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# Carboxyl-containing microporous organic nanotube networks as a platform for Pd catalysts†

Yang Xu, Tianqi Wang, Zidong He, Aiqing Zhong and Kun Huang\*

In this work, we present a novel synthesis of carboxyl-containing microporous organic nanotube networks (COOH-MONNs) by combination of hyper-cross-linking and molecular templating of core-shell bottlebrush copolymers. Highly dispersed palladium nanoparticles (Pd NPs) anchored on the COOH-MONNs (Pd@MONNs) have been prepared by *in situ* thermal decomposition of Pd(OAc)<sub>2</sub>. The Pd@MONNs composites were characterized by XRD, N<sub>2</sub> adsorption, TEM, ICP-AES and XPS. The results show that bulk production of highly dispersed palladium nanoparticles can be achieved by a thermal decomposition method. Moreover, the obtained Pd@MONNs exhibit high activities for the Suzuki–Miyaura cross-coupling reaction and can be easily recovered and reused. This approach of using MONNs as a platform for catalysts is expected to open doors for new types of catalytic support for practical applications.

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## 1. Introduction

The Suzuki-Miyaura cross-coupling reaction catalyzed by palladium nanoparticles (Pd NPs) is one of the most effective synthetic reactions in organic synthesis and pharmaceutical industries.1-3 Due to the large surface-to-volume ratio and ultrasmall size, Pd NPs exhibit remarkable high catalytic activities toward this reaction, a property not displayed in bulk palladium.<sup>4,5</sup> However, Pd NPs tend to agglomerate to form large particles, driven by high surface energy, which results in a loss of their catalytic activities.4 Considerable efforts and great achievements have been made to overcome this issue by immobilizing Pd NPs in or onto appropriate solid supports, such as silica,<sup>6</sup> zeolites,<sup>7</sup> activated carbon,<sup>8</sup> carbon nanotubes,9,10 polymers11 and some composite materials.12,13 Although these supported Pd catalysts have superior catalysis activities, the development of efficient and stable heterogeneous catalysts is still highly desirable.

Up to now, a variety of synthetic methods have been developed towards the fabrication of metal-loaded solid catalysts, such as chemical reduction,<sup>14,15</sup> supercritical fluid deposition method,<sup>16</sup> self-assembly,<sup>17</sup> electrochemical decoration<sup>18</sup> and thermal decomposition of metal salts.<sup>19–22</sup> Among them, thermal decomposition or pyrolysis of metal salts was considered as a straightforward and easy handling method to anchor metal nanoparticles on the appropriate solid supports. For example, Swadhin K. Mandal and co-workers<sup>21</sup> have developed a method through thermally decomposing metal salts to decorate palladium nanoparticles onto carboxylic acid functionalized single walled carbon nanotubes (SWNTs). Recently, Guo and co-workers<sup>22</sup> also reported a one-pot thermal decomposition method without addition of reductant or surfactant to synthesize multiwalled carbon nanotube (MWNT)-COOHstabilized Pd nanocatalysts (Pd–MWNT–COOH). These studies have shown that the COOH-modified materials had a high affinity for Pd NPs and exhibited a potential universality to fabricate different supported metal catalysts by thermal decomposition of metal salts.

In the past decade, porous materials have drawn everincreasing interest and have provided great new opportunities for heterogeneous catalysis. The fusion of porous materials and metal NPs technology has been a fruitful area in catalysis. The traditional porous materials such as silicas, zeolites and activated carbon have been extensively used as heterogeneous catalysts supports. Recently, microporous organic polymers (MOPs) as an emerging class of porous materials have received much attention as catalysts candidates owing to their high porosity. In addition, the bottom-up or post-synthetic modification approach for MOPs synthesis provides their excellent capability to incorporate targeted or multiple chemical functionalities into the porous framework for use as catalysts. For example, MOPs have been efficiently utilized as supports of metal NPs in photocatalysis, oxidation reactions, and Suzuki-Miyaura cross-coupling reactions.23,24 However, most of these MOPs mainly contain a sole micropore, which may limit the diffusion of the reactants and products, leading to undesirable catalytic activity. A potential method to solve this problem was to introduce meso/macropores into the sole microporous materials to form a structure with hierarchically pores.25

School of Chemistry and Molecular Engineering, East China Normal University, 500 N, Dongchuan Road, Shanghai, 200241, P. R. China. E-mail: khuang@chem.ecnu.edu.cn † Electronic supplementary information (ESI) available: Experimental data of Fig. S1-S6. See DOI: 10.1039/c6ra05753e



Scheme 1 Fabrication of Pd NPs catalysts supported on carboxylcontaining microporous organic nanotube networks.

