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# Carbon nanospheres with well-controlled nano-morphologies as support for palladium-catalyzed Suzuki coupling reaction

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#### Funding information

Natural Science Foundation of Hebei Province, Grant/Award Number: B2016204131. B2015204003.National Natural Science Foundation of China, Grant/Award Number: 21603054.

# **1 | INTRODUCTION**

Palladium-catalyzed Suzuki-Miyaura cross-coupling reaction has been one of the most powerful tools for constructing unsymmetric biaryl compounds.<sup>[1]</sup> Over the past few decades, homogeneous catalytic systems based on Pd have served as effective strategic tools for organic transformation and total synthesis.<sup>[2]</sup> However, the limited availability and high price of Pd have also become a problem for homogeneous catalytic systems. In order to reduce the cost of the catalyst and protect the environment, heterogeneous catalytic systems, as excellent recyclable systems, have been developed rapidly in recent years. However, it is well known that small metal nanoparticles tend to aggregate,<sup>[3]</sup> which may reduce their catalytic activity and restrict their practical application. In this context, scientists have developed various materials such as silica,<sup>[4]</sup> zinc ferrite.<sup>[5]</sup> metal-organic frameworks<sup>[6]</sup> and covalent organic frameworks<sup>[7]</sup> as supports for noble metals to address the aggregation problem. Carbon materials, owing to their special high surface area and excellent chemical, mechanical and thermal stabilities,<sup>[8]</sup> have been widely used as supports in Pd-catalyzed reactions, such as fullerene,<sup>[9]</sup> graphene,<sup>[10]</sup> carbon nanotubes<sup>[11]</sup> and porous carbon.<sup>[12]</sup>

Uniform carbon nanospheres (UCS) with well-controlled nano-morphologies were fabricated by hydrothermal carbonization of sucrose in the presence of kayexalate. Highly dispersed and ultrafine palladium nanoparticles were supported on the UCS through a facile co-reduction process with NaBH<sub>4</sub> as reducing agent. The obtained Pd@UCS exhibited efficient catalytic activity for the Suzuki coupling reaction. Moreover, the as-prepared catalyst could be recycled and reused at least five times without significant loss of its catalytic activity.

#### **KEYWORDS**

biomass, Pd, Suzuki coupling reaction, uniform carbon nanospheres

Carbon nanospheres not only possess the general advantages of carbon supports including high stability in both acidic and basic environments, but also have the potential to allow selective catalysis in some cases if faster mass transfer and diffusion are performed in the domain of the carbon nanospheres.<sup>[13]</sup> Moreover, carbon nanospheres can be simply prepared by the facile carbonization/activation route via use of renewable biomass precursors as carbon source.[8b] These strengths mean that biomass-derived carbon nanospheres are promising, green and environmentally friendly supports for noble metals. Recently, a carbon nanospheresupported Pt nanocatalyst was synthesized by Zhou and coworkers<sup>[14]</sup> using a facile one-pot hydrothermal synthesis with sucrose as carbon source and P123 as stabilizer. The results showed that the obtained Pt nanocatalyst could enhance the electrochemical performance for CH3OH oxidation. Xu and co-workers<sup>[15]</sup> immobilized Pd nanoparticles on carbon nanospheres, and the prepared catalyst provided an average rate of CO-free H<sub>2</sub> generation up to 43 1  $H_2 g_{Pd}^{-1} min^{-1}$  and a turnover frequency (TOF) of 7256 h<sup>-1</sup> at 60 °C with 100% selective dehydrogenation from aqueous formic acid. However, there is no report of the use of carbon nanospheres as support in Pd-catalyzed Suzuki crosscoupling reactions.

In the work reported herein, uniform size carbon nanospheres (UCS) were prepared via novel and simple hydrothermal carbonization (HTC) of sucrose at 180 °C with the help of kayexalate. After activation in air, UCS possessed a high surface area of 1346 m<sup>2</sup> g<sup>-1</sup>. Palladium metal nanoparticles were successfully immobilized on UCS by a facile co-reduction process. For the first time, the prepared Pd@UCS was used to catalyze the Suzuki coupling reaction, with the catalyst exhibiting efficient catalytic activity for this reaction. Furthermore, it could be recycled by simple centrifugation and reused at least five times without significant loss of its catalytic activity. To the best of our knowledge, this is the first report of UCS-supported Pd nanoparticles for the Suzuki coupling reaction.

