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FULL PAPER

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Functionalization of multi-walled carbon nanotubes by the baclofen drug to immobilize palladium nanoparticles and catalyze Sonogashira coupling reactions

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The baclofen-MWCNTs-Pd nanocatalyst was synthesized through covalent grafting of baclofen molecules onto surface-modified carbon nanotubes and immobilizing Pd nanoparticles by the baclofen ligands. The chemical structure of the produced nanocatalyst was studied by Raman spectroscopy, Fourier transform-infrared spectroscopy, energy-dispersive spectroscopy (EDS), elemental mapping and inductively coupled plasma analysis. Also, its surface morphology was determined using the scanning and transmission electron microscopy techniques. Furthermore, the obtained baclofen-MWCNTs-Pd nanocatalyst is demonstrated to exhibit very high activity as a heterogeneous phosphine-free catalyst in Sonogashira cross-coupling of aryl halides by giving good to excellent yields of different products. In addition, the nanocatalyst can be reused four times without any significant leaching or loss of activity.

KEYWORDS
baclofen, multi-walled carbon nanotubes, nanocatalyst, palladium, Sonogashira

1 | INTRODUCTION

Palladium (Pd) is a transition metal that has played important roles in almost all areas of organic synthesis. Particularly, the organometallic complexes containing Pd have managed to catalyze many well-known reactions, such as the Heck, Sonogashira, Stille, Suzuki and Buchwald–Hartwig cross-couplings reactions, the Wacker process,[1] and the reaction of Tsuji–Trost allylation.[2] Furthermore, this transition metal has been successfully applied to hydrogenolysis, hydrogenation, carbonylation, cycloisomerization, formation of the C–C, C–N, C–O and C–S bonds, and pericyclic reactions.[3]

In general, Pd-based materials have the potential of catalyzing many reactions, including the Sonogashira cross-coupling (SCC) reaction, which gives conjugated acetylenic compounds through coupling unsaturated organic halides with terminal acetylenes. The products obtained from the SCC reaction can be further employed as the intermediates required to synthesize pharmaceutics, natural products and diverse organic materials, for example, nanowires and nano-sized molecular architectures. The reaction of SCC has been most commonly performed using the Pd-based homogeneous catalysts that are generated from $PdCl_2$ or Pd $(OAc)_2$ and organic ligands. Such catalysts are devised to present high activity and selectivity towards definite reactions. The point is that homogeneous Pd catalysts cannot be easily separated from reaction mixtures. Therefore, they might contaminate the reaction products.[4] This issue is a great problem as the presence of metal contaminants in pharmaceutical ingredients can negatively affect public health. Consequently, pharmaceutical industries have to pay additional costs to remove the residual metals via post-reaction treatments. Alternatively, the catalyst nanoparticles (NPs) can be immobilized on solid supports to form heterogenous catalysts and facilitate their removal. The commonly applied supports include active carbon,

zeolites and carbon nanotubes (CNTs).[5] Among various solid supports, CNTs have attracted much interest due to their outstanding electrical, thermal, sensor and mechanical properties.[6]

Carbon nanotubes can be single- or multi-walled. The single-walled CNTs (SWCNTs) are formed through rolling of a single carbon sheet, while the multi-walled CNTs (MWCNTs) are obtained by rolling several carbon sheets. The MWCNTs are more abundant and less expensive, compared with the SWCNTs. The catalytic activity of CNTs can be improved by introducing heteroatom-containing functional groups onto their surface. In this respect, the boron, nitrogen, oxygen, sulfur and phosphorus atoms have been widely used. The negative aspect of CNT application is that CNTs are water-insoluble and manipulation of CNTs is difficult in most solvents. As an outcome, CNTs should be surface functionalized.[7]

One of the most feasible and commonly used methods of CNT surface modification is its oxidation by strong acids. This method introduces -COOH groups onto the surface of MWCNTs and creates MWCNT-COOH. It should be noted the -COOH functionalized CNTs can be further modified by reacting the -COOH groups with various organic molecules including biomolecules, for example, drugs, vitamins, amino acids, carbohydrates and proteins.[8–11] A potential candidate for modification of MWCNT-COOH is baclofen. This lipophilic drug is a gamma-aminobutyric acid (GABA) derivative that acts as a GABA-B agonist, inhibits the activity of presynaptic motor neurons, and results in an antispastic response.[12]

