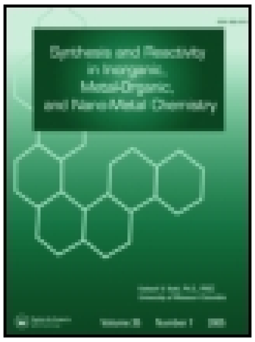


Taylor & Francis
Taylor & Francis Group

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

ISSN: 1553-3174 (Print) 1553-3182 (Online) Journal homepage: http://www.tandfonline.com/loi/lsrt20

Microwave-assisted synthesis of Pd nanoparticles and their catalysis application for Suzuki cross-coupling reactions

Jian Zhang & Xuefeng Bai

To cite this article: Jian Zhang & Xuefeng Bai (2016): Microwave-assisted synthesis of Pd nanoparticles and their catalysis application for Suzuki cross-coupling reactions, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, DOI: 10.1080/15533174.2016.1212228

To link to this article: http://dx.doi.org/10.1080/15533174.2016.1212228

Microwave-assisted synthesis of Pd nanoparticles and their catalysis application for Suzuki cross-coupling reactions

Jian Zhang[a], Xuefeng Bai[a,b]*

[a] School of Chemistry and Material Sciences, Heilongjiang University, Harbin 150080, China

[b] Institute of Petrochemistry, Heilongjiang Academy of Sciences, Harbin 150040, China

*Corresponding author. E-mail: tommybai@126.com

Abstract

Pd nanoparticles (PdNPs) were prepared via microwave-assisted chemical reduction (PdNPs-MW) and a conventional chemical reduction method (PdNPs-C) using ethanol as the reducing agent in the presence of polyvinylpyrrolidone (PVP), respectively. The as-prepared PdNPs were characterized by UV-Vis spectroscopy, TEM, XRD and XPS analysis. The results showed that PdNPs-MW had a uniform structure and narrower size distribution with diameters of 3.6-5.4 nm. An obvious increase in size of the Pd nanoparticles was apparent for PdNPs-C. The PdNPs-MW demonstrated 68.7% yield towards the Suzuki cross-coupling reaction of 4-bromobenzonitrile and phenylboronic acid for 10 min with a higher turnover frequency (TOF) of 41220 h^{-1} compared with the value of PdNPs-C (20580 h^{-1}).

Keywords: microwave-assisted chemical reduction; Pd nanoparticles; Suzuki cross-coupling reactions

1. Introduction

The Suzuki cross-coupling reactions of arylboronic acids and aryl halides provide an effective and attractive synthetic approach to biaryls [1-3], which play an important role as precursors in the synthesis of natural product, fine chemicals, pharmaceuticals, and advanced materials [4-5]. The transition metal palladium has become one of the most available catalysts in organic syntheses, which is mainly applied in cross-coupling reactions for the formation of C–C bonds.

The Pd catalysts used in Suzuki cross-coupling reactions has drawn a great deal of attention in both homogenous catalysis in the presence of different ligands [6-8] and heterogeneous catalysis in which the nanoparticles are supported on solid surfaces (e.g., polymer [9], silica [10], zeolite [11], graphene [12] or activated carbon [13]). The homogeneous catalysis suffers from a number of drawbacks which lie in the preparation of the ligands and separation of the catalyst, despite its remarkable catalytic activity. Alternatively, heterogeneous catalysis allows efficient separation and avoids the preparation of ligands, while the applications of heterogeneous catalysis are also limited due to a poor mass transfer result in a low reaction rates. By contrast, Pd nanoparticles highly dispersed in reaction system result in an excellent mass transfer exhibits high activity. Moreover, a reduction for preparation cost in the absence of ligands is satisfied. Pd nanoparticles used as a catalyst for Suzuki cross-coupling reactions have attracted a growing interest in recent years.

