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## Pd nanoparticles deposited on Isoniazid grafted multi walled carbon nanotubes: Synthesis, characterization and application for Suzuki reaction in aqueous media

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Abstract. In this article the new heterogeneous nanocatalyst based on palladium supported on Isoniazide-functionalized multi-walled carbon nanotubes (MWCNTs) has been introduced. The synthetic process of preparation of mentioned nanocatalyst (Isoniazide-MWCNTs/Pd) has been described. The formation of nanocatalyst was analyzed by FTIR, Raman spectroscopy, XRD, EDS, TEM, SEM, WDX, ICP and CHN analysis. Additionally, the (Isoniazide-MWCNTs/Pd) nanocatalyst was successfully employed in Suzuki cross coupling reactions with wide variety of functionalized substrates. Design of experiments indicates that the use of 0.2 mol% of Pd,  $K_2CO_3$  as the base, and aqueous ethanol are the best reaction conditions. Interestingly, the novel catalyst could be recovered and recycled four times without any significant loss in its catalytic activity.

Keywords: Multi-walled carbon nanotubes, Isoniazide, Palladium, Nanocatalyst, Suzuki

## Introduction

Carbon nanotubes (CNTs) nanotubes have attracted considerable interests due to their remarkable thermal conductivity,<sup>[1-3]</sup> mechanical,<sup>[4-6]</sup> and electrical properties.<sup>[6,7]</sup> In addition, their excellent chemical and mechanical stability and large surface area make them an ideal and potentially useful choice for applications in optics,<sup>[7,8]</sup> electronics,<sup>[9]</sup> catalysis,<sup>[10,11]</sup> polymer composites,<sup>[12]</sup> and many others.<sup>[13]</sup>

The immobilization methods used to deposit palladium into heterogeneous solid beds have been studied extensively, and diverse supports such as clay,<sup>[14]</sup> carbon nanofiber,<sup>[15]</sup> montmorillonite,<sup>[16]</sup> magnetic mesoporous silica,<sup>[17]</sup> zeolite,<sup>[18]</sup> and metal oxides<sup>[19]</sup> have been investigated. A current challenge in this area is the development of efficient immobilized systems that could simultaneously fulfill the usual targets of achieving high TON values and facilitate recovering and reuse as well as the need for obtaining Pd-free final products,<sup>[20,21]</sup> meeting the strict purity specifications for the pharmaceutical industry.<sup>[22,23]</sup>

Transition metal-catalyzed protocols, especially palladium reactions, have become powerful tools in chemical synthesis of many materials and compared with frequently used palladium(II) complexes catalysts, palladium nanoparticles were found to exhibit remarkable catalytic activities for Suzuki, Heck and Sonogashira cross-coupling reactions,<sup>[24-32]</sup> hydrogenation of many organic compounds,<sup>[33-35]</sup> oxidation of hydrocarbon,<sup>[36]</sup> isomerization,<sup>[37]</sup> and decomposition of nitrogen monoxide,<sup>[38]</sup> which have been extensively used in the synthesis of drugs and fine chemicals.<sup>[39-44]</sup>

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There have been a variety of reports describing the use of carbon materials for the immobilization of Pd nanoparticles, the catalytic activity of Pd nanoparticles can be retained, and the stability also can be improved to some extent.<sup>[45-47]</sup> In continuing our attempts toward the extension of efficient and environmentally benign heterogeneous catalysts,<sup>[48]</sup> herein, we will report a simple preparation of a novel Isoniazide-MWCNTs to deposition of palladium nanoparticles (Isoniazide-MWCNTs/Pd) (Scheme 1). After characterization, Suzuki cross coupling were selected to investigate its catalytic activity and recyclability.

#### Experimental

### Materials

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All the reagents were purchased from Aldrich and Merck used without any purification. SOCl<sub>2</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> (30 wt%, aq), deionized water, NaH (80%), anhydrous dimethylformamide (DMF), CaH<sub>2</sub>, and Isoniazide were obtained from Sigma Aldrich and Merck.

#### Preparation of the Isoniazide-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 h, 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 h. The solid was then separated by filtration and washed with anhydrous THF (30 mL), and dried in vacuum to obtain MWCNTs-COCI. The final product was then subjected to functionalization with Isoniazide. Isoniazide (amine-to-MWCNTs weight ratio was 5:1) were mixed with 10 mL solution of DMF and TEA (1 mL) and then stirred for 5 minute. 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<sub>2</sub>Cl<sub>2</sub> and deionized water for several times and dried in vacuum. The concentration of drug on MWCNTs is 0.18 mmol/g, which was determined by CHNS analysis.

