

RAPID COMMUNICATION

A facile approach to preparing palladium nanoparticles-embedded polyvinylpyrrolidone (PVP) heterogeneous hybrid nanofibers mats by electrospinning

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(Received 13 April 2013 • accepted 10 September 2013)

Abstract—Well-dispersed palladium nanoparticles (Pd NPs) were prepared under the condition that trisodium citrate was the reduction agent and polyvinylpyrrolidone (PVP) was the stabilizing agent via sol-gel process. By making good use of the advanced electrospinning technology we obtained Pd NPs/PVP composite nanofibers films. Optical properties were examined by UV-visible absorbance spectra (UV-vis) and Fourier transform infrared spectroscopy (FTIR). The morphology and distribution of Pd NPs in/on PVP matrix were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). The results showed that Pd NPs presented as spherical spots and distributed in/on PVP nanofibers uniformly; their diameter was 4-10 nm and decreased with the increase of PVP. The as-prepared Pd NPs/PVP hybrid mats possess catalytic activity, stability and reusability, as verified by performance in Heck reaction.

Key words: Sol-gel Process, Pd Nanoparticles, Electrospinning, Hybrid Nanofibers

INTRODUCTION

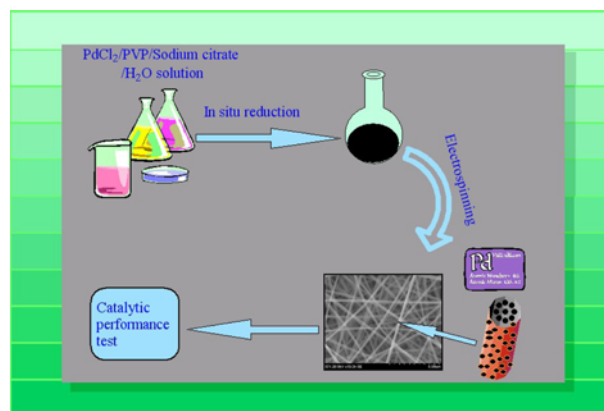
Nowadays, noble metal nanoparticles have not been ignored due to their fascinating physical and chemical properties. They have been flexibly constructed with the change of size and shape which influence the range of their applications deeply. They are ideal candidates in catalytic, photonics, information storage, fuel cell and life sciences fields [1-3].

Palladium nanoparticles (Pd NPs), palladium or its compounds can serve as good active center for cracking, hydrogenation and dehydrogenation as well as a large of reactions that can build carbon-carbon bonds such as Heck or Suzuki reactions. These coupling reactions are receiving unprecedented interest for their high catalytic activity, excellent selectivity and mild reaction conditions. In modern society, they can contribute in numerous ways, for example, minute organic synthesis, catalytic converters which convert harmful gases, petrochemical industry and so on [4-7]. There are many ways to acquire palladium nanoparticles, for example, chemical precipitation, microemulsion, ultrasonic, sol-gel, impregnation methods etc. In general, alcohols, glycols, polyacid, ascorbic acid, sodium borohydride and hydrazine can act as the reductant agent to prepare palladium nanoparticles [8-14].

In the 1990s, electrospinning technology came into its golden age. With the application of nanomaterials, nanofiber technology was put forward. So far, electrospinning technology has been proven to be a simple, versatile and cost-effective approach for fabricating long, continuous fibers and the only effective way to obtain continuous nanometer fiber productions. Nanofibers possess many exciting characteristics such as large surface area to volume ratio, excellent flexibility and superior mechanical performance. They are applied in

sensors, filter, protective materials in aerospace etc [15-18]. Among these, nanocomposite materials are the most promising area in the novel materials research direction. Many researchers pay attention to the preparation of inorganic/organic nanometer composite materials. The preparation of functional composite nanofibers, nanoparticles such as the noble metals, inorganic oxides and semiconductor are added to the polymer matrices. The stabilization strongly depends on the properties of polymer matrices. A versatile polymer has good mechanical strength, thermal stability and high dielectric constant [19-22].

It is well-known that polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), polycarbonate (PC) are the candidates in many potential applications, such as carriers. Demirv [23] prepared catalytic palladium nanoparticles on electrospun copolymers of acrylonitrile and acrylic acid (PAN-AA) mats via reduction of PdCl_2 with hydrazine. Gniewek prepared Pd/PVP colloid (stabilized with polyvinylpyrrolidone) with a diameter of 19.8 nm in $[\text{Bu}_4\text{N}]^+\text{Br}^-$ medium



Scheme 1. The schematic illustration of the preparation of Pd NPs/PVP composite nanofibers films catalyst.