The general trend of increased catalytic activity with the decrease in the particle size is frequently observed [14]. However, there remains challenging for the aggregation and precipitation of nano-sized particles out of solution during the preparation process in the absence of stabilizers. In order to get large quantities of uniform, stable, and monodisperse Pd nanoparticles in nano-scale range. The selection of a suitable stabilizer is an available way to avoid the aggregation of nanoparticles in the preparation process. A common method to prepare metal nanoparticles involves the reduction of metal ions in the presence of stabilizing ligands such as polymers [15], surfactants [16], dendrimers [17], phosphine [18] and thioether [19]. Polyvinylpyrrolidone (PVP) is one of most used polymers for stabilization due to its water-solubility, non-toxic and cheap price [20-21].

The particle size distribution and surface structure of the nanoparticles play an important role in the catalytic activity. Therefore, numerous efforts have been conducted to explore effective and facile synthetic method to get well-defined and uniform-sized metal NPs [22]. In addition to the conventional chemical reduction, microwaves-assisted chemical reduction provides a simple and fast way to prepare nanoparticles. The main advantage of microwave-assisted chemical reduction over other conventional water bath heating is that the reaction system achieves a uniform and rapid heating. Therefore, a more homogeneous nucleation as well as a shorter crystallization time can be obtained, generating metal particles in nanometer size with narrow size distribution and uniform structure.

In this paper, the Pd nanoparticles were prepared by microwave-assisted chemical reduction. The catalytic performances of obtained Pd nanoparticles for the Suzuki cross-coupling reaction were examined and compared with the Pd nanoparticles prepared by a conventional chemical reduction.

2. Materials and methods

2.1 Materials

All commercially available reagents were used without further purification. The $PdCl_2$, NaCl, ethanol and polyvinylpyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co. Ltd. K_2CO_3 was purchased from Tiajin Kermel Chemical Reagent Co. Ltd.

2.2 Characterization

The XRD patterns of the products were recorded with a Bruker D8 advance diffractometer with a Cu Kα (λ=0.15418 nm) radiation at 40 kV and 40 mA. TEM images were obtained using a FEI Tecnai G2 S-TWIN Transmission electron microscope operated at 200 kV. Samples for TEM were prepared by placing a droplet of a colloid suspension in ethanol on a 300-mesh copper grid and allowed to evaporate in air at room temperature. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific ESCALAB 250 using a monochromatic Al KR X-ray. Absorption measurements were carried out on a UV 2450 Shimadzu spectrophotometer. The spectra were recorded at room temperature using a quartz cuvette as sample-holder. Samples for UV-Vis spectroscopy were prepared by diluting the as prepared suspension of Pd nanoparticles with deionized water in order to load the same metal concentration for every sample into the cuvette.

2.3 Preparation of PdNPs with microwave-assisted chemical reduction

In a typical synthesis procedure, a 0.05M Na_2PdCl_4 solution was first prepared by adding 0.0887 g of $PdCl_2$ and 0.0585 g NaCl into 10 mL of deionized water. Then 0.555 g of polyvinylpyrrolidone (PVP) was added into the prepared Na_2PdCl_4 solution under stirring. After 0.5 h, 6 mL of ethanol was injected into solution with further stirring for another 0.5 h. Then the mixture was transferred to the microwave reaction vessel (XinYi MDS-6) equipped with a temperature sensor. The mixture was then subjected to microwave irritation for 2 h at 80°C. After the reaction, a black stable suspension of Pd nanoparticles was obtained. The as-prepared PdNPs was denoted as PdNPs-MW.

2.4 Preparation of PdNPs with conventional chemical reduction

The experiments were performed following the same procedure mentioned above except for the ethanol was slowly added as the reducing agent and the mixture was stirred for an additional 4h heating at 80°C in water bath. The resultant PdNPs was denoted as PdNPs-C.