#### Preparation of the Isoniazide-MWCNTs/Pd

The Isoniazide-MWCNTs (500 mg) were dispersed in  $CH_3CN$  (30 mL) by ultrasonic bath for 30 min. Subsequently, a yellow solution of  $PdCl_2$  (30 mg) in 30 mL acetonitrile was added to dispersion of Isoniazide-MWCNTs and the mixture was stirred for 10 hours at 25 °C. Then, the Isoniazide-MWCNTs/Pd(II) was separated by centrifugation and washed by  $CH_3CN$ ,  $H_2O$  and acetone respectively to remove the unattached substrates.

The reduction of Isoniazide-MWCNTs/Pd(II) by hydrazine hydrate was performed as follows: 50 mg of Isoniazide-MWCNTs/Pd(II) was dispersed in 60 mL of water, and then 100  $\mu$ L of hydrazine hydrate (80%) was added. The pH of the mixture was adjusted to 10 with 25% ammonium hydroxide and the reaction was carried out at 95 °C for 2 h. The final product Isoniazide-MWCNTs/Pd(0) was washed with water and dried in vacuum at 40 °C. Scheme 1 depicted the synthetic procedure of Isoniazide-MWCNTs/Pd(0). The concentration of palladium in the prepared catalyst was 1.8 wt% (0.19 mmol/g), which was determined by ICP-AES and EDS.

#### General procedure for the Suzuki-Miyaura reaction

Aryl halide (1 mmol), phenylboronic acid (1.1 mmol),  $K_2CO_3$  (2 mmol), catalyst (15 mg that contained 0.2 mol% Pd) and water/ethanol (1:1, 2 mL) were added to a 5 mL flask, and the mixture was stirred mechanically at 60 °C. The progresses of the reactions were monitored by TLC. After completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation and the crude product was extracted using ethyl acetate. The pure products were obtained by column chromatography on silica using the hexane and ethyl acetate as eluent.

#### **Results and discussion**

The Isoniazide-functionalized Multi-Walled Carbon Nanotubes (Isoniazide-MWCNTs) was conveniently synthesized from commercially available and cheap materials via reaction of acylated carbon nanotubes with Isoniazide. Next, palladium nanoparticles were deposited onto the surface of the Isoniazide-MWCNTs. The loading of Pd in the obtained material was determined by inductively coupled plasma (ICP) analysis to be 0.19 mmol/g. The pathways of Isoniazide-MWCNTs-Pd fabrication are shown in Scheme 1.



Scheme 1. Schematic diagram of Isoniazide-MWCNTs-Pd fabrication.

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FTIR spectroscopy provided further confirmation that the surface of the MWCNTs was modified by Isoniazide (Figure 1). Its shows the FT-IR spectra obtained for (a) MWCNTs-COOH, (b) Isoniazide, and (c) Isoniazide-MWCNTs. As it is seen in the curve **a**, the absorption bands at 1705 cm<sup>-1</sup> was attributed to the CO stretching of the carboxylic acid groups. In the curve **b**, the absorption band at ~1400-1600 cm<sup>-1</sup> is attributed to the C=C stretching of pyridine ring and the bands observed around 3411 cm<sup>-1</sup> and 3447 were assigned to the NH stretching vibrations. In the curve **c**, the absorption band at 1673 cm<sup>-1</sup> is attributed to the carboxyl stretching of the amide groups (-CONH-). Also, the bands observed around 2922 cm<sup>-1</sup> and 2858 were assigned to the bending vibration of C-H. The prominent IR bands at ~3180 and 3300 cm<sup>-1</sup> were ascribed to the NH stretching vibrations. These results indicated that the Isoniazide was successfully bonded to the surface of MWCNTs through amidation reaction.



Figure 1. FTIR spectra of (a) MWCNTs-COOH, (b) Isoniazide, and (c) Isoniazide-MWCNTs.

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Another method for assessment of functionalization reaction is Raman spectroscopy. Figure 2 shows the Raman spectra of the samples. Two main peaks in the Raman spectra were appeared in the samples at 1338 and 1596 cm<sup>-1</sup> which are known as D and G bonds, respectively. D band is related to disordered carbon atoms of MWCNTs corresponding to sp<sup>3</sup> hybridized and G band shows the sp<sup>2</sup>-hybridized of carbon atoms in the graphene sheets. Area ratio of the D to G bands ( $I_D/I_G$ ) can be used to assess the amount of defects in nano particles structure.  $I_D/I_G$  ratio was increased for Isoniazide-MWCNTs ( $I_D/I_G$ =1.35) which approves the successful conversion of MWCNTs to Isoniazide-MWCNTs. In the absence of amorphous carbon, the increase of  $I_D$  is related to increase of carbon containing sp<sup>3</sup> hybridized and implies to successful functionalization reaction.