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catalyzed Heck coupling of bromobenzene with butyl acrylate and methoxycarbonylation of iodobenzene reactions. Valmikanathan [24] introduced the synthesis of palladium (Pd)/polycarbonate (PC) nanocomposites as well as their morphological, optical, thermal and electrical properties. In Francis [25] silver (Ag) nanoparticles (3 nm) were synthesized in nylon matrix by electrospinning of nylon-6/Ag solution in 2, 2, 2-trifluoroethanol. But almost no reports pay attention to the preparation of Pd NPs/PVP hybrid nanofibers mats by electrospinning.

Hence, we obtained Pd NPs/PVP nanofibers films through in situ reduction and electrospinning technologies. Trisodium citrate was the reduction agent; PVP served as the stabilizing agent as well as matrix of nanofibers films-supported Pd NPs. The procedure of this experiment is in Scheme 1 of the supplementary materials.

EXPERIMENTAL

1. Reagents and Facilities

All the chemicals this experiment were used without further purification. Palladium chloride (PdCl_2 , AR), Iodobenzene ($\text{C}_6\text{H}_5\text{I}$, CP, 97%), N-butyl acrylate ($\text{C}_7\text{H}_{12}\text{O}_2$, CP, 98%) and Triethylamine ($\text{C}_6\text{H}_{15}\text{N}$, AR, 99%) were purchased from Sinopharm. Polyvinyl Pyrrolidone (PVP, $M_w=90,000$) was purchased from Sanland-chem International Inc. Trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, AR, 99.0%) was purchased from Tianjin Nankai chemical plant. Absolute ethyl alcohol ($\text{C}_2\text{H}_6\text{O}$, AR, 99.7%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. N, N-Dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, AR, 99.5%) was purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd.

UV-visible absorbance spectra (UV3150, UV-vis, Shimadzu Corporation); Fourier transform infrared spectroscopy (670, FTIR, Thermo Nicolet Corporation); transmission electron microscope (JEM-2010, TEM, JEOL); scanning electron microscope (S-3400, SEM, Hitachi Ltd.); gas chromatograph (7890A, GC, Agilent); gas chromatography-mass spectrometry (5975C, GC-MS, Agilent).

2. The Preparation of Nanopalladium Sol

In this experiment, all the glassware was strictly cleaned before experiment. The preparation process contained three steps, taking PVP and palladium chloride at mole ratio of 10 : 1 as an example. PVP (0.2 g) was dissolved in two grams purity water and intensively stirred 24 hours. Trisodium citrate (0.75 g) was also dissolved in purity water. Next, we mingled PVP aqueous solution with trisodium citrate aqueous solution into 50 ml 3-neck flask, under the protection of nitrogen, stirred rapidly and heated at 95 °C until boiling, then palladium chloride solution (26.6 g, 0.12% mass fraction) was added to this reaction system, and heated for several hours.

Reaction procedure was examined by UV-vis. After about 16 hours, UV-vis spectra showed all the bivalent palladium shifted to the zerovalent palladium, the color of solution ranged from bright

yellow to representative black. Finally, nanopalladium sol naturally cooled to room temperature.

3. Acquired Pd NPs/PVP Nanofibers Films by Electrospinning

Electrospinning is the most important way to obtain nanofibers and most hopeful for realizing the commercial production of nanofibers. By means of high voltage, in the process of the electrospinning the polymer solution or melt overcomes surface tension to form a jet trickle, at the same time, solvent evaporating, superfine nanofibers are prepared.

We removed some water of palladium sol and replenished a certain amount of PVP and ethanol solvent to palladium sol; it aimed for the percentage of PVP in this solution above 10% so that we could prepare Pd NPs/PVP nanofibers films by electrospinning. Molar ratio of Pd NPs and PVP accordingly declined to half of the original. Then, the Pd NPs/PVP sol was contained in a dropper which was twined by copper ring. The copper ring was connected to a high-voltage generator; the aluminum foil was connected to the negative electrode as well as the collector. We took advantage of 15 kV voltage and 15 cm distance from the tip of dropper to collector to obtain ultrafine black Pd NPs/PVP nanofibers films.