According to our previous works,[8,13] acidic groups and baclofen can be applied to modify the surface of MWCNTs. In this respect, we decided to focus on the amino group of baclofen to attach them onto MWCNT-COOH. The resultant baclofen-MWCNTs (BMWCNTs) can act as novel and efficient support for immobilization of Pd NPs. The corresponding catalyst, i.e. BMWCNT/Pd, is adopted as an active and reusable catalyst (Scheme 1) to catalyze the SCC reaction after its characterization using the field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy, transmission electron microscopy (TEM), inductively coupled plasma (ICP), CHNS and Fourier transform-infrared (FT-IR) techniques.

2 | EXPERIMENTAL

2.1 | Materials

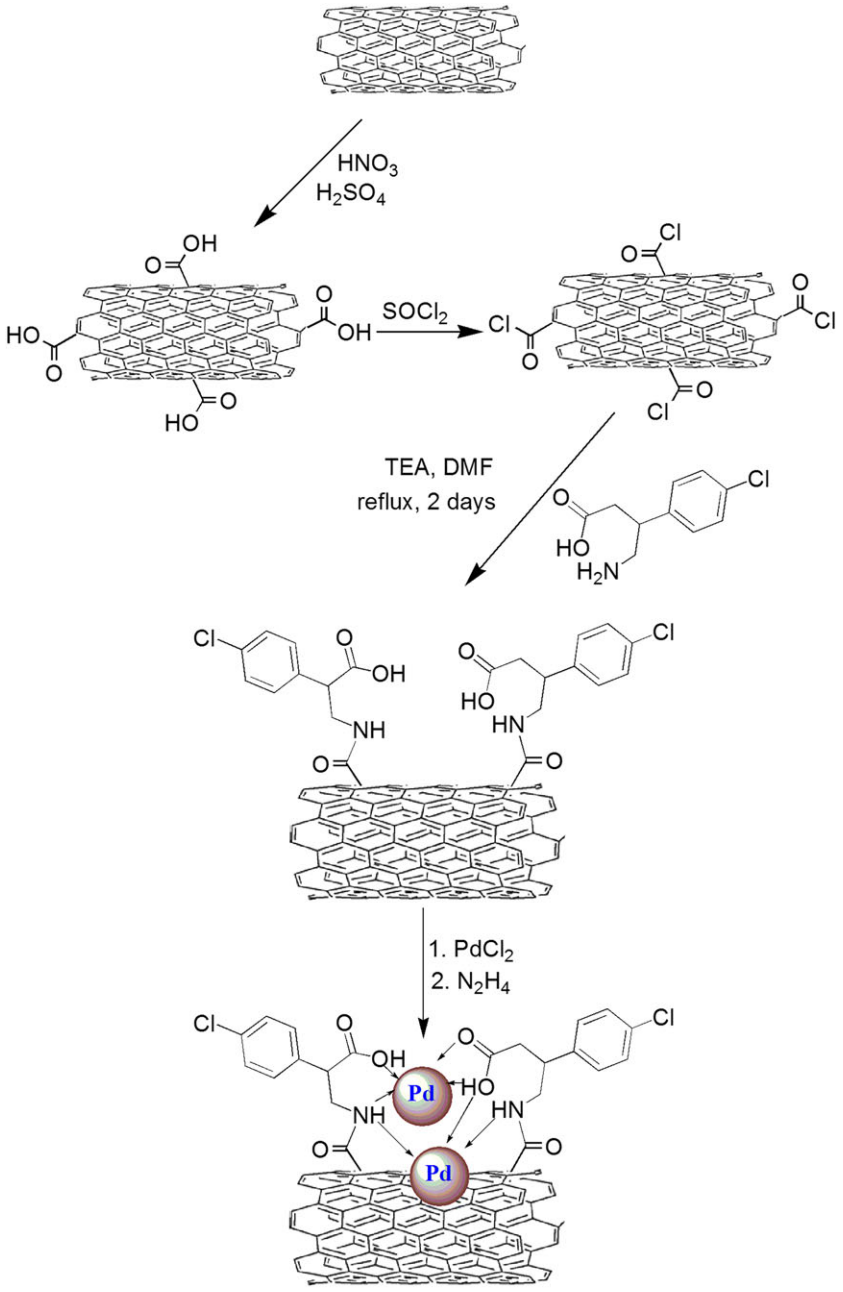
All the reagents were purchased from Aldrich and Merck, and were used without any purification. The pure MWCNTs without functional groups were purchased from Petrol Co. (Tehran, Iran). HCl, H_2SO_4, HNO_3, deionized water, NaH (80%), ethylenediamine, acetonitrile, $PdCl_2$ and *N*,*N*-dicyclohexylcarbodiimide (DCC) were obtained from Sigma Aldrich and Merck. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a Bruker D8 Advance diffractometer with CuKα radiation at 40 kV and 20 mA. FT-IR spectra were recorded with a Perkin Elmer 65 spectrometer in the range of 400–4000 cm^{-1}. TEM images at the accelerating voltage of 80 kV were taken with a Zeiss-EM10C. Morphology and particle dispersion was investigated by FE-SEM (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by energy-dispersive X-ray spectroscopy (EDS) performed in scanning electron microscopy (SEM).