Fig. 2. Raman spectra of the (a) MWCNTs, and (b) Isoniazide-MWCNTs.

The morphology of the Isoniazide-MWCNTs-Pd was characterized by field emission scanning electron microscopy (FE-SEM) in Figures 3. The image of pristine MWCNTs shows that the tube surfaces are clear and smooth (Figure 3a). It is observed that in the image 3b, the surface of CNTs uniformly coated, thus clearly indicative of Isoniazide units attached to MWCNTs. In The image 3c, the decorated palladium nanoparticles on the Isoniazide-MWCNTs surface were distinguishable.



Fig. 3. SEM images of (a) MWCNTs, (b) Isoniazide-MWCNTs, and (c) Isoniazide-MWCNTs-Pd.

Energy dispersion X-ray spectroscopy (EDX) was recorded and shown in Figure 4. The observed characteristic peak assigned to palladium metal in EDX spectrum, also evident the successful formation of palladium nanoparticles. Other existing elements revealed by the EDX analysis included carbon, oxygen, and nitrogen which confirmed that the Isoniazide present on the surface.



Fig. 4. Energy-dispersive X-ray spectroscopy (EDS) of the Isoniazide-MWCNTs-Pd.

The wavelength-dispersive X-ray spectroscopy (WDX)-coupled quantified FESEM mapping of the sample was also investigated (Fig. 5). The wavelength-dispersive X-ray spectroscopy (WDX) can provide qualitative information about the distribution of different chemical elements in the catalyst matrix. Looking at the compositional maps C and Pd, the presence of Pd NPs with good dispersion is clearly distinguished in the composite.



Fig. 5. FESEM image of Isoniazide-MWCNTs-Pd and elemental maps of C and Pd atoms.

Transmission electron microscopy (TEM) investigations are carried out to observe the morphology and distribution of palladium particles supported on Isoniazide-MWCNTs. The existence of Pd nanoparticles, deposited on *f*-CNTs was clearly distinguishable as dark spots in Fig. 6. From Fig. 6, we can see that Pd was well dispersed on the surface of Isoniazide modified MWCNTs. The results indicated that Isoniazide play an important role to improve the dispersibility of Pd. The mean diameter of Pd nanoparticles immobilized on *f*-CNTs was found to be around ~10 nm.



Fig. 6. TEM images of Isoniazide-MWCNTs-Pd.

Fig. 7 showed the X-ray diffraction spectroscopy (XRD) patterns of Isoniazide-MWCNTs-Pd. As shown in Fig. 7, the wide diffraction peak at  $2\theta = 26^{\circ}$  can be indexed to disorderedly stacked hexagonal graphite structure [49]. The well-defined peaks around 39°, 47°, 68° and

82° can be assigned to (111), (200), (220) and (311) crystal planes of Pd0 [49]. Thus the XRD results indicate efficient immobilization of fcc structured Pd nanoparticles on f-CNTs.



Fig. 7. XRD pattern of Isoniazide-MWCNTs-Pd.

The XPS spectroscopic analysis of the heterogeneous catalyst is a quantitative technique to indicate the electron properties of the species immobilized on the surface, such as oxidation state, the electron environment and the binding of the core electron (E binding) of the metal. Fig. 8 displays the Pd binding energy of Isoniazide-MWCNTs-Pd. The study of the Isoniazide-MWCNTs-Pd at the Pd 3p level shows peaks at 532.3 and 553.6 eV for Pd  $3p_{3/2}$ , which clearly indicates that the Pd nanoparticles are stable as metallic state in the nanocomposite structure. In comparison to the standard binding energy of Pd<sup>0</sup>, with Pd  $3p_{3/2}$  of about 532.4 eV and Pd  $3p_{1/2}$  of about 560.2 eV, it can be concluded that the Pd peaks in the Isoniazide-MWCNTs-Pd shifted to lower binding energy than Pd<sup>0</sup> standard binding energy. The previous studies<sup>50,51</sup> indicated that the position of Pd 3p peak is usually influenced by the local chemical/physical environment around Pd species besides the formal oxidation state, and shifts to lower binding energy when the charge density around it increases. Therefore, the peaks at 553.6 and 532.3 could be due to Pd<sup>0</sup> species bound directly to amino groups in the Isoniazide-MWCNTs.