4. Characterization

UV-visible absorbance spectra were conducted to detect the presence of zerovalent palladium with a variable wavelength from 190 to

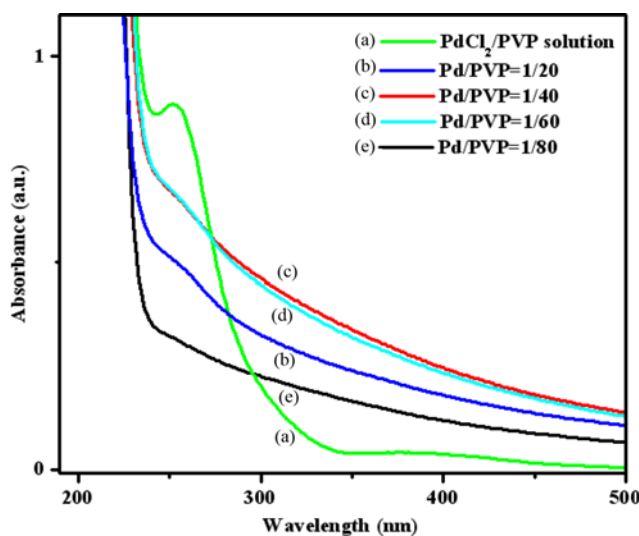


Fig. 1. UV-visible absorbance spectra images: (a) PdCl_2 /PVP solution. (b) The molar ratio of PVP to palladium chloride was 20 : 1. (c) The molar ratio of PVP to palladium chloride was 40 : 1. (d) The molar ratio of PVP to palladium chloride was 60 : 1. (e) The molar ratio of PVP to palladium chloride was 80 : 1.

Table 1. The experimental data of in situ reduction process

Sample	Sodium citrate (g)	Distilled water (g)	PdCl_2 (g)	PVP (g)	Reaction time (h)	$n_{\text{PVP}} : n_{\text{PdCl}_2}$
1	0.75	6	0.03192	0.4	16	20
2	0.75	6	0.03192	0.8	7	40
3	0.75	6	0.03192	0.12	6	60
4	0.75	6	0.03192	0.16	5	80

500 nm. We used a transmission electron microscope (TEM) to observe the shape, distribution and crystal structure of palladium nanoparticles on/in PVP nanofibers by electrospinning the samples on carbon-coated copper grids. A scanning electron microscope (SEM) characterized the morphology of Pd NPs/PVP nanofibers films which

were prepared on aluminum foil through electrospinning technology. Fourier transform infrared spectroscopy (FTIR) was used to examine the change of functional groups structure in the reaction.

