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Coupling reactions of aromatic halides with palladium catalyst immobilized on poly(vinyl alcohol) nanofiber mats

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ABSTRACT

Nanoporous poly(vinyl alcohol) (PVA) nanofiber mats prepared by means of electrospinning have been used for the immobilization of palladium catalyst. Thermal treatment of the palladium-loaded PVA nanofiber mats results in the cross-linking of the matrix PVA molecules as well as the reduction of the divalent palladium (Pd²⁺) into zerovalent palladium (Pd⁰) species. The palladium oxidation states were examined by X-ray photoelectron spectroscopic (XPS) analysis. The PVA nanofiber morphology was characterized by scanning electron microscopy (SEM). The catalytic activity and recyclability of the prepared heterogeneous palladium catalysts have been evaluated for the Ullmann, Heck–Mizoroki and Sonogashira coupling reactions of aromatic halides. The large structure of the Pd/PVA nanofiber mats can greatly facilitate its separation and recycling, and the high catalytic activity and stability of the prepared Pd/PVA nanofiber mats have been attributed to the chelation of palladium species with the abundant hydroxyl functional groups on the PVA matrix surface area.

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1. Introduction

The importance of palladium catalyst in synthetic organic chemistry can hardly be overestimated because palladium catalysis has become a routine tool for the preparation of fine chemicals and pharmaceutically active compounds in both academic studies and industrial productions [1]. However, the majority of the palladium catalysis is performed in the homogeneous system, in which the catalyst suffers from the difficult separation from the reaction media, nonreusability and deactivation due to aggregation of palladium particles [2]. Moreover for the homogeneous catalysis, the final products are frequently contaminated by residual transition metal at an unacceptable level, which could be difficult to remove, especially for large scale productions of pharmaceuticals where metal contamination is closely monitored [3]. Thus, it is not surprising why relatively few homogeneous catalysis systems have been commercialized [4].

Catalyst reuse can greatly increase the overall productivity and cost effectiveness while minimizing both waste generation and contamination of the metal traces in the final products, resulting in a greener and more sustainable chemical transformation process [5]. But the heterogenization of a homogeneous catalysis will significantly reduce the accessible catalytic centers because the catalytic reactions can take place only on the heterogeneous surface, rather than all catalytic centers are accessible in the homogeneous system. Therefore, the solid matrices are generally fabricated into small fine particles to maximize the surface area to enhance the catalytic activities. However, the separation and recycling of the particulate catalysts from the reaction media are usually a tedious and time-consuming process due to the high pressure drop by filtration.

On the other hand, the palladium leaching is a common problem for the heterogeneous palladium catalysts [6,7]. Surface derivatization of the solid matrices with special ligand functional groups including phosphine and N-heterocyclic carbine could improve the chelation with the transition metal species to minimize the leaching, but the ligand synthesis as well as the surface modification are usually very challenging [2,8,9]. Nevertheless, only few lowleaching and ligand-free heterogeneous palladium catalysts have been reported in the literature [10]. Recently, we have demonstrated that the ground powder of the natural pearl shells is an excellent solid support for the immobilization of the palladium catalyst [11]. The high stability of the heterogeneous palladium catalyst has been attributed to the chelation of palladium species with the abundant hydroxyl and amino functional groups of the shell powder surface area. These results promoted us to explore the inexpensive, non-toxic and biodegradable poly(vinyl alcohol) (PVA) as the supported matrix to immobilize palladium catalyst because PVA has plentiful surface hydroxyl functional groups. To the best of our knowledge, electrospun PVA nanofiber mats have not yet been used for the preparation of the heterogeneous palladium catalysts.

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Fig. 1. Scanning electron microscopic (SEM) images of the electrospun nanofiber mats prepared using different PVA weight concentrations: (a) 3.0%, (b) 5.0%, (c) 6.0% and (d) 7.0%.