### 2 | EXPERIMENTAL

#### 2.1 | Materials and Methods

All chemicals were used as received without any purification. Palladium chloride  $(PdCl_2)$  and kayexalate were obtained from Aladdin Reagent Company Limited. Sucrose, sodium borohydride  $(NaBH_4)$ , ethanol and other reagents were purchased from Huaxin Co. Ltd (Baoding, China).

The morphologies and sizes of samples were observed using transmission electron microscopy (TEM) with an FEI Tecnai f20 at 200 kV and scanning electron microscopy (SEM) with an S-4800 SEM instrument. X-ray diffraction (XRD) patterns were recorded using a Dandong TD-3500 X-ray diffractometer with Cu K $\alpha$  irradiation at 40 kV and 150 mA. Brunauer–Emmett–Teller (BET) surface areas of samples were measured at 77 K by nitrogen adsorption using a V-Sorb 2800 surface area and porosity analyzer. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi spectrometer with a monochromatic Al K $\alpha$  X-ray source at 15 kV. The Pd content was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Thermo Elemental IRIS Intrepid II.

#### 2.2 | Synthesis of UCS

In a typical synthesis, 8 g of sucrose and 40 mg of kayexalate were added into 50 ml of deionized water. After ultrasonication for 10 min, the mixture was transferred into a Teflon-lined stainless steel autoclave, and heated at 180 °C for 8 h. After cooling naturally, the material was washed with water and ethanol several times, and dried in a vacuum at 60 °C overnight. The resultant product was activated in air (0.01 MPa) at 800 °C for 1 h.

# 2.3 | Synthesis of Pd@UCS

UCS (100 mg) was dispersed in 8.335 ml of  $H_2PdCl_4$  (1 mg ml<sup>-1</sup>) solution and stirred at room temperature for 12 h. Then, 5 ml of NaBH<sub>4</sub> (4 mg ml<sup>-1</sup>) was added into the mixture solution drop by drop in 5 min under vigorous stirring. After 2 h of sustaining stirring, the resulting solid was washed with water and ethanol two times each. Finally, the product was dried in vacuum at 60 °C overnight.

# **2.4** | General Procedure for Suzuki–Miyaura Reaction

Typically, a mixture of aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), solvent (5 ml) and Pd@UCS (2.6 mg, 0.12 mol%) was stirred at 50 °C in a round-bottom flask for the desired reaction time. Subsequently, the mixture was diluted with water (10 ml), and extracted with ethyl acetate (10 ml) three times. After drying using anhydrous MgSO<sub>4</sub>, the product was concentrated by vacuum and purified by flash chromatography on silica gel with petroleum ether–ethyl acetate as eluent.

# 2.5 | Recyclability Test

For the recycling test, after the reaction of bromobenzene and phenylboronic acid was completed, the catalyst was isolated from the reaction solution by centrifugation and washed with water, then dried in a vacuum at 60 °C overnight. The dried catalyst was used again to catalyze the reaction of bromobenzene and phenylboronic acid.

# **3 | RESULTS AND DISCUSSION**

The morphologies and sizes of samples were observed using SEM and TEM. Because of the presence of kayexalate, UCS with sizes ranging from 50 to 100 nm are obtained by HTC (Figure 1a,b). From the TEM image of the catalyst (Figure 1c), it can be seen that highly dispersed Pd (2–3.5 nm) nanoparticles are immobilized on the surface of UCS. The Pd content of the catalyst was determined by means of ICP-AES, amounting to 2.92%.

Figure 2 shows the XRD patterns of samples. The broad peak at 24° and weak peak at 45° belong to (002) and (100) reflections of the graphite-type lattice, respectively, which result from UCS. The pattern of Pd@UCS exhibits peaks at 40.1° and 46.9° arising from Pd. The diffraction peaks of reused Pd@UCS are similar to those of fresh Pd@UCS, which demonstrates that the catalyst maintains its original structure after being used in catalytic reactions. The presence of Pd metal was further confirmed using XPS. In Figure 3, the characteristic peaks of Pd 3d<sub>3/2</sub> and



**FIGURE 1** (a) SEM image of UCS. TEM images of (b) UCS, (c) Pd@UCS and (d) recycled Pd@UCS (recovered after five recycles)



FIGURE 2 XRD patterns of UCS, Pd@UCS and recycled Pd@UCS



FIGURE 3 XPS analysis of Pd@UCS

Pd  $3d_{5/2}$  are seen at 341.3 and 336.1 eV, which could confirm that Pd on UCS is present in the metallic state. However, the presence of PdO species is confirmed by the peaks at 337.8 and 343.2 eV, which is probably due to the oxidation of metallic Pd left in an oxygen-containing environment.