Herein, we present a novel synthesis of carboxyl-containing microporous organic nanotube networks (COOH-MONNs) by combination of hyper-cross-linking and molecular templating of core–shell bottlebrush copolymers (Scheme 1). The well-dispersed Pd NPs could be anchored into the COOH-MONNs by *in situ* thermal decomposition of  $Pd(OAc)_2$ , in which the carboxyl groups served as anchors were generated and tuned from the controllable synthesis of the materials. To the best of our knowledge, direct thermal decomposition of  $Pd(OAc)_2$  in the presence of carboxyl-containing porous organic polymers without the addition of surfactants or reducing reagents has rarely been reported. On this basis, the as-prepared novel Pd NPs catalysts (Pd@MONNs) may be promising heterogeneous catalysts towards Suzuki–Miyaura cross-coupling reaction under mild conditions.

### 2. Experimental

#### 2.1. Materials

All reagents were used as received unless stated otherwise. Glycidyl methacrylate (GM, Acros 97%) was distilled before use. Dichloromethane (DCM) and *N*,*N*-dimethylformamide (DMF) were dried using CaH<sub>2</sub> and distilled. Styrene (Aldrich 99%) was purified by passing over basic alumina. 2,2-Azoisobutyronitrile (AIBN) and D,L-lactide were purified by recrystallization from methanol and ethyl acetate, respectively. *S*-1-Dodecyl-*S*'-( $\alpha$ , $\alpha$ '-dimethyl- $\alpha$ ''-acetic acid) trithiocarbonate<sup>26</sup> and 2-cyanoprop-2-yl-4-cyanodithiobenzoate (CPD)<sup>27</sup> were synthesized according to literature procedures.

#### 2.2. Instrumentations

All <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III<sup>™</sup> 500 spectrometer (500 MHz) by using CDCl<sub>3</sub> as a solvent. GPC data were obtained from Waters GPC system equipped with a Waters 1515 isocratic HPLC pump, a 2414 refractive index (RI) detector, and two Waters' HPLC columns. Tetrahydro-furan was used as the solvent for polymers and eluent for GPC with a flow rate of 1 ml min<sup>-1</sup> at 30 °C. The GPC instrument was calibrated with narrowly dispersed linear polystyrene standards. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F TEM instrument. Samples

were prepared by dip-coating a 400 mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. A Quantachrome Autosorb IQ surface area and porosity analyzer was utilized to study the pore structure of the samples. Before measurements, the polymer samples were degassed for more than 10 h at 120 °C. The Brunauer-Emmett-Teller surface area and the micropore surface area were determined by the BET equation and the tplot equation, respectively. The pore size distribution was analyzed by original density functional theory (DFT). X-ray photoelectron spectroscopy (XPS) spectra were obtained on an ESCALAB 250Xi spectrometer. The powder X-ray diffraction (XRD) pattern of the sample was collected using a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu K radiation. The infrared (IR) spectra were recorded using Thermo NICOLET is 50. TG analyses were carried out with a NETZSCH STA449F3 simultaneous thermal analyzer at a heating rate of 10 K min<sup>-1</sup> from 30 to 800 °C in a nitrogen atmosphere.

#### 2.3. Synthetic procedures

**2.3.1.** Synthesis of PGM. GM (2 ml), CPD (18 mg), AIBN (2.4 mg) and benzene (2 ml) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 16 h. The mixture was diluted with DCM, precipitated into methanol 3 times and dried under vacuum at room temperature for 24 h. Yield = 1.77 g (89%). GPC (PS standards):  $M_n = 1.5 \times 10^4$  g mol<sup>-1</sup>,  $M_w/M_n = 1.07$ . <sup>1</sup>H NMR: n(GM) = 200.