2. Results and discussion

2.1. Preparation and characterization of heterogeneous Pd/PVA nanofiber mats

Although PVA can strongly chelate with the transition metal species because of the numerous surface hydroxyl functional groups, it is very difficult to fabricate it into suitable solid matrix with a large surface area due to the semi-crystalline structure and high melting point (230 °C) [12]. Electrospinning is a versatile polymer processing technique using a high electrical charge to draw ultrafine nanofibers with diameters in the nanometer to submicrometer range. The resultant porous nanofiber mats have very high surface area to volume ratios, resulting in a wide range of applications such as in water purifications, medical tissue repair, drug delivery, etc. [13,14]. The large structure of the nanofiber mats supported catalyst also has the advantage of much easier separation and recycling over the fine particles supported catalyst from the reaction media.

A series of PVA samples with different concentrations have been prepared to examine the nanofiber morphology by the optimization of the electrospinning conditions including electrical voltage, tip-target distance, flow rate and polymer substrate concentration [12,15]. The scanning electron microscopy (SEM) images of the yielded PVA nanofiber mats are shown in Fig. 1. Spindle-like beads (Fig. 1a and b) were observed for the nanofiber mats prepared using 3.0 and 5.0% of the PVA weight concentrations. The bead formation could be attributed to the inefficient chain entanglement at relatively low PVA substrate concentrations [16]. Droplets were obtained instead of nanofiber mats regardless of the electrospinning voltage when over 8.0% PVA weight concentration was used. Interestingly, a uniform and bead-free structure of the nanofiber mats could be achieved when the PVA weight concentration was at 6.0 or 7.0% [17]. The PVA weight (6.0%) concentration was chosen for the subsequent preparation of the PVA nanofiber mats

because the nanofiber diameter $(148 \pm 71 \text{ nm})$ of the mats obtained using 6.0% PVA weight concentration is significantly smaller than that $(504 \pm 290 \text{ nm})$ obtained using 7.0% PVA weight concentration (Fig. 1).

Palladium deposition was achieved by dissolution of PVA polymer substrate in disodium tetrachloropalladate (Na₂PdCl₄) acetic acid solution, followed by electrospinning. Many experimental methods have been developed for reduction of the divalent Pd²⁺ precatalyst into zerovalent palladium (Pd⁰) active species in literature [18]. We have shown that the divalent Pd²⁺ species can be readily reduced into the active Pd⁰ species in alcoholic media [19]. Thus, we believed that the precatalyst divalent Pd²⁺ species should be reduced by the hydroxyl functional groups of the solid matrix PVA molecules. Indeed, characteristic color change was observed from brown to black during a thermal treatment at the temperature over 150° C. The color change is clearly associated with the formation of the zerovalent palladium (Pd⁰) active species (black), i.e. Pd/PVA nanofiber mats. The reduction of the divalent Pd²⁺ into Pd⁰ species has further been confirmed by the XPS analysis as shown in Fig. 2, which evidently indicates that the thermal treatment decreases the palladium electron binding energy (3d_{5/2} and $3d_{3/2}$) by ~1.1 eV. These observations are consistent with the characteristic electron binding energy shift reported in the literature for the reduction of the divalent palladium into the metallic palladium species [20,21].

The reduction of the divalent Pd^{2+} species must be concomitantly coupled with the oxidation of the PVA matrix molecules. The FT-IR spectra (Fig. 3) indicate that the carbonyl absorption peak at ~1733 cm⁻¹ is significantly increased during the reduction of the divalent Pd^{2+} species into the zerovalent palladium active species, suggesting that some of the PVA hydroxyl groups have been oxidized into the carbonyl functional groups as shown in Scheme 1. X-ray diffraction (XRD) analysis (not shown) indicates that there is no characteristic diffraction peak at 40° for the metallic palladium, suggesting that the zerovalent



Fig. 2. X-ray photoelectron spectra (XPS): (a) precatalyst Na₂PdCl₄/PVA nanofiber mats and (b) Pd/PVA nanofiber mats.



Fig. 3. FT-IR/ATR spectra: (a) PVA nanofiber mats and (b) Pd/PVA nanofiber mats.



palladium metal dispersed on the PVA nanofiber mats has amorphous structure [6].