2.2 | Covalent grafting of baclofen to MWCNTs

Pristine MWCNTs (p-MWCNTs) were refluxed under stirring in the mixture of 1:3 (*v*/v) HNO_3 and H_2SO_4 at 70°C for 30 hr, which was followed by centrifugation and repeated washings with DI water. The dried carboxylated MWCNTs (MCNTs-COOH) were suspended in a solution of thionyl chloride (excess) and DMF (1 mL). The suspension was stirred at 65°C for 24 hr. The solid was then separated by filtration and washed with anhydrous THF (30 mL), and dried in vacuum to obtain MWCNTs-COCl. The final product was then subjected to functionalization with baclofen. Baclofen (drug-to-MWCNTs weight ratio was 5:1) was mixed with a 10 mL solution of DMF and TEA (1 mL), and then stirred for 5 min. The obtained acyl chloride MWCNTs that dispersed in DMF (20 mL) by ultrasonic bath for 15 min were subsequently added to the suspension. The reaction mixture was kept at 120°C for 2 days. The solid was then separated by filtration and washed with CH_2Cl_2 and deionized water several times and dried in vacuum. The concentration of drug on MWCNTs was 0.13 mmol g^{-1}, which was determined by CHNS analysis.

2.3 | Preparation of the baclofen-MWCNTs/Pd

The baclofen-MWCNTs (500 mg) were dispersed in CH_3CN (30 mL) by ultrasonic bath for 30 min. Subsequently, a yellow solution of $PdCl_2$ (15 mg) in 30 mL acetonitrile was added to the dispersion of baclofen-MWCNTs, and the mixture was stirred for 10 hr at 25ºC. Then, the baclofen-MWCNTs/Pd (II) was separated



SCHEME 1 Schematic diagram of baclofen-multi-walled carbon nanotubes (MWCNTs)/Pd fabrication

by centrifugation and washed by CH_3CN, H_2O and acetone, respectively, to remove the unattached substrates.

The reduction of baclofen-MWCNTs/Pd (II) by hydrazine hydrate was performed as follows: 50 mg of baclofen-MWCNTs/Pd (II) 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 100°C for 2 hr. The final product baclofen-MWCNTs/Pd(0) was washed with water and dried in vacuum at 40°C. Scheme 1 depicted the synthetic procedure of baclofen-MWCNTs/Pd. The concentration of palladium in the prepared catalyst was 0.13 mmol g^{-1}, which was determined by ICP-AES.