**2.3.2.** Hydrolysis of PGM. PGM (600 mg), THF (12 ml) and acetic acid (24 ml) were mixed in a 250 ml two-necked roundbottom flask. The reaction mixture was stirred and placed in an oil bath at 60 °C, followed by the slow addition of 35 ml water over the course of 1 h. After stirring for 24 h, the solvent was removed on a rotary evaporator. The isolated polymer was precipitated from methanol into diethyl ether 3 times and dried under vacuum at 25 °C for 24 h. Yield = 0.52 g (95%). <sup>1</sup>H NMR: conversion = 95+%.

**2.3.3.** Synthesis of PGM-g-PLA. Hydrolyzed PGM (50 mg) and <sub>D,L</sub>-lactide (1.80 g) were added to a dried 50 ml roundbottom flask. Dried DMF (4.5 ml) was then added and the mixture was stirred until all polymer dissolved. 1,8-Diazbicyclo [5.4.0] undec-7-ene (DBU, 54 µl) was then injected into the flask. After stirring at room temperature for 1.5 h, the reaction was quenched by adding 162 mg benzoic acid. The resulting polymer was precipitated from THF into methanol/water (1 : 1) 3 times and dried under vacuum at 25 °C for 24 h. Yield = 1.25 g (75%). GPC (PS standards):  $M_n = 1.9 \times 10^5$  g mol<sup>-1</sup>,  $M_w/M_n = 1.11.$  <sup>1</sup>H NMR: n(PLA) = 25.

2.3.4. Synthesis of PGM-g-(PLA-b-PS)/PGM-g-(PLA-b-tBA-b-PS). Hydroxyl end groups of the PLA brush were then modified to install trithiocarbonate functionalities as described in the literature.<sup>29</sup> PGM-g-PLA-TC (30 mg) was mixed with AIBN (0.24 mg), styrene (1.98 ml) and toluene (1.98 ml) in a reaction vessel and degassed by 3 freeze–pump–thaw cycles. The reaction was then conducted at 50 °C for 15 h and stopped by cooling to room temperature and opening the flask to air. The resulting reaction mixture was then precipitated from DCM to methanol 3 times and dried under vacuum at 25 °C for 24 h. Yield = 125 mg. GPC (PS standards):  $M_{\rm n} = 4.8 \times 10^5$  g mol<sup>-1</sup>,  $M_{\rm w}/M_{\rm n} = 1.21$ . <sup>1</sup>H NMR: n(styrene) = 67.

PGM-g-(PLA-*b*-*t*BA-*b*-PS) was prepared as same as the above procedures. The synthesis of PGM-g-PLA-*b*-*t*BA was as follow. PGM-g-PLA-TC (80 mg) was mixed with AIBN (0.42 mg), *tert*butyl acrylate (*t*BA 1.10 ml) and 1,4-dioxane (3.20 ml) in a reaction vessel and degassed by 3 freeze–pump–thaw cycles. The reaction was then conducted at 50 °C for 22 minutes and stopped by cooling to room temperature and opening the flask to air. The resulting reaction mixture was then precipitated from THF to the solution methanol/water (1 : 2) 3 times and dried under vacuum at 25 °C for 24 h. Yield = 125 mg. GPC (PS standards):  $M_n = 9.3 \times 10^5$  g mol<sup>-1</sup>,  $M_w/M_n = 1.25$ . <sup>1</sup>H NMR: n(tBA) = 3.

2.3.5. Hyper-cross-linking and core etching (MONNs). Here, we choose PGM-g-(PLA-b-PS) as an example to demonstrate the general procedure for the hyper-cross-linking and core etching. PGM-g-(PLA-b-PS) (110 mg) was dissolved into 11 ml dried 1,2-dichloroethane (DCE) under nitrogen in a 100 ml round-bottom flask. After purging with N2 for 10 minutes, formaldehyde dimethyl acetal (FDA) (134 µl) and anhydrous FeCl<sub>3</sub> (340 mg) were added. The reaction mixture was left under a N2 flow for a further 10 minutes. The reaction was then sealed and heated under reflux at 80 °C for 24 h. The solid products were washed 3 times with methanol. To assure complete removal of any PLA-related residues (and deprotection of tBA to produce more carboxyl), the product was then heated in hydrochloric acid (5 M) at 60 °C for 24 h. The final product was collected and washed with methanol 3 times and dried under vacuum at 60 °C for 24 h. Yield = 108 mg.