5. The Study of Catalytic Performance

In a typical procedure, 10 ml N, N-Dimethyl Formamide (DMF),

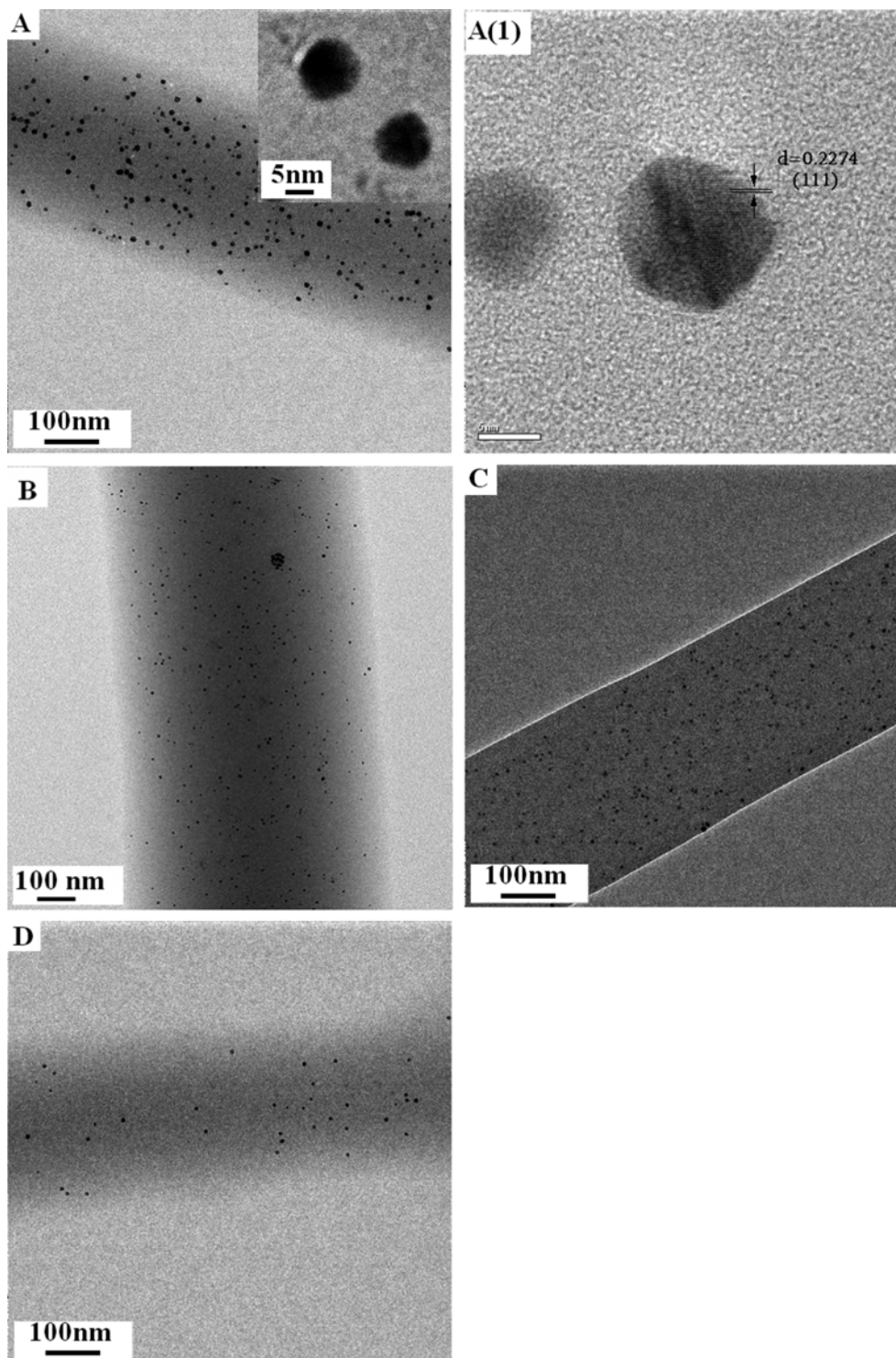


Fig. 2. Transmission electron microscope images of Pd NPs/PVP composite nanofibers: (a) the molar ratio of PVP to palladium chloride was 20 : 1. A (1) the high-resolution TEM (HRTEM) analysis of Pd NPs/PVP composite nanofibers, PVP and palladium chloride at mole ratio of 20 : 1; (b) The molar ratio of PVP to palladium chloride was 40 : 1. (c) The molar ratio of PVP to palladium chloride was 60 : 1. (d) The molar ratio of PVP to palladium chloride was 80 : 1.

0.408 g iodobenzene, 0.5464 g triethylamine and 0.22 g Pd NPs/PVP nanofibers films catalyst (It had been crosslinked 5 hours in oven at 150 °C, PVP and palladium chloride at mole ratio of 20 : 1) were added simultaneously into a 50 ml round bottom flask, intensively stirred. After 15 min, 0.3845 g n-butyl acrylate was added to this system, under the protection of nitrogen, heated at 125 °C. After 24 hours, the reaction was terminated and cooled to room temperature; products were examined by 7890A Gas Chromatograph (GC), 5975C Gas Chromatography-Mass Spectrometry (GC-MS), chromatographic condition; the temperature of injection port and detector was 220 °C; the temperature of oven adopted temperature programming, the highest temperature was 220 °C; chromatographic column was J&W 113-3032, SE-30; every time sample volume was 0.3 μ L.

The catalyst was filtered and separated easily, washed thoroughly with absolute alcohol and distilled water three times and dried below 50 °C in an oven; it could be used repeatedly.

RESULTS AND DISCUSSION

By combining sol-gel with electrospinning technologies, we obtained Pd NPs/PVP composite nanofibers films. In this experiment, PVP served as both protecting agent and carrier. The experimental data are shown in Table 1. In this reaction system, bivalent palladium was reduced to zerovalent palladium gradually. A comparison of the UV-vis spectra of samples is displayed in Fig. 1. It shows UV-vis spectra of PdCl_2 /PVP solution and Pd NPs/PVP solution. The mole ratios of PVP to palladium chloride were 20 : 1, 40 : 1, 60 : 1 and 80 : 1, respectively. As shown in Fig. 1, the characteristic absorption peaks of Pd^{2+} or PdCl_4^{2-} at 256 nm and 382 nm vanished in the reaction progress, which revealed that bivalent palladium was reduced to zerovalent palladium completely in the end and the formation of the plasma absorption spectra of the Pd NPs.

Transmission electron microscope images of Pd NPs/PVP composite nanofibers mats are in Fig. 2; The mole ratios of PVP to palladium chloride were 20 : 1 with the high-resolution TEM (HRTEM) analysis A (1), 40 : 1, 60 : 1 and 80 : 1 respectively. The images reveal that palladium nanoparticles were distributed on or embedded in PVP nanofibers evenly in the method of spherical dark spots; the agglomeration of Pd NPs was not obvious; their diameters were 4–10 nm and decreased with the increase of PVP, so the concentration of PVP influenced the size of palladium nanoparticles directly. It was the critical role in this experiment. To further investigate the change trend of nanoparticle size, the statistical analysis of Pd NPs under different molar ratios of PVP to PdCl_2 is shown (Fig. 3). The results show the average particles size of Pd NPs ranged from 5 to 9 nm and decrease gradually with the increase of PVP. It agrees with Fig. 2. Obviously, higher percentage protective agent of PVP led to nanoparticles mutually bonded together; precipitation and bigger nanoparticle size emerged. Besides, we can see the nanoparticles were only one type of facet. They verged to spheroid, which is desirable, particularly for applications in catalysis. At the same time, we realized the atom economy. The high-resolution TEM (HRTEM) analysis, as shown in Fig. 2 A (1), shows the distinct lattice fringes of $d=0.2274$ nm which match with the crystallographic plane of Pd (111) and confirm the existence of zerovalent Palladium further.