2.4 | General procedure for the Sonogashira coupling reactions

In a typical reaction, 10 mg of the baclofen-MWCNTs/Pd (17 mg = 0.2 mol% Pd) was placed in a 25-mL Schlenk tube, 1 mmol of the aryl halide in 3 mL of DMF was added, and phenyl acetylene (1.5 mmol) and Et_3N (2 mmol). The mixture was then stirred for the desired time at 100°C. The progress of the reaction was monitored by thin-layer chromatography. After the reaction was over, the catalyst was removed by centrifuge. The filtrate was then extracted with ethyl acetate followed by washing with brine solution. The organic part thus obtained was dried by sodium sulfate and the solvent was then

removed by rotary evaporation under reduced pressure. The product thus obtained was further purified before spectroscopic analysis.

3 | RESULTS AND DISCUSSION

To synthesize the catalyst, the steps described in Scheme 1 were followed. As illustrated in Scheme 1, first the MWCNTS were oxidized by adding a HNO_3/H_2SO_4 mixture. Then, the oxidized CNTs were activated with $SOCl_2$ to graft the baclofen molecules onto the acylated CNTs. After that, the Pd NPs were deposited onto the surface of the BMWCNTs. The deposited Pd NPs were quantified by ICP analysis, which indicated that the BMWCNT/Pd particles contain 0.13 mmol g^{-1} palladium. The synthesized nanocatalyst was characterized using powder XRD, EDS, FT-IR spectroscopy, elemental mapping, Raman spectroscopy, CHN analysis, and the FESEM and TEM techniques.

The chemical structure of the bare and surface-modified MWCNTs was analyzed by FT-IR spectroscopy. The FT-IR spectra recorded for: (a) the MWCNTs; (b) the MWCNTs-COOH; and (c) the BMWCNTs are shown in Figure 1. As curve **b** of Figure 1 displays, the oxidized MWCNTs have given rise to a vibrational band at 1705 cm^{-1}. This band is related to the stretching vibration of carbonyl in the carboxylic acid groups. In addition, this CNT sample has outlined a broad peak of OH vibration from 2400 to 3450 cm^{-1}. These two peaks confirm the presence of the hydroxyl and carboxyl functional groups on the surface of the acid-treated MWCNTs. In the case of the BMWCNTs (curve **c** of Figure 1), there are three prominent vibrational bands at 1668, 2933 and 3433 cm^{-1} that refer to the -C=O stretching of the amide groups (-CONH-), the bending vibration of CH_2 and stretching of NH, respectively. These results declare bonding of baclofen to the surface functionalized MWCNTs through amidation.

The success of the functionalization reactions was also assessed by performing Raman spectroscopy. The recorded Raman spectra are exhibited in Figure 2. As can be seen, the Raman spectra of the samples include two main Raman bands at 1338 and 1596 cm^{-1}, which are indicative of type D and G bonds, respectively. The D band corresponds to the disordered MWCNT atoms with sp^3 hybridization, while the G band represents the sp^2-hybridized carbons of graphene sheets. The extent of defects in the MWCNTs can be determined with respect to the area ratio of the D to G bands (I_D/I_G). Based on the Raman spectra, the I_D/I_G ratio of the BMWCNTs ($I_D/I_G = 1.36$) is more than that of the bare MWCNTs. This finding verifies successful modification of the MWCNTs with the baclofen molecules. Furthermore,