**2.3.6.** Preparation of the Pd catalyst (Pd@MONNs). MONNs (60 mg) and palladium acetate (21 mg) (COOH : Pd = 1 : 2) were uniformly dispersed into 30 ml dry DMF under nitrogen atmosphere in a 100 ml round-bottom flask with the aid of stirring. To carry out the thermal decomposition of palladium acetate, the mixed system was heated at 95 °C for 4 h, and then cooled to 25 °C under nitrogen atmosphere. After the reaction finished, the solid product was centrifuged and washed several times with ethanol (10 ml × 3), acetone (10 ml × 2) until the filtrate was clear and dried under vacuum at 60 °C for 24 h. Yield = 62 mg.

2.3.7. Preparation of the comparative Pd catalyst (Pd@MOP). PGM-g-(PLA-*b*-PS) (70 mg) was dissolved in 16 ml THF, and 1 M NaOH methanol solution (2 ml) was then added to the mixture. The reaction solution was stirred at room temperature for 12 h. The solvent was evaporated and the polymer was precipitated from THF to methanol 2 times and dried under vacuum at 25 °C for 24 h. GPC data (Fig. S8D, ESI<sup>†</sup>) shown that the core of PGM-*g*-(PLA-*b*-PS) has been etched with the PS–COONa block fragment remained. The corresponding microporous organic polymer (MOP) was constructed *via* hyper-cross-linking of the PS–COONa block fragment and the Pd catalyst (Pd@MOP) was prepared at the same condition as Pd@HMONNs.

#### 2.4. Catalysis of the Suzuki-Miyaura coupling reaction

The Suzuki-Miyaura coupling reactions were carried out under the catalysis of Pd@MONNs. 5 mg Pd@MONNs catalyst, K2CO3 (1.5 mmol), and borophenylic acid (0.75 mmol) were added into a round-bottom flask under nitrogen atmosphere. Halobenzene (if halobenzene was liquid) (0.5 mmol), H<sub>2</sub>O (0.8 ml), and ethanol (1.2 ml) were successively added using syringes, and the mixture was stirred at 50 °C (aryl chlorides reactions at 80 °C). After the reaction finished, the catalyst solid was separated from the reaction mixture by centrifuging. The product was extracted with ethyl acetate and the liquid was concentrated. The conversion of product was quantified by gas chromatograph test. If it is necessary, the product could be purified by column chromatography. Then the separated catalyst was washed several times with distilled water (5 ml  $\times$  2), methanol (5 ml  $\times$ 2) and dried under vacuum at 60 °C for next run. The content of Pd species leached off from the catalyst was determined by ICP analysis.

## 3. Results and discussion

Scheme 1 describes the synthetic strategy of Pd NPs catalysts supported on carboxyl-containing microporous organic nanotube networks (Pd@MONNs). First, the core-shell bottlebrush copolymer precursors were synthesized *via* a "grafting-from" approach with the help of ring-opening and reversible additionfragmentation chain transfer (RAFT) polymerizations. Next, the outer polystyrene (PS) side chains in molecular bottlebrush were then hyper-cross-linked *via* a Friedel–Crafts alkylation reaction.<sup>28,30</sup> By removal of the polylactide<sup>28</sup> core retained in the pores and further acidification, the COOH-MONNs were obtained and abundant inherent carboxyl groups were produced on the pore walls. The number of carboxyl groups could be tuned by introduced a functional block between the PLA core and PS shell layer, such as poly(*tert*-butyl acrylate) (PtBA).