2.5 General procedure for Suzuki reactions

Aryl halides (4 mmol, 1 eq.) was dissolved in a mixture of 48 mL H_2O: EtOH (1:1) and placed in a three-necked bottle (100 mL). To this were added the phenylboronic acid (6 mmol, 1.5 eq.) and potassium carbonate (8 mmol, 2 eq.). PdNPs catalyst (0.4 mmol‰ Pd) was then added and the mixture was vigorously stirred at 60°C under air atmosphere for 10 min. The reaction mixture (5 mL) was added to 0.2 mol/L sodium hydroxide solution (5 mL) and extracted with ethyl acetate (10 mL). The organic layers were combined, dried in air to give a solid product which was detected in high performance liquid chromatograph (HPLC).

3. Results and discussion

The progression of the reaction and forming of the PdNPs-MW and PdNPs-C are recorded by the UV-vis spectrum, respectively. As shown in Fig. 1, a strong characteristic absorption peak at around 420 nm which is attributed to the Pd (II) ions in the absence of reducing agent. With the increase of reduction time, the intensity of the absorption peak turns weak and the yellow color of Pd (II) solution gradually changed into black indicating the forming of Pd (0). For the

PdNPs-MW, the peak at 420 nm totally disappears with a reduction time for 2 h indicating the reduction of Pd (II) to Pd (0) is completed. However, a longer reduction time is needed for the PdNPs-C. The result demonstrates that microwave irritation is an effective and fast method to generate Pd nanoparticles.

The particles size distribution of the Pd nanoparticles displays an important influence on their catalytic activities. The TEM images and particles size distribution of as-prepared PdNPs-MW and PdNPs-C are presented in Fig. 2. From the image, the clear crystal lattice fringes with a spacing of 0.226 nm corresponding to the (111) facets of palladium are shown in Fig. 2 (b). Besides, the PdNPs-MW with near spherical shapes uniformly distributed in the system; these particles have a narrow size distribution with diameters ranging from 3.6 to 5.4 nm according to the particle size distribution histogram, and the average particle sizes is about 4.71 nm. However, the PdNPs-C of different morphology such as tetrahedron, cube and polyhedron with an obvious increase in particle size are observed. The particle size of PdNPs-C is between 1.3 and 26.8 nm (average diameter of 9.54). A possible reason for this is the ability to heat the catalytic system uniformly in microwave irritation reduction progress forming the Pd nanoparticles with uniform structure and narrow size distribution. Otherwise, the conventional chemical reduction method possess a longer reduction time than microwave result in a further growth of Pd nanoparticles.

The XRD patterns of PdNPs-MW and PdNPs-C dried powders are displayed in Fig. 3. Three characteristic peaks observed at $2\theta = 40.1°$, $46.6°$, $68.1°$ which are corresponding to Pd (111), Pd (200), Pd (220) lattice phases, respectively. The position of all diffraction peaks matched well with the standard face centered cubic structure according to the JCPDS card no. 46-1043. However, the diffraction peaks of PdNPs-MW are weaker and broader than those of

PdNPs-C, indicating that the PdNPs-MW has a smaller Pd nanoparticles size than PdNPs-C. In addition, the peaks with 2θ of 28.3°, 31.7°, 56.4° which are ascribed to (111), (200) and (222) of NaCl are also observed in all samples.

XPS is employed to obtain the information on the electronic state of the surface region of the Pd nanoparticles. As shown in Fig. 4, the observed binding energies of Pd3d5/2 and Pd3d3/2 at 335.0 eV and 340.4 eV indicate the presence of Pd (0). The binding energy is coincident with the value reported in literatures which is 335.1 eV and 340.4 eV, respectively. However, the binding energy values at 337.2 eV (3d5/2) and 342.4 eV (3d3/2) are assigned to Pd^{2+}. Similarly, four peaks of PdNPs-C are ascribed to Pd (0) and Pd^{2+}. Besides, the reduction degree of 66% obtained under microwave reduction method is slightly higher than the value of 65% obtained under conventional reduction method.