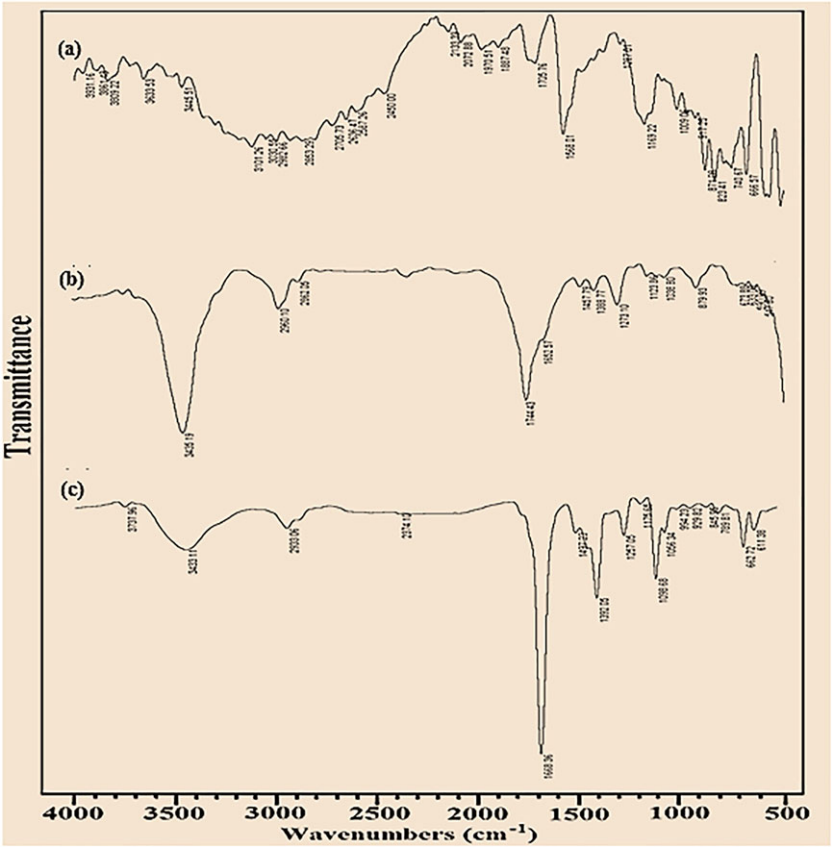


FIGURE 1 Fourier transform-infrared (FT-IR) spectra of (a) multi-walled carbon nanotubes (MWCNTs), (b) MWCNTs-COOH, (c) baclofen-MWCNTs

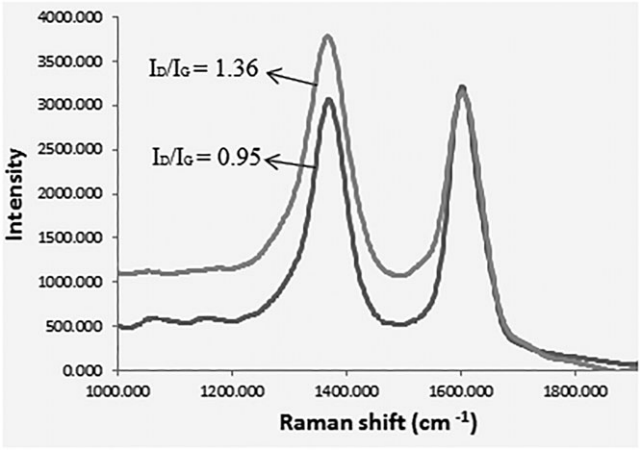


FIGURE 2 Raman spectra of the multi-walled carbon nanotubes (MWCNTs), and the baclofen-MWCNTs

the observed increase of I_D can be attributed to the increased number of sp^3-hybridized carbon atoms as there is no amorphous carbon in the samples. This observation can be accepted as evidence for successful functionalization of the MWCNTs.

The TEM image of the BMWCNT/Pd catalyst is shown in Figure 3. This image unravels that the MWCNTs are covered with a homogenous layer of Pd NPs. Notably, the Pd NPs are not aggregated onto the CNTs. Consequently, the baclofen molecules should have played a key role in promoting dispersibility of the Pd NPs.

The surface morphology and elemental composition of the catalyst were determined by FESEM coupled with EDS. The resultant FESEM image is depicted in Figure 4. Based on the FESEM image, the surface of the MWCNTs is uniformly coated with the applied functional groups and Pd NPs.

The catalyst was analyzed by EDS to determine its chemical composition. The obtained spectrum (Figure 5) demonstrates the well-resolved peaks of C, O, N and Pd. Therefore, the EDS spectrum approves successful immobilization of the Pd NPs onto the surface of the BMWCNTs, in agreement with the FESEM results.