Subsequently, we also investigated scanning electron microscope

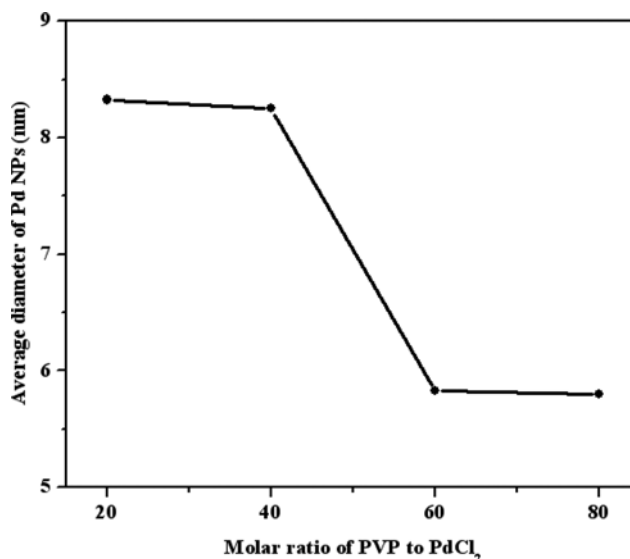


Fig. 3. The size of Pd NPs varied with the molar ratio of PVP to PdCl_2 .

(SEM) images of Pd NPs/PVP composite nanofibers films. Fig. 4 compares with PVP and palladium chloride at mole ratio of 20 : 1, 40 : 1, 60 : 1 and 80 : 1; they revealed that morphology and the diameters of Pd NPs/PVP composite nanofibers mats were about 80–350 nm; obviously, the diameters decrease with the increase of palladium nanoparticles in the solution. The charge density increases with the increase of metal nanoparticles in the solution, so the ejected jets have stronger elongation forces in the electrical field, the outcome as shown in Fig. 4. We prepared ultrafine nanofibers whose morphology was very excellent, equal in size, width, and proportion. The white dots are sodium chloride.

Fig. 5 shows the FTIR of different reaction stages: (a) PdCl_2 /PVP solution (b) Pd NPs/PVP solution. The FTIR pattern shows that there was chemical bonding between the PVP matrix and the Pd NPs taking place in the reaction. The oxygen atoms of PVP have lone pair electrons generating coordinate bond with the empty orbits of outer electrons of Pd^{2+} (or PdCl_4^{2-}); that is, C=O of PVP can bond to Pd forming Pd-O chemical bond. The way of PVP-coated metal nanoparticles can efficiently prevent the aggregation of nanoparticles. So as-prepared Pd NPs are very small, were well-dispersed and stable. Comparing (a) with (b), stretching vibration peaks of carbonyl moved from $1,613\text{ cm}^{-1}$ to $1,621\text{ cm}^{-1}$ during the reduction process of Pd^{2+} species into Pd^0 species. It is confirmed that C=O of PVP can bond to Pd and form Pd-O chemical bond. Because PVP is a kind of water-soluble polymer, the hydroxyl stretching vibration peaks at $3,418\text{ cm}^{-1}$ are very significant in this spectrum image.

The experimental data of Heck reaction are shown in Table 2. The mole ratio of PVP to palladium chloride was 20 : 1. We applied the catalyst so that the molar ratio of PVP to PdCl_2 was 20 in the Heck reaction because this catalyst possessed more excellent morphology and uniform dispersibility relatively, so we selected it as a candidate to prove the catalytic activity in Heck reaction of this kind of catalyst. Pd NPs/PVP composite nanofibers mats were crosslinked 5 hours in oven at 150 Celsius degree before they were applied in the Heck reaction. The results showed the conversion of PhI was