PVA polymers are generally cross-linked through chemical reactions with bifunctional reagents such as glutaraldehyde [22] or glyoxal [23] to minimize dissolution for the applications in polar solvents because the cross-linking can significantly reduce the intrinsic solubility and dissolution of polymeric materials [22–24]. Interestingly, the PVA molecules were found to be cross-linked during the thermal treatment for the reduction of the precatalyst Na₂PdCl₄/PVA nanofiber mats. The PVA nanofiber mats were still noticeably swollen in dimethyl sulfoxide (DMSO) solution after being treated at 150 °C for 1 h, whereas they were over crosslinked after being treated at 210 °C for 1 h. Thus, the precatalyst Na₂PdCl₄/PVA nanofiber mats were heated at 170 °C for 1 h for the



Fig. 4. Nanofiber diameter distributions for (a) precatalyst Na_2PdCl_4/PVA nanofiber mats and (b) Pd/PVA nanofiber mats.

cross-linking of the PVA nanofiber molecules and the reduction of the divalent Pd^{2+} into zerovalent Pd^0 species.

The SEM images (Fig. S1 of the supplementary material) show that the fiber diameters of the Pd/PVA are considerably smaller than those of the precatalyst Na₂PdCl₄/PVA nanofiber mats. The fiber diameter distributions for the Na₂PdCl₄/PVA and Pd/PVA nanofiber mats can be obtained from their SEM images and the results are summarized in Fig. 4. The shrinking of the mats fiber diameter by the thermal treatment can be attributed to the partial dehydration of the hydroxyl functional groups among the PVA polymer chains, resulting in the cross-linking of the supplementary material) shows that the weight loss from the dehydration is not significant up to 250 °C for the palladium-loaded PVA nanofiber mats, indicating that the oxidative degradation of the applications performed in this study.

2.2. Reductive homocoupling of aromatic iodides as catalyzed by Pd/PVA nanofiber mats

Symmetrical biaryls are important intermediates in organic chemistry, but they are traditionally synthesized by the coppermediated Ullmann reductive homocoupling [25]. The Ullmann reactions generally require drastic reaction conditions such as the high temperatures (over 200 °C) together with the consumption of a stoichiometric amount of copper metal into toxic copper halide waste [26]. The palladium catalyzed reductive homocoupling has been demonstrated as a much more convenient and efficient method for the biaryl synthesis [27].

The Pd/PVA heterogeneous catalyst was first tested and optimized for the model reductive homocoupling of iodobenzene in DMSO solution. The initial reaction conditions were adapted from the parameters optimized for the homogeneous and heterogeneous catalytic systems [19,28]. While cesium fluoride (CsF) is the most efficient base [19,28], potassium acetate (KOAc) is the most efficient base among the screened bases including CsF, acetates, carbonates, bicarbonates and hydroxides for the Pd/PVA nanofiber mats catalysis in DMSO solution.

Several representative solvent systems have been examined for the Pd/PVA nanofiber mats catalyzed homocoupling of iodobenzene and the results are summarized in Table 1. Surprisingly, no biphenyl product was observed when carried out in the aqueous solution (entry 1). Entry 6 of Table 1 shows that the reductive homocoupling of iodobenzene gives the complete conversion of

Table 1

Solvent effects on the Pd/PVA nanofiber mats catalyzed reductive homocoupling of iodobenzene^a.

Entry	Solvent	Conversion ^b (%)	Yield (%) ^b	
			Biphenyl	Benzene
1	Water ^c	~0	~0	~0
2	Xylene	0.82	0.8	0
3	Ethanol	19.7	5.8	13.9
4	3-Pentanol	54.6	2.8	51.8
5	DMF	29.5	27.6	1.7
6	DMSO	100	87.0	10.9
7	Xylene + DMSO ^d	100	91.0	9.0

^a Reaction conditions: 1.0 mmol iodobenzene, 0.05 mmol Pd/PVA nanofiber mats catalyst, 7.5 mmol potassium acetate in 5.0 ml of solvent at $110 \degree$ C for 7.0 h unless otherwise indicated.

^b lodobenzene conversion, biphenyl and benzene yields were determined from the GC/MS measurements based on the amount of iodobenzene.

^c At 100 °C for 10 h.