Powder XRD was employed to reveal the crystal structure of the BMWCNT/Pd particles. The obtained XRD pattern is presented in Figure 6. In this figure, the XRD peak observed at 26.5° represents the (002) crystal plane of hexagonal graphite, and its appearance after surface modification of the MWCNTs indicates that the functionalization process has not altered or destroyed

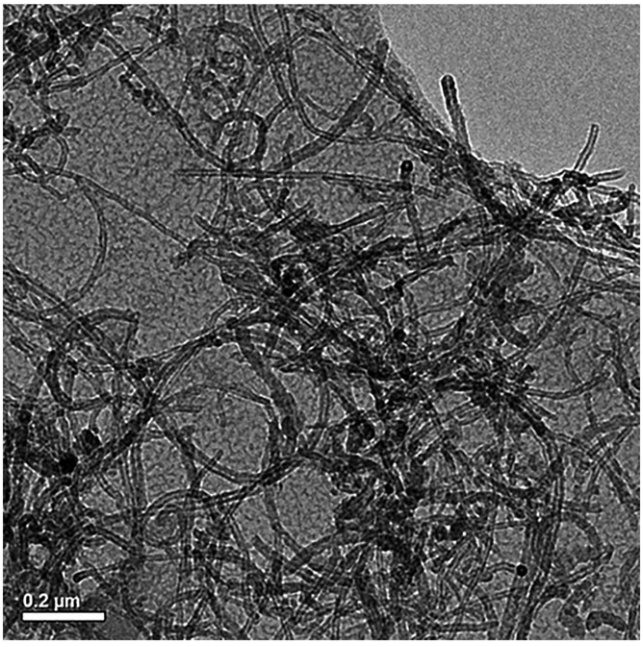


FIGURE 3 Transmission electron microscopy (TEM) image of baclofen-multi-walled carbon nanotubes (MWCNTs)/Pd

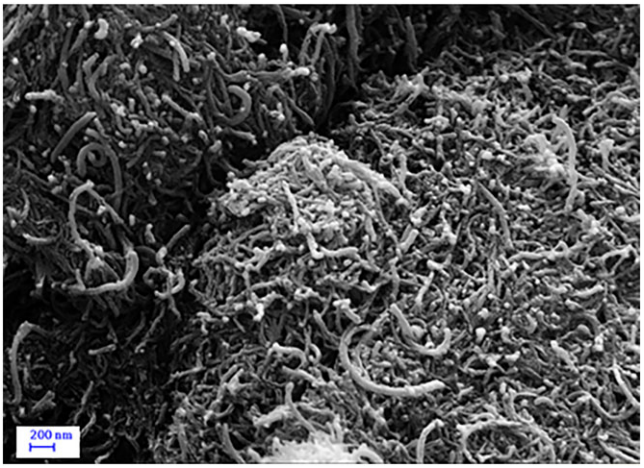


FIGURE 4 Field emission scanning electron microscopy (FE-SEM) image with its elemental mapping of baclofen-multi-walled carbon nanotubes (MWCNTs)/Pd

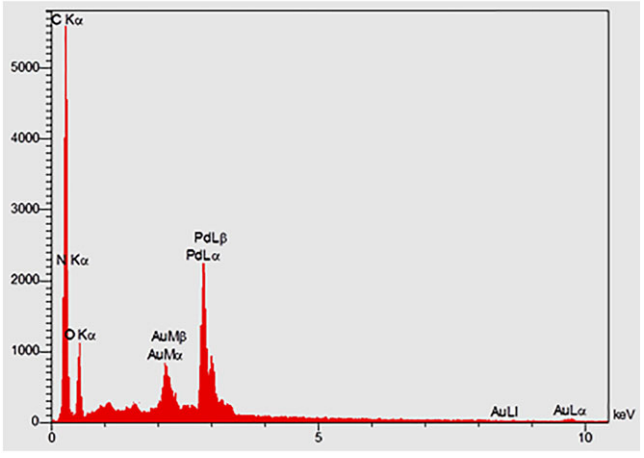


FIGURE 5 Energy-dispersive spectroscopy (EDS) data of the baclofen-multi-walled carbon nanotubes (MWCNTs)/Pd