The N<sub>2</sub> adsorption–desorption isotherms of UCS and Pd@UCS are shown in Figure 4. The BET surface areas of UCS and Pd@UCS are 1345.7 and 934.6 m<sup>2</sup> g<sup>-1</sup>, respectively. The slight decrease in surface area could be attributed to the fact that the majority of Pd nanoparticles are supported on the surface of UCS, and a small number within UCS.

The synthesized Pd@UCS material was investigated as a catalyst for typical Suzuki–Miyaura carbon–carbon coupling reaction. In the optimization experimental study, the reaction



FIGURE 4  $N_{\rm 2}$  adsorption–desorption isotherms of UCS and Pd@UCS

of phenyl bromide and phenylboronic acid was selected as a model reaction. As is evident from Table 1, the reaction does not proceed either when the Pd@UCS catalyst is absent (Table 1, entry 1) or when pure UCS is used as catalyst (Table 1, entry 2), which demonstrates that Pd

**TABLE 1** Optimization of factors influencing the Suzuki–Miyaura reaction of bromobenzene with phenylboronic acid<sup>a</sup>

Entry	Solvent	Base	Pd (mol%)	Yield (%)
$1^{b}$	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	_	_
2 <sup>c</sup>	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	_	_
3 <sup>d</sup>	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	0.12	95
4	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	0.12	99
5	EtOH-H <sub>2</sub> O (3:2)	Na <sub>2</sub> CO <sub>3</sub>	0.12	90
6	EtOH-H <sub>2</sub> O (3:2)	KOH	0.12	10
7	EtOH-H <sub>2</sub> O (3:2)	NaOH	0.12	10
8	EtOH-H <sub>2</sub> O (3:2)	Et <sub>3</sub> N	0.12	13
9	EtOH-H <sub>2</sub> O (3:2)	NaAc	0.12	10
10	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	0.06	87
11	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	0.09	94
12	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	0.15	99
13	EtOH-H <sub>2</sub> O (4:1)	K <sub>2</sub> CO <sub>3</sub>	0.12	73
14	EtOH-H <sub>2</sub> O (1:4)	K <sub>2</sub> CO <sub>3</sub>	0.12	5
15	EtOH-H <sub>2</sub> O (2:3)	K <sub>2</sub> CO <sub>3</sub>	0.12	83
16 <sup>e</sup>	EtOH-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub>	0.12	83

<sup>a</sup>Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvent (5 ml), 50 °C, 1 h.

<sup>b</sup>In absence of catalyst.

<sup>c</sup>Catalyzed by UCS.

<sup>d</sup>30°C, 6 h.

<sup>e</sup>0.5 h.

nanoparticles have a key role in the reaction. The reaction could be carried out at room temperature; however, the reaction time is 4 h with a yield of 95% (Table 1, entry 3). With the reaction temperature increasing to 50  $^{\circ}$ C, the reaction can be completed after 1 h with a yield of 99% (Table 1, entry 4).

It is well known that the base has a great influence on Suzuki reactions. Various bases including organic and inorganic ones have been considered. The screening experiments show that  $K_2CO_3$  as a base affords the coupling product in the highest yield (99%) at 50 °C in 1 h (Table 1, entries 4–9). The dosage of Pd@UCS and type of solvent were also studied, and the results show that 0.12 mol% Pd@UCS is sufficient to guarantee complete conversion with EtOH– $H_2O$  (5 ml, 3:2 v/v) as the solvent (Table 2, entries 4 and 10–15).

With the optimized conditions in hand, the catalytic activity of Pd@UCS for Suzuki coupling reactions was investigated with various aryl halides and arylboronic acids, and the results are summarized in Table 2. High catalytic activities are observed for bromobenzene and electron-rich and electron-poor aryl bromide, both affording the corresponding biphenyl compounds in good yields under the optimized reaction conditions. It is worth noting that the reaction of 3-methylbenzeneboronic acid with bromobenzene needed less reaction time (Table 2, entry 8) than that of phenylboronic acid, indicating that benzeneboronic acid containing electron-donating group is beneficial for the reaction. However, 2-methylbenzeneboronic acid needs a relatively long reaction time, which can be ascribed to the steric hindrance effect (Table 2, entry 7). Unfortunately, a low yield was obtained with the reaction of aryl chloride (Table 2, entry 9) because of the strength of the C-Cl bond.

In order to evaluate the catalytic activity of the Pd@UCS catalyst for the reaction of bromobenzene and phenylboronic acid, it was compared with other reported Pd catalysts in terms of dosage of catalysts, reaction time and temperature, yield of product and TOF of the reaction (Table 3). The Pd@UCS catalyst could efficiently catalyze the Suzuki coupling reaction giving the highest yield without using any additive and toxic solvent.

