *6*, 88916-88924.
- [11] a) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467-4470; b) R. Chinchilla, C. Nájera, *Chem. Rev.* **2007**, *107*, 874-922; c) R. Chinchilla, C. Nájera, *Chem. Soc. Rev.* **2011**, *40*, 5084-5121; d) M. M. Heravi, S. Sadjadi, *Tetrahedron* **2009**, *65*, 7761-7775; e) A. Kollhofer, H. Plenio, *Chem. Eur. J.* **2003**, *9*, 1416-1425; f) R. Ciriminna, V. Pandarus, G. Gingras, F. Béland, P. D. Carà, M. Pagliaro, *ACS Sustain. Chem. Eng.* **2013**, *1*, 57-61; g) F. Bellina, M. Lessi, *Synlett* **2012**, *23*, 773-777.
- [12] a) L. M. Tan, Z. Y. Sem, W. Y. Chong, X. Liu, K. Hendra, W. L. Kwan, C. L. K. Lee, *Org. Lett.* **2013**, *15*, 65-67; b) M. Gholinejad, N. Jeddi, B. Pullithadathil, *Tetrahedron* **2016**, *72*, 2491-2500; c) S. Diyarbakir, H. Can, O. Metin, *ACS Appl. Mater. Interfaces* **2015**, *7*, 3199-3206; d) A. Corma, H. García, A. Primo, *J. Catal.* **2006**, *241*, 123-131; e) W. Xu, H. Sun, B. Yu, G. Zhang, W. Zhang, Z. Gao, *ACS Appl. Mater. Interfaces* **2014**, *6*, 20261-20268; f) P. Cintas, G. Cravotto, E. C. Gaudino, L. Orto, L. Boffa, *Catal. Sci. Technol.* **2012**, *2*, 85-87; g) M. Gholinejad, J. Ahmadi, *ChemPlusChem* **2015**, *80*, 973-979; h) E. M. Beccalli, G. Broggini, S. Gazzola, A. Mazza, *Org. Biomol. Chem.* **2014**, *12*, 6767-6789; i) D. Sengupta, J. Saha, G. De, B. Basu, *J. Mater. Chem. A* **2014**, *2*, 3986-3992.
- [13] C. B. Ma, Z. T. Zhu, H. X. Wang, X. Huang, X. Zhang, X. Qi, H. L. Zhang, Y. Zhu, X. Deng, Y. Peng, Y. Hand and H. Zhang, *Nanoscale* **2015**, *7*, 10162-10169.
- [14] S. Liu, J. Tian, L. Wang, Y. Zhang, X. Qin, Y. Luo, A. M. Asiri, A. O. Al-Youbi, X. Sun, *Adv. Mater.* **2012**, *24*, 2037-2041.
- [15] S. Yuan, J. Gu, Y. Zheng, W. Jiang, B. Liang and S. O. Pehkonen, *J. Mater. Chem. A* **2015**, *3*, 4620-4636.
- [16] J. Sun, Y. Fu, G. He, X. Sun, X. Wang, *Catal. Sci. Technol.* **2014**, *4*, 1742-1748.
- [17] a) T. Ghodselahe, M. A. Vesaghi, A. Shafiekhani, A. Baghizadeh, M. Lameii, *Appl. Surf. Sci.* **2008**, *255*, 2730-2734; b) C. Gonzalez-Arellano, R. Luque and D. J. Macquarrie, *Chem. Commun.* **2009**, *11*, 1410-1412;

- c) Y. H. Kim, D. K. Lee, H. G. Cha, C. W. Kim, Y. C. Kang and Y. S. Kang, *J. Phys. Chem. B* **2006**, *110*, 24923-24928.
- [18] J. Y. Park, Y. S. jung, J. Cho, W. K. Choi, *Appl. Surf. Sci.* **2006**, *252*, 5877-5891.
- [19] a) S. Martinez, M. Moreno-Man, A. Vallibera, U. Schubert, A. Roig, E. Molins, *New J. Chem.* **2006**, *30*, 1093-1097; b) H. Firouzabadi, N. Iranpoor, M. Gholinejad, *Tetrahedron* **2009**, *65*, 7079-7084.
- [20] M. A. Bhosale, B. M. Bhanage, *RSC Adv.* **2014**, *4*, 15122-15130.
- [21] S. Zaman, A. Zainelabdin, G. Amin, O. Nur, M. Willander, *J. Phys. Chem. Solids* **2012**, *73*, 1320-1325.
- [22] S. Li, W. Zhang, M.-H. So, C.-M. Che, R. Wang and R. Chen, *J. Mol. Catal. A: Chem.*, **2012**, *359*, 81-87.
- [23] a) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609-679; b) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A: Chem.* **2003**, *198*, 317-341; c) B. Karimi, P. Fadavi Akhavan, *Inorg. Chem.* **2011**, *50*, 6063-6072.
- [24] Massart, R. *IEEE Trans. Magn.* **1981**, *17*, 1247-1248.
- [24] a) A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Henderickx, J. G. de Vries, *Org. Lett.* **2003**, *5*, 3285-3288; b) C. Deraedt, A. D. Didier, *Acc. Chem. Res.* **2014**, *47*, 494-503; c) G. Collins, M. Schmidt, C. Dwyer, G. McGlacken, J. D. Holmes, *ACS Catal.* **2014**, *4*, 3105-3111.

Layout 2:

FULL PAPER



Mohammad Gholinejad,^{*,[a]} Jahantab Ahmadi,^[a] Carmen Najera,^{*,[b]} Mohammad Seyedhamzeh,^[a] Fatemeh Zareh,^[a] Mohsen Kompany-Zareh^[a]

Page No. – Page No.

Graphene Quantum Dots Modified Fe₃O₄ Nanoparticles Supported PdCu with Enhanced Catalytic Activity for Sonogashira Reaction