^d Volume ratio of xylene and DMSO is 1:1.

Table 2

Pd/PVA nanofiber mats catalyzed reductive homocoupling of various substituted aromatic halides^a.



1	C ₆ H ₅ I	94.0
2	2-CH ₃ C ₆ H ₄ I	80.8
3	4-CH ₃ C ₆ H ₄ I	93.3
4	2-ClC ₆ H ₄ I	91.4
5	3-ClC ₆ H ₄ I	90.1
6	4-FC ₆ H ₄ I	95.3
7	$2-IC_5H_4N^c$	97.6
8	C_6H_5Br	17.4 ^d

^a Reaction conditions: 1.0 mmol aromatic halide, 0.05 mmol Pd/PVA nanofiber mats, 7.5 mmol potassium acetate in 5.0 ml of DMSO/xylene (v:v=1:1) at $110 \degree$ C in 7 h. unless otherwise indicated.

^b Biaryl yields were determined from the GC/MS measurements based on the amount of aromatic halide substrate.

^c 2-Iodopyridine.

^d In 40 h.

iodobenzene and 87% biphenyl yield in DMSO in about 7 h, whereas the biphenyl yield is only 27% when carried out in DMF under the same conditions (entry 5). Dehalogenation is the primary pathway for the Pd/PVA nanofiber mats catalyzed reduction of iodobenzene in ethanol (entry 3) and 3-pentanol (entry 4), which are similar to the results observed for the homogeneous palladium catalysis [19]. Although the biphenyl product is negligible in xylene (entry 2), addition of xylene into DMSO solution does not suppress the homocoupling pathway, but instead slightly improves it (entry 7). These observations are further supported by the time-courses of the biphenyl and benzene yields as shown in Fig. S3 of the supplementary material. Addition of the less polar xylene could also reduce the swelling of the PVA nanofiber mats especially for the relatively slow homocoupling reactions in DMSO.

Table 2 summarizes that the optimized Pd/PVA nanofiber mat catalysis is also applicable to other aromatic iodides although the homocoupling biphenyl yield is very low for bromobenzene. The new palladium catalytic system works well for the reductive homocoupling of the aromatic iodides bearing either an electron donating or an electron accepting substituent. The relatively lower homocoupling yield of 2-methyliodobeneze could be attributed to the steric hindrance of the *o*-methyl group (entry 2), but the steric effects seem to be less severe for the relatively small chlorine (entry 4). Excellent biaryl yield was also obtained for the Pd/PVA nanofiber mats catalyzed reductive homocoupling of 2-iodopyridine (entry 7).

Table 3

Heck-Mizoroki cross-coupling reactions of various aromatic halides with different acrylates^a.

Entry Aryl halides Vinylic substrates Time (h) Yield (%) (<i>cis:tra</i>	\sim	
Entry Aryl halides Vinylic substrates Time (h) Yield (%) (cis:tra		
	ans) ^b	
1 C ₆ H ₅ I <i>n</i> -Butyl acrylate 2.0 97.5 (0.4:99.6)		
2 3-FC ₆ H ₄ I <i>n</i> -Butyl acrylate 2.0 94.6 (2.5:97.5)		
3 4-FC ₆ H ₄ I <i>n</i> -Butyl acrylate 2.0 97.0 (1.2:98.8)		
4 4-BrC ₆ H ₄ I <i>n</i> -Butyl acrylate 2.0 97.5 (0.2:99.8)		
5 4-CH ₃ C ₆ H ₄ I <i>n</i> -Butyl acrylate 4.0 94.5 (0.5:99.5)		
6 C ₆ H ₅ I Methyl acrylate 4.0 97.1 (0.3:99.7)		
7 C ₆ H ₅ Br <i>n</i> -Butyl acrylate 2.0 1.6 (0:100)		
36 14.3 (0:100)		

^a Reaction conditions: 1.0 mmol aromatic halide, 2.0 mmol acrylate, 0.02 mmol Pd/PVA nanofiber mats, 3.0 mmol potassium acetate in 5.0 ml DMSO at 110 °C.