Scheme 2 presents the synthesis routes of well-defined core-shell bottlebrush copolymers, as previously described



Scheme 2 Synthesis routes of the bottlebrush copolymer precursors of (A) MONNs-1 and (B) MONNs-4.

method.<sup>31,32</sup> From the <sup>1</sup>H NMR spectra (Fig. S1, ESI<sup>†</sup>), the backbone of poly(glycidyl methacrylate) (PGM) with an average degree of polymerization of 200 and a polydispersity index (PDI) of 1.07 was obtained. For PGM-g-(PLA-b-PS), every branch was composed of a PLA block with an average of 25 repeat units and a PS block with an average of 67 units. As a regulation technique, poly(tert-butyl acrylate) (PtBA) was selected as a middle functional block to introduce the core-shell bottlebrush copolymers. From the <sup>1</sup>H NMR spectrum of PGM-g-(PLA-b-PtBA*b*-PS), the characteristic signal of *t*BA at 2.26 ppm was observed and the number of PtBA and PS groups was 3 and 70, respectively. GPC analysis of all polymers exhibited low polydispersities  $(M_w/M_n < 1.30)$ , which revealed the formation of well-defined copolymer precursors (Fig. S2, ESI<sup>†</sup>). Subsequently, the resulting precursors were hyper-cross-linked via a Friedel-Crafts alkylation. In this work, the pendant phenyl groups from PS shell layer were hyper-cross-linked by anhydrous FeCl<sub>3</sub> with the extra cross-linker of formaldehyde dimethyl ether (FDA). After that, the hyper cross-linked polymer networks were then subjected to hydrochloric acid to remove the PLA core. Under this circumstance, the one-fold carboxyl groups will be produced after the PLA core removed (MONNs-1). In addition, the functional block of PtBA can be deprotected to yield poly-(acrylic acid) (PAA) layer, where extra threefold carboxyl groups were added into the above system (MONNs-4). These transformations were evidenced by FTIR spectra, where the PLA carbonyl stretch peak (1758 cm<sup>-1</sup>) completely disappeared after hydrolysis (Fig. S3, ESI<sup>†</sup>). The carbonyl stretch peak of PtBA at 1728 cm<sup>-1</sup> was replaced by a broad signal from 1716 to 1732 cm<sup>-1</sup>, which was attributed to free and H-bonded carbonyl vibrations of carboxyl groups on the nanotube interior.33

Transmission electron microscopy (TEM) analysis revealed that the cylindrical morphology of bottlebrush copolymer precursors was maintained after the core removal process. Especially, the hollow tubular network structure could be clearly observed (Fig. 1A and C). The average length of the obtained tubular units in polymer networks was measured to be  $38 \pm 5$ 

nm, whereas the internal cavity average diameter was about 5 nm. The Brunauer-Emmet-Teller (BET) surface area and total pore volume of MONNs-1 determined by nitrogen adsorptiondesorption isotherms were 996 m<sup>2</sup> g<sup>-1</sup> and 1.74 cm<sup>3</sup> g<sup>-1</sup>, respectively (Fig. 2). The presence of microporous structures was confirmed by an adsorption uptake at low relative pressure  $(P/P_0 < 0.001)$  in the N<sub>2</sub> adsorption–desorption. A sharp rise at medium and high relative pressure  $(P/P_0 = 0.8-1.0)$  indicated the presence of macropores in the support. However, a pronounced hysteresis loop observed in the desorption isotherm indicated the existence of accessible mesopores in the polymeric matrices (Fig. 2A). The micropore was within the hyper-cross-linking PS shell layer, mesopore was produced by the selectively removed PLA core layer, while the meso/ macropore resulted from a 3D continuous bottlebrush polymeric cross-linked network. The pore-size distribution was also calculated by the nonlocal density functional theory (NLDFT) model. Two dominating pore-size distributions about 1.4-1.8 and 5.0 nm were observed, further confirming that uniform mesopores existed in hollow microporous organic nanotubes, which agreed with the results of TEM (Fig. 2B). Because of the same degrees of graft of PLA and PS, the BET data of MONNs-4 are similar shown in the above results (Table 1). Based on their rigid network structures, high surface areas and excellent hierarchical porosity, the obtained supports can be expected to be superior platforms for the heterogeneous catalysts.