To evaluate the catalytic activity of PdNPs-MW and PdNPs-C, Suzuki cross-coupling reaction was carried out as the model reactions. The influence of using EtOH/H_2O, EtOH and H_2O as the solvent in the Suzuki reaction was studied. As shown in Table 1, the reaction in pure water was sluggish and the low yields of 14.4% for PdNPs-MW and 10.8% for PdNPs-C were obtained in neat ethanol (Table 1, entries 2, 3). The satisfactory result in terms of yield is obtained by using EtOH/H_2O (1:1) co-solvent (Table 1, entry 1). The merit of the co-solvent is attributed to the good solubility of the organic reactants and the inorganic base.Thus, we adopt EtOH/H_2O (1:1) as the solvent for this catalytic reaction.

To survey the generality of the catalytic protocol, we investigated the reaction using Suzuki cross-coupling reactions of aryl halides with phenylboronic acid in the presence of K_2CO_3 using EtOH/H_2O (1:1) as solvent. Unsurprisingly, aryl bromides are more reactive than aryl chlorides.

Although extending the reaction time and increasing the reaction temperature, the poor yields were obtained for aryl chlorides (Table 1, entries 8-10). On the other hand, the PdNPs-MW obtains a higher catalytic activity with higher turnover frequency (TOF) than PdNPs-C by comparing the yield for same substrates under the same reaction conditions. For instance, the reaction between 4-bromobenzonitrile and phenylboronic acid, PdNPs-MW provides a 68.7% yield of the coupling product. A lower yield of 34.3% is obtained by using PdNPs-C as catalyst. These results display a higher catalytic activity towards Suzuki cross-coupling reaction for PdNPs-MW with a higher TOF of 41220 h^{-1} (Table 1, entry 1). The excellent catalytic activity of PdNPs-MW may be attributed to the uniform structure and small particle size of Pd nanoparticles (3.6-5.4 nm). We then further extended the scope of reaction substrates to heteroaryl bromides, and 22.8%-32.2% yields were observed (Table 1, entries 11-13).

4. Conclusions

In summary, a simple, versatile and fast synthesis method to generate highly active Pd nanoparticles was prepared by microwave-assisted chemical reduction method. The obtained PdNPs of near spherical shapes have a narrow size distribution with particle size of 3.6-5.4 nm. Moreover, the PdNPs-WM were of smaller particle size and more dispersed than PdNPs-C result in a higher catalytic activity for Suzuki cross-coupling reactions.

References

[1]. N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457-2483.

[2]. A. Suzuki, J. Organomet. Chem. 576 (1999) 147-168.

[3]. J.P. Wolfe, R.A. Singer, B.H. Yang, S.L.J. Buchwald, J. Am. Chem. Soc. 121 (1999) 9550-9561.

[4]. S.R. Chemler, D. Trauner, Angew. Chem. Int. Ed. 40 (2001) 4544-4568.

[5]. H.U. Blaser, A. Indolese, J. Mol. Catal. A: Chem. 173 (2001) 3-18.

[6]. K.H. Chung, C.M. So, S.M. Wong, C.H. Luk, Z.Y. Zhou, C.P. Lau, F.Y. Kwong, Chem. Commun. **48 (**2012) 1967-1969.

[7]. A. Dewan, Z. Buragohain, M. Mondal, G. Sarmah, G. Borah, U. Bora, Appl. Organomet. Chem. 28 (2014) 230-233.

[8]. F. Godoy, C. Segarra, M. Poyatos, E. Peris, Organometallics 30 (2011) 684-688.

[9]. M.M.D. Anna, M. Mail, P. Mastrorilli, A. Rizzuti, C. Ponzoni, C. Leonelli, J. Mol. Catal. A: Chem. 366 (2013) 186-194.

[10]. C. Sarmah, D. Sahu, P. Das, Catal. Today 198 (2012) 197-203.

[11]. M.G. Speziali, A.G.M Silva, D.M.V Miranda, A.L. Monteiro, Appl. Catal. A: Gen. 462 (2013) 39-45.

[12]. N. Li, Z. Wang, K. Zhao, Z. Shi, S. Xu, Z. Gu, J. Nanosci. Nanotech. 10 (2010) 6748-6751.