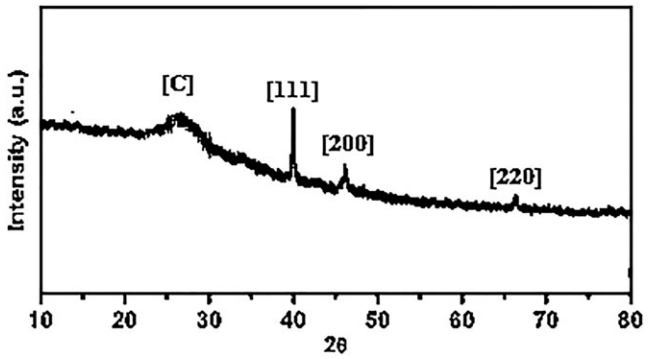


FIGURE 6 X-ray diffraction (XRD) pattern of the baclofen-multi-walled carbon nanotubes (MWCNTs)/Pd

the original structure of the MWCNTs. On the other hand, the diffraction peaks positioned at about 39, 47 and 67° are related to the (111), (200) and (220) planes of face-centered cubic (*fcc*) Pd particles.[14] Therefore, the XRD pattern illustrates efficient immobilization of *fcc* Pd nanostructures on the BMWCNTs.

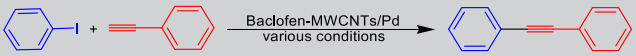
The BMWCNT/Pd catalyst was applied to the SCC reaction to investigate its catalytic performance. The reaction conditions were optimized by concentrating on the reaction of iodobenzene with phenylacetylene, as a model reaction (Table 1). The optimized parameters included base type, solvent type, catalyst dose and reaction temperature. Based on the results reported in Table 1, the use of the DMF solvent, the Et_3N base and 0.2 mol% catalyst at a temperature of 100°C (Table 1, Entry 7) are expected to provide the maximal product yield via the BMWCNT/Pd-catalyzed SCC reactions.

After optimizing the reaction conditions, the efficiency of BMWCNT/Pd was evaluated by applying it to the SCC reaction of different aryl halides. The results are outlined in Table 2. According to this table, the prepared catalyst can efficiently catalyze the reaction of the examined aryl iodides (Entries 1–6) and aryl bromides (Entries 7–13) with phenylacetylene to give good to excellent yields of their SCC-associated products. However, the activity of the catalysts towards SCC of the studied aryl chlorides is insignificant.

To assure about heterogeneity of the catalyst, the SCC reaction of iodobenzene and phenylacetylene was monitored through two different experiments. In the first experiment, the cross-coupling reaction was terminated after 60 min. At this point, the BMWCNT/Pd particles were centrifuged and the reaction was followed for another 60 min using the centrifugation supernatant. In the second experiment, the same reaction was conducted but the terminated reaction was not continued. It was observed that both experiments lead to the same product yield (60%). Therefore, the catalyst is heterogeneous.

Inductively coupled plasma analysis was also used to determine the leaching of Pd NPs into the reaction

TABLE 1 Optimization of the reaction conditions for the reaction of iodobenzene with phenylacetylene[a]

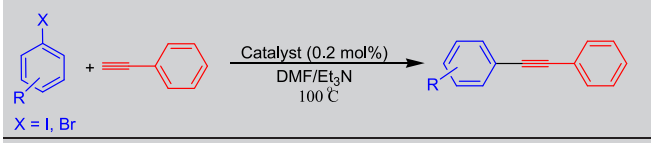


Entry	Solvent	Base	Pd (mol%)	T (°C)	t (hr)	Yield (%)[b]
1	DMF	K_2CO_3	0.2	100	10	70
2	H_2O	K_2CO_3	0.2	100	10	50
3	EtOH	K_2CO_3	0.2	80	10	60
4	CH_3CN	K_2CO_3	0.2	70	10	65
5	Solvent-free	K_2CO_3	0.2	100	10	65
6	DMF	Na_2CO_3	0.2	100	10	70
7	DMF	Et_3N	0.2	100	2	96
8	DMF	$NaHCO_3$	0.2	100	4	75
9	DMF	K_3PO_4	0.2	100	4	60
10	DMF	No base	0.2	100	12	Trace
11	DMF	Et_3N	0.2	50	6	80
12	DMF	Et_3N	0.2	120	2	96
13	DMF	Et_3N	0.1	100	6	75
14	DMF	Et_3N	0.3	100	2	96
15	DMF	Et_3N	0.0	100	24	0

[a]Reaction conditions: iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol), catalyst, base (2 mmol) and solvent (3 mL).