With the as-prepared supports in hand, the confinement of MONNs and coordination ability of carboxyl groups with Pd NPs were investigated (Pd@MONNs). As shown in Scheme 1, a facile method, *in situ* thermal decomposition of Pd(OAc)<sub>2</sub> in a solution of MONNs dispersed in *N*,*N*-dimethylformamide (DMF), was used. TEM images showed that Pd NPs were well dispersed in the MONNs-1 and MONNs-4, and their average diameters are  $3.98 \pm 0.5$  and  $4.16 \pm 0.6$  nm, respectively, which are small enough to anchored into the interior cavities of MONNs-1 and MONNs-4 (Fig. 1B and D). In the powder X-ray diffraction (XRD) pattern of Pd@MONNs-1, only a weak peak about (111) plane of the Pd NPs was detected (Fig. S4, ESI†), revealing the Pd NPs are



Fig. 1 TEM images of (A) MONNs-1; (B) Pd@MONNs-1; (C) MONNs-4 and (D) Pd@MONNs-4. The size distributions of Pd NPs were calculated from TEM images and were illustrated in the inset histograms ((B):  $(3.98 \pm 0.5)$  nm; and (D):  $(4.16 \pm 0.6)$  nm).



Fig. 2 Nitrogen adsorption–desorption isotherms and NLDFT pore size distributions of MONNs-1 (A, B) and Pd@MONNs-1 (C, D).

Table 1 Surface area and pore volume of the samples

<sup>*a*</sup> BET specific surface area calculated from N<sub>2</sub> adsorption isotherm. <sup>*b*</sup> Microporous volume obtained from *t*-plots method. <sup>*c*</sup> Total pore volume at  $P/P_0 = 0.995$ .

small and well dispersed in the support.<sup>34</sup> The BET surface area of Pd@MONNs-1 was reduced to 850 m<sup>2</sup> g<sup>-1</sup> (Table 1), indicating the successful immobilization of Pd NPs into the support (Fig. 2C and D).<sup>24</sup> Thermogravimetric analysis (TGA) analyses showed Pd contents in Pd@MONNs-1 and Pd@MONNs-4 are 10 wt% and 13 wt%, which are in good agreement with ICP analyses (9.7 wt% and 12.5 wt%) respectively (Fig. S5, ESI†). The different Pd loading in Pd@MONNs-1 and Pd@MONNs-4 may be owing to the different number of carboxyl groups.

To further investigate the coordination ability of carboxyl groups with Pd NPs, Pd@MONNs-1 was selected for subsequent X-ray photoelectron spectroscopy (XPS) characterizations. As shown in Fig. 3, their wide-scan survey spectrum possess four peaks centered at 284.1, 336.0, 533.4, and 561.5 eV, corresponding to C 1s, Pd 3d, O 1s, and Pd 3p, respectively (Fig. 3A). In the high-resolution XPS spectrum, the peaks of Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> binding energies were observed slightly higher than the bulk Pd 3d levels ( $3d_{5/2} = 334.7$  eV and  $3d_{3/2} = 340.3$  eV), at 336.1 and 341.7 eV (Fig. 3B). The peaks shift positively suggested that the catalyst contains almost Pd metal and an interaction between the Pd NPs with the support.<sup>21,35</sup> Highresolution C 1s XPS spectrum of MONNs-1 and Pd@MONNs-1 were shown in Fig. 3C and D. The deconvolution of the C 1s curve for Pd@MONNs-1 was almost the same as the curve of MONNs-1, indicated that the load of Pd NPs on the supports has not influenced its stable structure. However, in comparison

with MONNs-1, the intensity of oxygen-containing groups (C=0) in the Pd@MONNs-1 decreased obviously, which can be attributed to the strong binding of oxygen-containing groups with Pd NPs.<sup>22</sup> These results confirmed that Pd NPs were successfully anchored into the MONNs-1 by coordination to carboxyl groups, and that the bonding interaction appeared between Pd NPs and the C=O.