Fig. 8. XPS spectra of Isoniazide-MWCNTs-Pd for Pd 3p.

The prepared Isoniazide-MWCNTs supported heterogeneous Pd-catalyst was then evaluated in the C-C bond formation reaction of aryl halides with phenyl boronic acid as Suzuki-Miyaura coupling reaction. For optimization of the reaction, the Suzuki coupling reaction of 4-methylbromobenzene with phenyl boronic acid was chosen as a model for optimizing reaction parameters such as the solvent, base, temperature and the amount of the catalyst. Optimization conditions studies are summarized in Table 1. As expected, no target product could be detected in the absence of the catalyst (Table 1, entry 11). However, addition of the catalyst to the mixture has rapidly increased the synthesis of product in high yields. The reactions were conducted using  $H_2O/EtOH$  (1:1) as the best solvent. Among the bases evaluated, K<sub>2</sub>CO<sub>3</sub> was found to be the most effective. The effect of catalyst loading was investigated employing several quantities of the catalyst ranging from 0.1 mol% to 0.3 mol% (Table 1, entries 7,8 and 9). The best yield was obtained with 0.015 g (0.2 mol%) of the catalyst (Table 1, entry 8). Also, the optimum temperature for the reaction was 60 °C (entry 8 versus entries 12, 13 and 14). In the case of 50 °C, the yield of the desired product was lower than the one at 60 °C. However, when the temperature increased to 100 °C, the yield of the desired product did not increase obviously.

**Table 1.** The optimization of reaction parameters for the Suzuki reaction of 4-methylbromobenzene with phenylboronic acid.<sup>a</sup>

H₃C		Br +	B(OH) <sub>2</sub>	various conditions $\rightarrow$ (			CH <sub>3</sub>		
	Entry	Pd (mol%)	Solvent	Base	T (°C)	Time (h)	Yield (%) <sup>b</sup>		
-	1	0.2	DMF	$K_2CO_3$	80	3	75		
	2	0.2	Toluene	$K_2CO_3$	60	4	60		
	3	0.2	EtOH	$K_2CO_3$	60	2	75		
	4	0.2	$H_2O$	$K_2CO_3$	90	5	60		
	5	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	NaOAc	60	2	65		

6	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	Et <sub>3</sub> N	90	4	80
7	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	$K_2CO_3$	60	2	75
8	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	$K_2CO_3$	60	1	98
9	0.3	EtOH/H <sub>2</sub> O <sup>c</sup>	$K_2CO_3$	60	1	96
10	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	No base	60	12	10
11	0.0	EtOH/H <sub>2</sub> O <sup>c</sup>	$K_2CO_3$	60	12	0.0
12	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	$K_2CO_3$	25	6	60
13	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	$K_2CO_3$	50	2	80
14	0.2	EtOH/H <sub>2</sub> O <sup>c</sup>	$K_2CO_3$	100	1	98

<sup>a</sup>Reaction conditions: 4-methylbromobenzene (1.0 mmol), phenylboronic acid (1.0 mmol), catalyst, base (2 mmol) and solvent (3 mL).

<sup>b</sup>Isolated yield. <sup>c</sup>3 mL (1:1)

Several coupling reactions of various aryl halides (I, Br and Cl) with phenyl boronic acid were evaluated using 0.2 mol% of Isoniazide-MWCNTs-Pd under the optimized conditions and the results presented in the Table 2. Phenyl iodides, bromides and chlorides all reacted efficiently with phenylboronic acid (Table 2, entries 1-17). Aryl halides with electron-withdrawing or releasing groups reacted with phenylboronic acid to afford the corresponding products in high yields. Notably, heteroaryl halides such as 2-bromothiophene and 2-iodothiophene with phenylboronic acid gave the corresponding coupled products in 90% and 96% yields, respectively (Table 2, entries 16 and 17). The coupling reaction of aryl chlorides with phenyl boronic acid required extended reaction time than aryl iodides and bromides, producing the desired products in moderate yield (Table 2, entries 3, 6, 9).