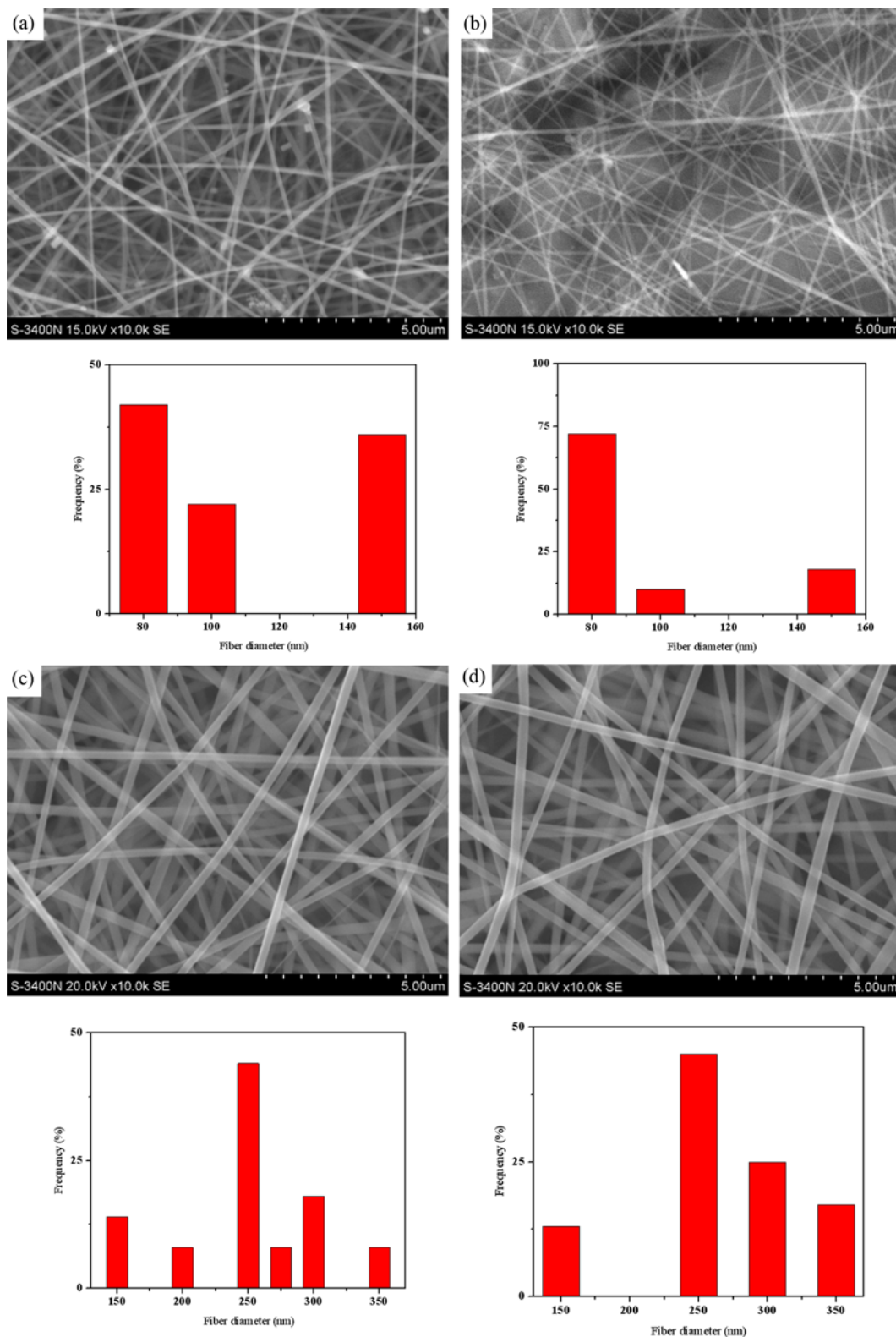


Fig. 4. SEM images of Pd NPs/PVP composite nanofiber films: (a) the molar ratio of PVP to palladium chloride was 20 : 1. (b) The molar ratio of PVP to palladium chloride was 40 : 1. (c) The molar ratio of PVP to palladium chloride was 60 : 1. (d) The molar ratio of PVP to palladium chloride was 80 : 1.

100%; the selectivity of n-butyl cinnamate esters was 42%. This proved that this kind of catalyst possessed catalytic activity, stability and reusability.

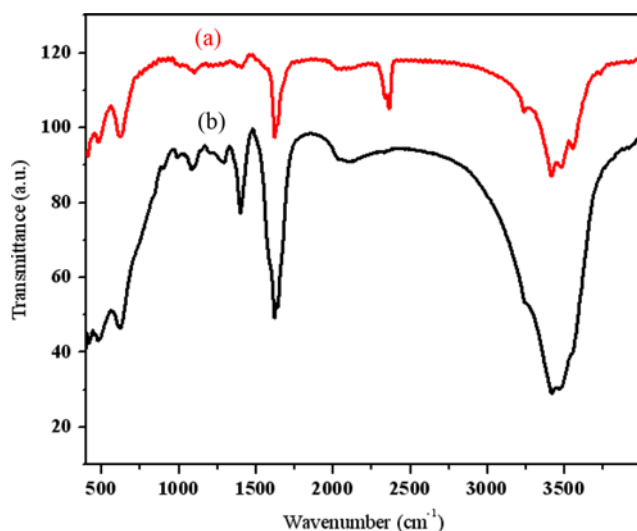
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CONCLUSION