To evaluate the catalytic efficiency and stability of Pd@MONNs, we selected the Suzuki-Miyaura coupling of piodoanisole and phenylboronic acid as a model reaction (Fig. 4). Considering the subject of environment-friendly reaction processes, the model reaction was conducted in a relatively mild aqueous media, K<sub>2</sub>CO<sub>3</sub> (3 equiv.) as a base at 50 °C in EtOH/H<sub>2</sub>O (3:2) solutions. Fig. 4A shows kinetic profiles of the catalytic reactions, which were monitored by Gas Chromatography-Mass Spectrometer (GC-MS). For Pd@MONNs-1, full conversion of this reaction afforded within 5 h, while the use of Pd@MONNs-4 under the same conditions gave obviously rise to a complete conversion within 3 h. The higher activity of Pd@MONNs-4 than Pd@MONNs-1 probably results from the higher Pd contents of Pd@MONNs-4. The increase of the carboxyl groups for MONNs-4 supports maybe offer multidentate anchor sites to Pd NPs, which shows better immobilization ability than one-fold carboxyl groups.36,37 This observation also demonstrated that Pd NPs were coordinated with carboxyl groups, which can be tuned from the controllable synthesis of the materials. Recyclability is a considerable quality of heterogeneous catalyst, which is necessary for industrial applications. Pd@MONNs-1, as a general example, was successfully reused with no obvious loss of activity after eight runs and recovered by simple filtration (Fig. 4B). The XPS and TEM image of Pd@MONNs-1 after eight runs revealed that the oxidation state of Pd in Pd@MONNs-1 presented 0 and +2 states and still remained a well-dispersed form with slightly increased in size, as well as the morphology of the support was well maintained (Fig. S6 and S7, ESI<sup>†</sup>). To further investigate the stability of the catalyst, a brief hot





Fig. 3 XPS spectra of Pd@MONNs-1: (A) wide-scan survey, (B) curve fit of Pd 3d, (C) curve fit of C 1s of MONNs-1 and (D) curve fit of C 1s of Pd@MONNs-1.



Fig. 4 (A) Kinetic profiles of Pd@MONNs-1 and Pd@MONNs-4 in the model Suzuki–Miyaura coupling reaction of *p*-iodoanisole and phenylboronic acid. (B) Recycle performances of the typical Pd@MONNs-1 catalyst in the model reaction. Reaction conditions: *p*-iodoanisole (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 (2 ml, 3 : 2 v/v), Pd@MONNs-1 (5 mg, 9.7 wt%) or Pd@MONNs-1 (5 mg, 12.5 wt%), 50 °C, under a N<sub>2</sub> atmosphere. For recycle tests, the reaction time was set at 5 h. The conversion yields were monitored by GC.

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filtration test for Pd@MONNs-1 was adopted. When the *p*-iodoanisole conversion reached 55% (1 h), the solid Pd@MONNs-1 catalyst was filtered and removed from the reaction mixture. Then the mother liquor of the mixture was allowed to react for another 4 h under the similar conditions. No significant change in conversion was observed, indicating that the catalyst active phase was not the dissolved homogeneous Pd atoms leached from the support. ICP analyses of the Pd content in the filtrate demonstrated nearly no Pd leaching (0.7 ppm) occurred for the Pd@MONNs-1, which agrees with the result of the hot filtration test.

To expand the scope of practical applications, the Pd@MONNs-1 was selected as a typical catalyst for further examined in Suzuki-Miyaura coupling reaction of various types of aryl halide and aryboronic acids. As shown in Table 2, when the coupling reaction of p-iodoanisole and phenylboronic acid was carried out in the presence of Pd@MONNs-1 (5 mg, 9.7 wt%) at 50 °C, 99% GC yield of product was obtained in 5 h (entry 1). No corresponding product was formed in the control experiment of the above reaction in the presence of MONNs-1 only (entry 2). When various types of aryl bromides and arylboronic acids were used as substrates, the corresponding products were obtained over 85% (entry 3-7). These results suggest that the electronic effects of reactants have no obvious influence on the desired coupling products obtained under the given reaction conditions. As we all know, the use of aryl chlorides reactants is a particular challenge for the coupling reaction due to their inactivated characters. It was noteworthy that the couplings of various arylboronic acids with chlorobenzene easily converted with 84-89% yields at 80 °C (entry 8, 9), which showed a remarkable universality for the Suzuki-Miyaura coupling reactions with our new catalysts.