The recycling and reusability of the Pd@UCS catalyst were further investigated because they are very important characters for heterogeneous catalysts. The reaction of bromobenzene with phenylboronic acid was carried out under optimized conditions. It can be seen in Figure 5 that the catalyst maintains high catalytic activity after five reaction runs, indicating good stability. A TEM image of the recovered catalyst after five recycles is shown in Figure 1(d), where there is no aggregation phenomenon occurring, which demonstrates that the Pd nanoparticles remain well dispersed after five runs. 
 TABLE 2
 Suzuki coupling reactions catalyzed by Pd@UCS<sup>a</sup>

$R_1 \longrightarrow X + (HO)_2 B \longrightarrow R_2 \xrightarrow{Pd@UCS} R_2 \xrightarrow{Pd@UCS} R_2 \xrightarrow{R_1} R_2$							
Entry	Aryl halide	Arylboronic acid	Time (h)	Yield (%)			
1	Br	B(OH)2	1	99			
2	H <sub>3</sub> C-	B(OH)2	2	91			
3	CH <sub>3</sub> Br	B(OH)2	3	94			
4	H <sub>3</sub> CO-	B(OH) <sub>2</sub>	3	90			
5	O <sub>2</sub> N-Br	B(OH) <sub>2</sub>	1	98			
6	H <sub>3</sub> CCO-Br	B(OH) <sub>2</sub>	1	96			
7	Br		0.67	89			
8	Br	H <sub>3</sub> C B(OH) <sub>2</sub>	0.67	98			
9	<−ci	B(OH)2	12	19			
10	Br	B(OH) <sub>2</sub>	4	98			
11	Br	B(OH) <sub>2</sub>	4	97			
12	CH <sub>3</sub> Br	B(OH) <sub>2</sub>	4	90			

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<sup>a</sup>Reaction conditions: aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), EtOH-H<sub>2</sub>O (3:2, 5 ml) and Pd@UCS (0.12 mol%), 50 °C.

 TABLE 3
 Suzuki coupling reaction of bromobenzene with phenylboronoic acid catalyzed by various catalysts

Entry	Catalyst	Dosage (mol%)	Temp. (°C)	Time (h)	Yield (%)	TON	TOF $(h^{-1})$	Ref.
1	Pd/Nf-G	0.3	80	3	88	293.3	97.8	[16]
2	Fe <sub>3</sub> O <sub>4</sub> @PUNP-Pd	0.1	90	1	95	950	950	[17]
3	MOF-253-Pd	0.23	100	10	94	408.7	40.9	[18]
4	Pd-MCM-41	0.05	80	12	90	1 800	150	[19]
5	Pd/Y-MOF	0.054	80	8	59	1 092.6	136.6	[20]
6	Pd/PMA-MIL-101	1.3	130	24	50	38.5	1.6	[21]
7	Pd@p-SiO <sub>2</sub>	0.003	200	3	65	21 666.7	7 222.2	[22]
8	Pd/UiO-66-NH <sub>2</sub>	0.25	60	0.5	90	360	720	[23]
9	Pd/H <sub>2</sub> P-Bph-COF	0.5	110	1.5	98	196	130.7	[24]
10	Pd@UCS	0.12	50	1	99	825	825	This study



FIGURE 5 Recyclability of Pd@UCS for Suzuki reaction

#### 4 | CONCLUSIONS

In summary, UCS were synthesized using a renewable biomass – sucrose – with HTC and activation methods. The as-prepared catalyst, Pd@UCS, showed highly efficient catalytic activity for the Suzuki coupling reaction. Moreover, the catalyst could be recovered by simple centrifugation and reused for at least five times without significant loss of its catalytic activity. The use of UCS as a catalyst support might bring new opportunities in the development of efficient heterogeneous Pd catalysts. Studies aimed at extending the scope of Pd@UCS to other Pd-catalyzed reactions are currently underway in our laboratories.

#### ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (21603054), the Natural Science Foundation of Hebei Province (B2015204003, B2016204131), the Young Top-notch Talents Foundation of Hebei Provincial Universities (BJ2016027) and the Natural Science Foundation of Agricultural University of Hebei (LG201404, ZD201506, ZD201613) is gratefully acknowledged.

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How to cite this article: Dong W, Cheng S, Feng C. et al. Carbon nanospheres with well-controlled nanomorphologies as support for palladium-catalyzed Suzuki coupling reaction. *Appl Organometal Chem.* 2017;e3741. https://doi.org/10.1002/aoc.3741