^b Cross-coupling yields were determined from the GC/MS measurements based on the amount of aromatic halide substrate.

2.3. Heck–Mizoroki cross-coupling as catalyzed by Pd/PVA nanofiber mats

Heck–Mizoroki reaction is the palladium catalyzed crosscoupling of aromatic halides with alkenes, which allows an *E*-selective carbon-carbon bond formation between sp^2 hybridized carbons [29]. The reaction has been considered as one of the most powerful and straightforward methods for the construction of the sp^2-sp^2 carbon–carbon bonds [30]. The exceptional attractiveness of the Heck–Mizoroki reaction for the organic chemical synthesis of substituted alkenes has stimulated tremendous interest in searching for more environmentally benign and ligand-free heterogeneous catalysts [31].

The prepared Pd/PVA nanofiber mats have been examined to catalyze the Heck–Mizoroki cross-coupling reactions of several representative aromatic halides with *n*-butyl acrylate or methyl acrylate in DMSO solution at 110 °C. Examination of Table 3 shows that the Pd/PVA nanofiber mats catalysis affords excellent cross-coupling yields (>95%) and selectivity (>97%, *trans*-products) in 2–4 h, indicating that the prepared Pd/PVA nanofiber mats are an efficient, selective and specific heterogeneous catalyst for the Heck–Mizoroki cross-coupling reactions of aromatic iodides with acrylates. However, the related catalytic activity is relatively low for the cross-coupling reaction of bromobenzene (entry 7 of Table 3).

2.4. Sonogashira cross-coupling as catalyzed by Pd/PVA nanofiber mats

In view of the high catalytic activity and selectivity for the Heck-Mizoroki cross-coupling with aromatic iodides (Table 3), we extended our interests to explore the Pd/PVA nanofiber mats to catalyze the Sonogashira cross-coupling because both the Heck-Mizoroki and Sonogashira reactions involve the palladium catalyzed cross-coupling of aromatic halides with unsaturated hydrocarbon. The Sonogashira reaction is known as the most powerful and straightforward method for the construction of the sp²-sp carbon-carbon bonds [32]. The prepared Pd/PVA nanofiber mats have been examined for the Sonogashira reaction of phenylacetylene with several representative aromatic halides. Although the cross-coupling yield is relatively low for bromobenzene (entry 6 of Table 4), the Pd/PVA nanofiber mats catalyzed cross-coupling reactions afford excellent cross-coupling yields (88-99%) for the aromatic iodides in DMSO solution, indicating that the prepared Pd/PVA nanofiber mats are also an efficient heterogeneous catalyst for the Sonogashira cross-coupling reaction of aromatic iodides.

Table 4

Pd/PVA nanofiber mats catalyzed reductive Sonogashira cross-coupling reactions of various aromatic halides with phenylacetylene^a.



^a Reaction conditions: 1.0 mmol aromatic halide, 1.2 mmol phenylacetylene, 7.5 mmol potassium acetate, 0.02 mmol Pd/PVA nanofiber mats in 5.0 ml DMSO at 110 °C in 4 h, unless otherwise indicates.

^b Cross-coupling yields were determined from the GC/MS measurements based on the amount of aromatic halide substrate.

^c In 9 h.

2.5. Separation and recyclability of the Pd/PVA nanofiber mats catalyst

The heterogeneous catalysts have the advantage for their relatively easy separation and recycle of the expensive transitional metals. The prepared Pd/PVA nanofiber mats not only have large structure for easier separation, but also have excellent stability as shown for the Ullmann homocoupling and Heck-Mizoroki cross-coupling reactions. The catalytic activities of the recovered Pd/PVA nanofiber mats retained over five cycles for the Ullmann homocoupling of iodobenzene. Even more recycling times without loss of the catalytic activities have been obtained for the Pd/PVA nanofiber mats catalyzed Heck-Mizoroki cross-coupling of iodobenzene with *n*-butyl acrylate as shown in Fig. 5. The palladium contents have been determined to be 0.276 ± 0.003 , 0.223 ± 0.001 and 0.164 ± 0.002 g for each gram of the fresh catalyst, the recovered catalysts after three and six recycles respectively, indicating that the average palladium leaching is about 6.5% for each cycle of application. These results clearly demonstrate that the palladium leaching from the Pd/PVA nanofiber mats is not significant during the reaction and washing process. The remarkable stability of the prepared Pd/PVA nanofiber mats must be associated with the