To prove the unique advantage of MONNs as catalyst support, a new Pd catalyst (Pd@MOP) with dominated micropore structure was synthesized for comparison. Its synthetic

Table 2Pd@MONNs-1 catalyzed Suxuki-Miyaura reactions of varioussubstrates $^{a}$ 

Pd catalyst

$R_1 \longrightarrow X + R_2 \longrightarrow B(OH)_2 \xrightarrow{K_2CO_3} R_1 \longrightarrow R_2$ EtOH/H <sub>2</sub> O					
Entry	R <sub>1</sub>	Х	$R_2$	Time (h)	Yield <sup>b</sup> (%)
1	CH <sub>3</sub> O	Ι	н	5	>99
$2^{c}$	CH <sub>3</sub> O	Ι	Н	5	0
3	$CH_3O$	Br	Н	5	91
4	Н	Br	Н	5	89
5	CH <sub>3</sub> CO	Br	Н	10	86
6	CN	Br	Н	5	90
7	Н	Br	CH <sub>3</sub> O	5	97
$8^d$	Н	CI	Н	5	$84^e$
$9^d$	Н	CI	CH <sub>3</sub> O	10	$89^e$

<sup>*a*</sup> Reaction conditions: aryl halides (0.5 mmol), arylboronic acids (0.75 mmol),  $K_2CO_3$  (1.5 mmol), EtOH/H<sub>2</sub>O (2 ml, 3 : 2 v/v), Pd@MONNs-1 (5 mg, 9.7 wt%), 50 °C, under a N<sub>2</sub> atmosphere. <sup>*b*</sup> GC yield. <sup>*c*</sup> Only MONNs-1 without Pd. <sup>*d*</sup> 80 °C. <sup>*e*</sup> Isolated yield.

procedure is similar to that of the Pd@MONNs-1 except with linear PS polymers to replace the PGM-g-(PLA-b-PS) bottlebrush copolymers. The BET surface area and total pore volume of the resulted Pd@MOP were 0.86 m<sup>2</sup> g<sup>-1</sup> and 706 cm<sup>3</sup> g<sup>-1</sup>, respectively (Fig. S8A and S8B, ESI<sup>†</sup>). However, no pronounced hysteresis loop observed in the desorption isotherm indicated that the comparative Pd@MOP catalyst mainly consisted of a microporous structure (Fig. S8A, ESI<sup>†</sup>). TEM image also showed that Pd@MOP has a disordered structure and the Pd species tend to agglomeration on the MOP surface with a non-uniform distribution (Fig. S8C, ESI<sup>†</sup>). Compared with Pd@MONNs, the full conversion of the model reaction with Pd@MOP catalyst for the first time needs 12 h under the same reaction conditions. This might be attributed to the dominated micropore structure of Pd@MOP, which may limit the diffusion of the reactants and products, leading to undesirable catalytic activity. In addition, the poor distribution of the bulk Pd species also reduced the recyclability of Pd@MOP, which showed an obvious loss of activity after the second runs. Therefore, the Pd@MONNs, with unique microporous nanotube networks structure and well-dispersed Pd NPs, have shown better catalytic activity and stability than the obtained disordered microporous Pd@MOP catalysts.

## 4. Conclusions

In conclusion, we reported an efficient way to prepare Pd NPs catalysts anchored into the carboxyl-containing microporous organic nanotube networks (COOH-MONNs) by in situ thermal decomposition of  $Pd(OAc)_2$ . The high surface areas (996 m<sup>2</sup>)  $g^{-1}$ ), large pore volume (1.74 cm<sup>3</sup> g<sup>-1</sup>) and various pore sizes distributions of supports ensured the high dispersion of Pd NPs active sites as well as improved the diffusion of reactants and products. In addition, the carboxyl groups served as anchors can be directly generated and tuned from the controllable synthesis of the materials, which offer excellent regulation to the contents of Pd NPs. Pd@MONNs, with unique structure, exhibited a high catalytic activity and excellent stability during the catalytic process of the Suzuki-Miyaura coupling reactions. Encouraged by the excellent catalytic performance of Pd@MONNs, our further research will be devoted to the preparation of high-efficiency catalysts based on MONNs for more practical catalytic applications.

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