A large number of researchers generally believe that polymeric

Table 2. The experimental data of Heck reaction

Catalyst	PhI (g)	N-butyl acrylate (g)	Base (g)	Reaction time (h)	Catalyst (g)	Conversion rate of PhI (%)	Selectivity of n-butyl cinnamate esters (%)
20 : 1	0.408	0.3845	0.5464	24	0.22	100	42

**Fig. 5. Fourier transform infrared spectroscopy image. (a) PdCl₂/PVP solution; (b) Pd NPs/PVP solution.**

complexes are commonly more stable in catalytic reactions than traditional catalysts because of polymers asymmetric structure and empty coordination structure. In addition, these are the most critical factors of catalyst high activity and easy recycle. We prepared heterogeneous Pd NPs/PVP hybrid nanofibers films which combined in situ with effective electrospinning technologies, then applied them in the Heck reaction. The results revealed that palladium nanoparticles were distributed on/in PVP nanofibers evenly in the method of spherical spots; their diameters were 4-10 nm and decreased with the increase of PVP, and diameters of Pd NPs/PVP composite nanofibers films were 80-350 nm, with the diameters decreasing with the increase of palladium nanoparticles in the solution. At the same time, Pd NPs/PVP composite nanofibers films catalyzed Heck reaction easily under low temperature and pressure with excellent stability and reusability. Palladium particles were anchored to nanofiber membranes, the leaching of palladium also was avoided, and improved the use efficiency of noble metal.

ACKNOWLEDGEMENTS

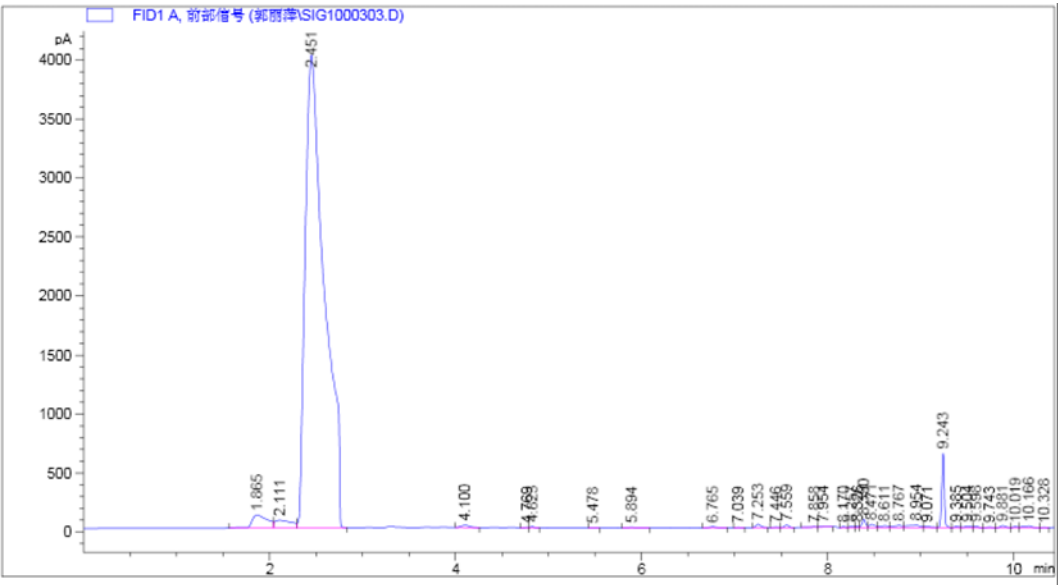
The authors gratefully acknowledge the support of the National Natural Science Foundation of China (21266016), and the Inner Mongolia Natural Science Foundation (2012MS0202).