Fig. 5. Dependence of Heck–Mizoroki cross-coupling yields with the recycled numbers for the Pd/PVA nanofiber mats catalyzed cross-coupling of iodobenzene with *n*-butyl acrylate. Reaction conditions: 1.0 mmol iodobenzene, 2.0 mmol acrylate, 0.02 mmol Pd/PVA nanofiber mats, 3.0 mmol potassium acetate in 5.0 ml DMSO at 110° C for 2.0 h.

Table 5

Heck–Mizoroki cross-coupling reactions of iodobenzene with *n*-butyl acrylate as catalyzed by different palladium catalysts^a.

Entry	Palladium catalyst	Yield ^b (%)
1	PVA/PdCl ₂ nanofiber mats	93.4
2	PdCl ₂	73.4
3	Pd(PPh ₃) ₂ Cl ₂	93.2
4	Pd(dppf)Cl ₂	99.0

^a Reaction conditions: 1.0 mmol iodobenzene, 2.0 mmol *n*-butyl acrylate, 3.0 mmol potassium acetate and 0.02 mmol palladium catalyst in 5.0 ml DMSO at 110 °C for 0.5 h.

 $^{\rm b}$ Cross-coupling yields as determined from the GC/MS measurements based on the amount of iodobenzene.

chelation of palladium species with the abundant hydroxyl groups on the PVA matrix surface.

2.6. Comparison of heterogeneous and homogeneous palladium catalytic activities

Heterogeneous catalysis is generally less active than the corresponding homogeneous one primarily due to the limited surface-bound catalytic centers [30]. Several commonly used and commercially available homogeneous palladium catalysts together with the prepared Pd/PVA nanofiber mats have been tested to catalyze the Heck–Mizoroki cross-coupling reaction of iodobenzene with *n*-butyl acrylate under the same reaction conditions. Examination of Table 5 shows that the PVA nanofiber mats supported palladium catalyst has comparable catalytic activity with these commonly used homogeneous palladium catalysts, suggesting that the chelation of palladium species with the abundant hydroxyl functional groups on the PVA matrix surface may enhance the catalytic activities to compensate the less surface-bound catalytic centers.

3. Conclusions

In summary, a highly active and recyclable heterogeneous palladium catalyst (Pd/PVA nanofiber mats) has been prepared by the immobilization of palladium species onto the cross-linked poly(vinyl alcohol) nanofiber mats, which are not only insoluble in most organic solvents and water, but can also function as a reducing agent and stabilizer. The prepared Pd/PVA nanofiber mats have been demonstrated as an efficient and selective heterogeneous catalyst for the reductive Ullmann homocoupling, the Heck-Mizoroki cross-coupling and Sonogashira cross-coupling of aromatic halides. The large structure of the nanofiber mats enables easier separation and recycling of the heterogeneous catalyst than the fine powders supported catalysts from the reaction media. The remarkable stability and recyclability of the prepared Pd/PVA nanofiber mats have been attributed to the chelation of palladium species with the abundant hydroxyl functional groups on the PVA matrix surface. The high catalytic activities combined with the easier separation and recycle make this unique environmentally benign heterogeneous palladium catalyst to be attractive for large industrial-scale applications.