**Table 2.** Scope of the Suzuki-Miyaura reaction.<sup>a</sup>

X	Isoniazide-MWCNTs-Pd (14 mg)						
		H	I₂O-E	tOH,∣	K <sub>2</sub> CO <sub>3</sub> , 60	°C 2	
R 🗸	~ В(	OH) <sub>2</sub>					Ŕ
	Entry	RC <sub>6</sub> H <sub>4</sub> X	R	Х	Time (h)	Yield $(\%)^{b}$	-
	1	Н	Н	Ι	1.0	98	-
	2	Н	Η	Br	2.0	98	
	3	Н	Η	Cl	24	70	
	4	4-CH <sub>3</sub>	Η	Ι	1.5	96	
	5	4-CH <sub>3</sub>	Η	Br	2.0	96	
	6	4-CH <sub>3</sub>	Η	Cl	24	60	
	7	4-COCH <sub>3</sub>	Η	Ι	1.0	98	
	8	4-COCH <sub>3</sub>	Η	Br	2.0	96	
	9	4-COCH <sub>3</sub>	Η	Cl	24	55	
	10	4-CH <sub>3</sub> O	Η	Ι	2.0	98	
	11	4-CH <sub>3</sub> O	Η	Br	3.5	92	
	12	$4-NH_2$	Η	Ι	1.5	90	
	13	$4-NH_2$	Η	Br	2.5	80	
	14	4 <b>-</b> OH	Η	Ι	3.0	96	
	15	4 <b>-</b> OH	Н	Br	5.0	90	
	16	2-Thienyl	Η	Ι	2.5	96	
	17	2-Thienyl	Η	Br	4.0	90	

<sup>a</sup>Reactions were carried out under aerobic conditions in 3 mL of H<sub>2</sub>O/EtOH (1:1), 1.0 mmol arylhalide, 1.0 mmol phenylboronic acid and 2 mmol K<sub>2</sub>CO<sub>3</sub> in the presence of catalyst (0.015 g, 0.2 mol% Pd) at 60 °C. <sup>b</sup>Isolated yield.

11

It was found that the catalyst Isoniazide-MWCNTs-Pd could be separated conveniently by centrifugation and reused at least 4 times without significant lose in catalytic activity for the Suzuki coupling reaction between phenylboronic acid and 4-methylbromobenzene in the presence of  $K_2CO_3$  (Fig. 9). After completion of the reaction, catalyst was separated by centrifugation from the reaction mixture and washed several times with deionized water and ethanol. Then, it was and dried in an oven at 50 °C and the recycled catalyst was saved for the next reaction.



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**Fig. 9.** Recyclability of catalyst in the Suzuki-Miyaura reaction (Reaction conditions: 4-methylbromobenzene (1.0 mmol), phenylboronic acid (1.0 mmol), catalyst (0.015 g),  $K_2CO_3$  (2 mmol) and 3 mL of H<sub>2</sub>O/EtOH (1:1) at 60 °C).

Leaching of palladium from the solid catalyst was examined employing a hot filtration test. The reaction of 4-methylbromobenzene with phenylboronic acid in the presence Isoniazide-MWCNTs-Pd catalyst at 60 °C was performed and a solid precipitate was formed by adding 2 mL ethanol, which was collected by centrifugation. Then, the solid-free filtrate was allowed to continue to react under the same conditions for another 60 min. No increase in the amount of the product was observed, which suggested that the leaching of Pd species from the solid support is low and the prepared catalyst is stable. Moreover, the leaching of Pd into the reaction solution after four runs was determined by ICP analysis to be 1.24 %, which indicates the stability of the catalyst during the reaction. Also, the Pd loading in the reused catalyst was determined by inductively coupled plasma (ICP) analysis to be 0.17 mmol/g. This result indicated that the palladium catalyst is heterogeneous and remained on the support at elevated temperatures during the reaction. Based on these evidences, a reaction mechanism for Suzuki coupling with the prepared nanocatalyst was proposed (Scheme 2).



Scheme 2. Possible mechanism of Suzuki coupling reaction.

#### Conclusions

In this study, Isoniazide was successfully bonded on the surface of MWCNTs by reaction of acylated carbon nanotubes with Isoniazide. Based on the results of IR, SEM, XRD, WDX, ICP, TEM, Raman and CHN analysis confirmed the functionalization of MWCNTs with Isoniazide. The prepared Isoniazide-MWCNTs were used to deposition of Pd NPs as novel nanocatalyst. The catalyst showed high activity in Suzuki coupling reaction of aryl halides (X = I, Br, Cl). The catalyst showed good stability and was recycled for several times without significant loss in its catalytic activity. These advantages make the process highly valuable from the synthetic and environmental points of view.

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# **Graphical Abstract**

Pd nanoparticles deposited on Isoniazid grafted multi walled carbon nanotubes: Synthesis, characterization and application for Suzuki reaction in aqueous media

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The prepared Isoniazide-MWCNTs were used to deposition of Pd NPs as novel nanocatalyst. The catalyst showed high activity in Suzuki coupling reaction of aryl halides (X = I, Br, Cl).