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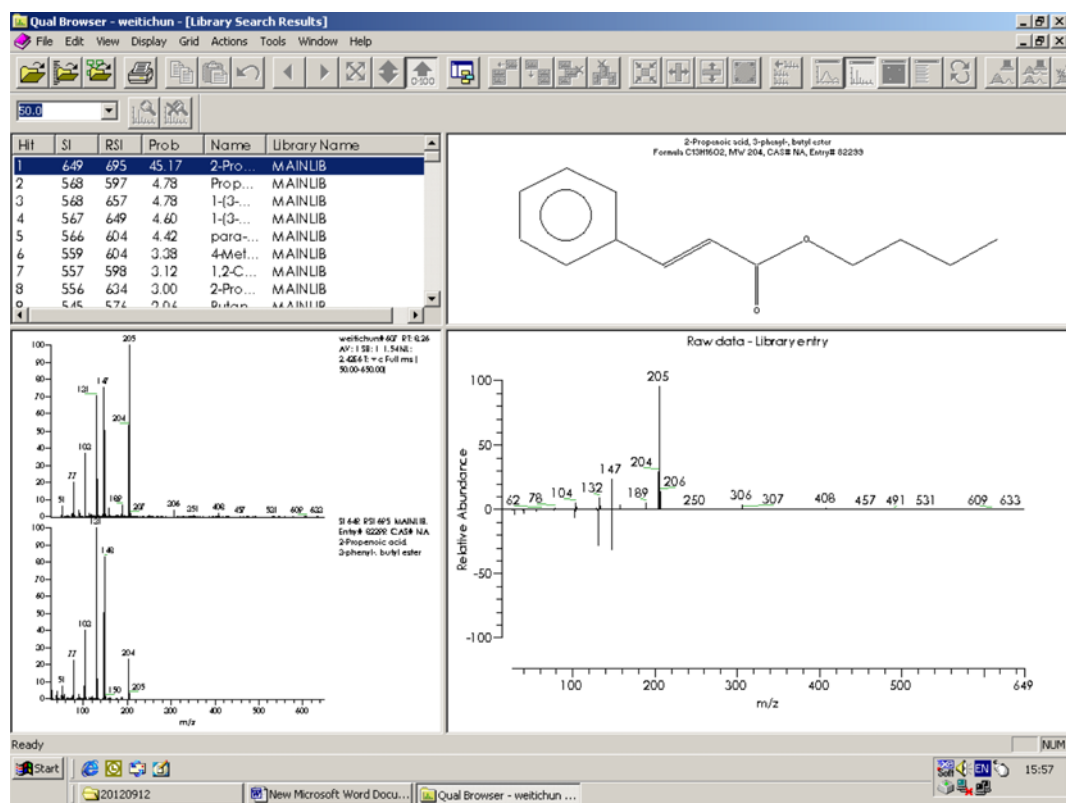
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APPENDIX



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	1.865	BV	0.1611	1320.06995	110.72389	2.12813
2	2.111	VV	0.1605	810.30444	65.44278	1.30632
3	2.451	VB	0.1829	5.70399e4	4012.01611	91.95570
4	4.100	BB	0.0821	109.47511	18.76124	0.17649
5	4.769	BV	0.0461	9.64796	3.39588	0.01555
6	4.823	VB	0.0347	27.94035	11.78149	0.04504
7	5.478	BB	0.0336	2.80374	1.38629	0.00452
8	5.894	BB	0.0965	32.07660	5.46461	0.05171
9	6.765	BB	0.0834	41.53019	7.29378	0.06695
10	7.039	BB	0.0316	4.44842	2.29440	0.00717
11	7.253	BB	0.0524	96.79633	27.29753	0.15605
12	7.446	BV	0.0535	8.72686	2.51157	0.01407
13	7.559	VB	0.0482	64.52232	20.79600	0.10402
14	7.858	BV	0.0615	15.53287	3.32766	0.02504
15	7.954	VB	0.0682	29.25954	6.30165	0.04717
16	8.170	BV	0.0384	15.90787	6.09760	0.02565
17	8.257	VV	0.0453	32.65611	11.11626	0.05265
18	8.326	VV	0.0347	27.21439	11.90125	0.04387
19	8.390	VV	0.0404	184.93472	68.81855	0.29814
20	8.471	VV	0.0628	111.55544	25.64373	0.17984
21	8.611	VV	0.0754	89.42815	15.24597	0.14417
22	8.767	VV	0.0854	123.82893	18.91381	0.19963
23	8.954	VV	0.1088	189.00197	22.31444	0.30470
24	9.071	VV	0.0686	49.74266	10.08327	0.08019
25	9.243	VV	0.0296	1225.81848	632.58295	1.97618
26	9.385	VV	0.0494	37.59859	11.43356	0.06061
27	9.504	VV	0.0649	61.60758	13.33705	0.09932
28	9.598	VV	0.0437	38.21493	13.24620	0.06161
29	9.743	VV	0.0654	19.29076	4.29444	0.03110
30	9.881	VV	0.0611	68.67981	16.66224	0.11072
31	10.019	VV	0.0517	31.58993	9.51610	0.05093
32	10.166	VV	0.0950	98.64159	13.86900	0.15902
33	10.328	VV	0.0442	11.01125	3.99401	0.01775

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