[b]Isolated yields.

TABLE 2 Sonogashira reaction of various aryl halides using baclofen-MWCNTs/Pd as a catalyst[a]



Entry	R	X	Time (hr)	Yield (%)[b]
1	H	I	2	96
2	4-CH_3O	I	2	95
3	4-CH_3	I	2	95
4	2-CH_3	I	3	85
5	4-Cl	I	2	95
6	3-NO_2	I	2	90
7	H	Br	3	96
8	4-CH_3O	Br	4	92
9	4-CH_3	Br	5	90
10	2-CH_3	Br	6	80
11	4-Cl	Br	5	90
12	3-NO_2	Br	5	85
13	4-$COCH_3$	Br	6	92

[a]Reaction conditions: arylhalide (1 mmol), phenylacetylene (1.2 mmol), Et_3N (2 mmol), DMF (3 mL), catalyst (0.2 mol%) and 100°C.

[b]Isolated yield.

solution following 5 cycles, which was shown to be 1.14%, and showed the constancy of the catalyst over the reaction.

Reusability of the catalyst was assessed to ensure its industrial applicability. In this respect, the BMWCNT/Pd particles were used to catalyze the model reaction (Table 1). After that, the utilized catalyst was centrifuged, washed several times with deionized water and ethanol, dried at 40°C in an oven and reused in another cycle of the reaction. This test was performed in

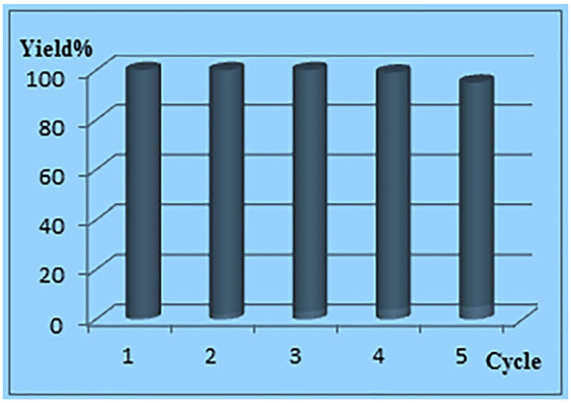


FIGURE 7 The recycling of the baclofen-multi-walled carbon nanotubes (MWCNTs)/Pd for the Sonogashira coupling reaction under similar conditions

TABLE 3 Comparison of the activity of different processes in the Sonogashira coupling reaction of 4-methylbromobenzene with phenylacetylene

Catalyst	Reaction conditions	Yield (%)	Ref.
Baclofen-MWCNTs/Pd	Et_3N, DMF, 100°C, 5 hr	90	this study
SiO_2-pA-*Cyan-Cys*-Pd	NaOAc, DMF-H_2O, 80°C, 7 hr	84	[15]
$CoFe_2O_4$/Pd	K_3PO_4, DMF, 80°C, 6 hr	13	[16]
NS-MCM-41-Pd	Et_3N, NMP, 90°C, 72 hr	40	[17]

the same batch system. As Figure 7 shows, the synthesized catalyst can be reused four times with negligible loss of efficiency.

Finally, the performance of BMWCNT/Pd in catalyzing the SCC reaction of 4-methylbromobenzene and phenylacetylene was compared with the activity of the other catalysts that have been reported in the literature. With respect to Table 3, BMWCNT/Pd can lead to higher conversion rates and yields, relative to the other catalysts.

4 | CONCLUSIONS

In this research, the baclofen drug was successfully grafted onto acylated MWCNTs to immobilize Pd NPs. The structure of the resultant MWCNTs was confirmed by the FT-IR and Raman spectroscopies, and TEM, FESEM, EDS, XRD, elemental mapping and ICP analysis. The obtained particles were then applied as a novel nanocatalyst to catalyze the Sonogashira coupling reaction. The catalyst demonstrated high catalytic efficiency for cross-coupling of aryl bromides and iodides, in addition to presenting high structural stability and recyclability without any significant loss of activity.

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