4. Experimental

4.1. General remarks

Poly(vinyl alcohol) (M_n = 77,000) and xylene were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Palladium catalysts were supplied by Shanghai D&R Fine Chemical Company (Shanghai, China). Acetic acid and DMSO were obtained from Guangdong Xilong Chemical Company (Guangdong, China). All solvents and chemicals are analytical grade or the best grade available and used without further purification. The quantitative analysis was performed on an Agilent GC/MS instrument with a programmable split/splitless injector, which was set at 270 °C. The oven-temperature was initially started at 140 °C and then ramped to 270 °C at a rate of 10 °C/min, and maintained for 2.0 min at each step. NMR spectra were recorded in CDCl₃ (Bruker, AVANCE III 400 MHz, Switzerland) and the proton chemical shifts are reported in ppm relative to TMS as the internal reference. Multiplicities are reported as: singlet (s), doublet (d), and multiplet (m). The morphologies of the electrospun PVA nanofiber mats were recorded on a scanning electron microscope (Jeol, jsm-6360lv, Japan). Samples for the SEM analysis were first coated with a 2-3 nm layer of gold to make them conductive. The nanofiber diameter was determined from the SEM micrographs. FT-IR/ATR spectra were recorded on a FT-IR spectrometer (Nicolet, Nexus-470, USA) with the accessories of attenuated total reflection. XPS measurements were carried out at room temperature and relative elemental ratios on the sample surface were determined on an Al/Mg anode with a power of 250 W (VG, ESCALAB, UK). TGA was performed using a thermogravimetric analyzer (Mettler, SDTA851, Switzerland) from 20 to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere.

4.2. Preparation of Pd-Loaded PVA nanofiber mats

Appropriate amount of PVA polymer substrate was suspended in a 13.0 M acetic acid aqueous solution, which was allowed to stir at room temperature until complete dissolution. The resultant solution was then slowly mixed with the Na₂PdCl₄ solution, which was prepared with 4.2 g of PdCl₂ (23.5 mmol) and 4.0 g of NaCl (68.4 mmol) in 13.0 M acetic acid. The final solution was subjected to electrospinning for the PVA nanofiber mats through a syringe (20 ml) with a blunt-end capillary (1.1 mm ID) as spinneret at a flow rate of 1.0 ml/min. A voltage of 21 kV (Tianjin Dongwen High-Voltage Power Supply Company, Tianjin, China) was applied with a distance of 12 cm between the syringe tip and the collector. The resulting nanofiber mats were dried at room temperature under vacuum for 12 h. The cross-linking of the electrospun PVA nanofiber mats was optimized at the temperature of 150, 170 and 210 °C for 1 h under an argon atmosphere.

4.3. General procedure for the Pd/PVA nanofiber mats catalyzed Ullmann-type reductive homocoupling

To 5.0 ml of a given solvent in a 20 ml round bottom flask with a magnetic stir bar, were added with aromatic halide (1.0 mmol), Pd/PVA nanofiber mats (0.05 mmol) and base (7.5 mmol). The resulting solution was allowed to stir at 110 °C and the reaction progress was monitored by TLC and/or GC/MS analysis. The reaction mixture was cooled down to room temperature after completion, and then quenched with 10 ml of water and extracted three times with ethyl acetate (3×20 ml). The combined organic layer was washed with water, saturated brine, and then dried over anhydrous Na₂SO₄. Solvent was removed under a reduced pressure. The residue was purified to afford the homocoupling product by silica gel chromatography with a mixture of petroleum ether and ethyl acetate. All of the homocoupling products were characterized by ¹H NMR spectroscopy and mass spectroscopy.

4.4. General procedure for the Pd/PVA nanofiber mats catalyzed Heck–Mizoroki and Sonogashira cross-couplings

To 5.0 ml DMSO solution in a 20 ml round bottom flask with a magnetic stir bar, were added with aromatic halide

(1.0 mmol), acrylate (2.0 mmol) or phenylacetylene (1.2 mmol), Pd/PVA nanofiber mats (0.02 mmol) and an appropriate amount of potassium acetate base. The resulting solution was allowed to stir at 110 °C and the reaction progress was monitored by TLC and/or GC/MS analysis. The reaction mixture was cooled down to room temperature after completion, and then quenched with 10 ml of water and extracted three times with ethyl acetate (3×20 ml). The combined organic layer was washed with water, saturated brine, and then dried over anhydrous Na₂SO₄. Solvent was removed under a reduced pressure. The residue was purified to afford the cross-coupling product by silica gel chromatography with a mixture of petroleum ether and ethyl acetate. All of the cross-coupling products were characterized by ¹H NMR spectroscopy and mass spectroscopy.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.11.018.

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