[13]. E.J. García-Suárez, P. Lara, A.B. García, M. Ojeda, R. Luque, K. Philippot, Appl. Catal. A: Gen. 468 (2013) 59-67.

[14]. Y. Li, E. Boone, M.A. El-Sayed, Langmuir 18 (2002) 4921-4925.

[15]. S. Niembro, A. Shafir, A. Vallribera, R. Alibés, Org. Lett. 10 (2008) 3215-3218.

[16]. W. Zhou, J. Y. Lee, J. Phys. Chem. C 112 (2008) 3789-3793.

[17]. D. Astruc, Tetrahedron: Asymmetry 21 (2010) 1041-1054.

[18]. D. Sahu, P. Das, RSC. Adv. 5 (2015) 3512-3520.

[19]. M. Ganesan, R.G. Freemantle, S.O. Obare, Chem. Mater.19 (2007) 3464-3471.

[20]. P.J. Ellis, I.J.S. Fairlamb, S.F.J. Hackett, K. Wilson, A.F. Lee, Angew. Chem. Int. Ed. 122 (2010) 1864-1868.

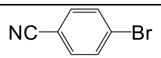
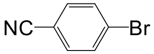
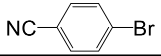
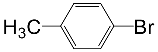
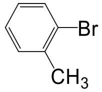
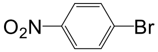
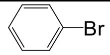
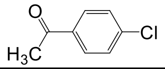
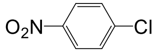
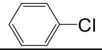
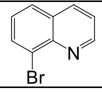
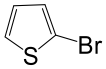
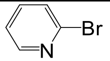
[21]. B. Tamami, H. Allahyari, S. Ghasemi, F.J. Farjadian, Organometal. Chem. 696 (2011) 594-599.

[22]. X. Wang, J. Zhuang, Q. Peng, Y. L, Nature 437 (2005) 121-124.

Table 1 Representative Suzuki cross-coupling reaction performed using the PdNPs catalyst.[a]

$$\mathbf{R\text{-}Ar\text{-}X + Ar'\text{-}B(OH)_2 \xrightarrow[K_2CO_3,\ EtOH/H_2O]{PdNPs\ catalyst} R\text{-}Ar\text{-}Ar'}$$

X=Br, Cl R=CH_3, CN, NO_2, $COCH_3$ Ar'=Ph

Entry	ArX	Time	Temp/℃	Solvent (v/v)	Yield [b]/%	Yield [c]/%
1[d]		10min	60	$EtOH/H_2O$ (1:1)	68.7	34.3
2		10min	60	Neat EtOH	14.4	10.8
3		10min	60	Pure water	Trace	Trace
4		10min	60	$EtOH/H_2O$ (1:1)	99.0	91.0
5		10min	60	$EtOH/H_2O$ (1:1)	95.0	82.0
6		10min	60	$EtOH/H_2O$ (1:1)	85.1	58.3
7		10min	60	$EtOH/H_2O$ (1:1)	39.1	28.8
8[e]		6h	80	$EtOH/H_2O$ (1:1)	26.5	20.8
9[e]		6h	80	$EtOH/H_2O$ (1:1)	18.2	14.6
10[e]		6h	80	$EtOH/H_2O$ (1:1)	13.4	11.5
11[e]		6h	80	$EtOH/H_2O$ (1:1)	32.2	27.5
12[e]		6h	80	$EtOH/H_2O$ (1:1)	25.5	22.8
13[e]		6h	80	$EtOH/H_2O$ (1:1)	30.7	28.6

[a] Reaction conditions: aryl bromides (4 mmol), phenylboronic acid (6 mmol), PdNPs (0.4 mmol‰), K_2CO_3 (8 mmol), ethanol/H_2O (24 mL/24 mL) .

[b] catalyst: PdNPs-MW

[c] catalyst: PdNPs-C

[d] TOF values in (mol aryl bromides)(molPd)$^{-1}$h^{-1} of the PdNPs was determined on the basis of the yield of biphenyl.

[e] 4mmol‰ of Pd was used.

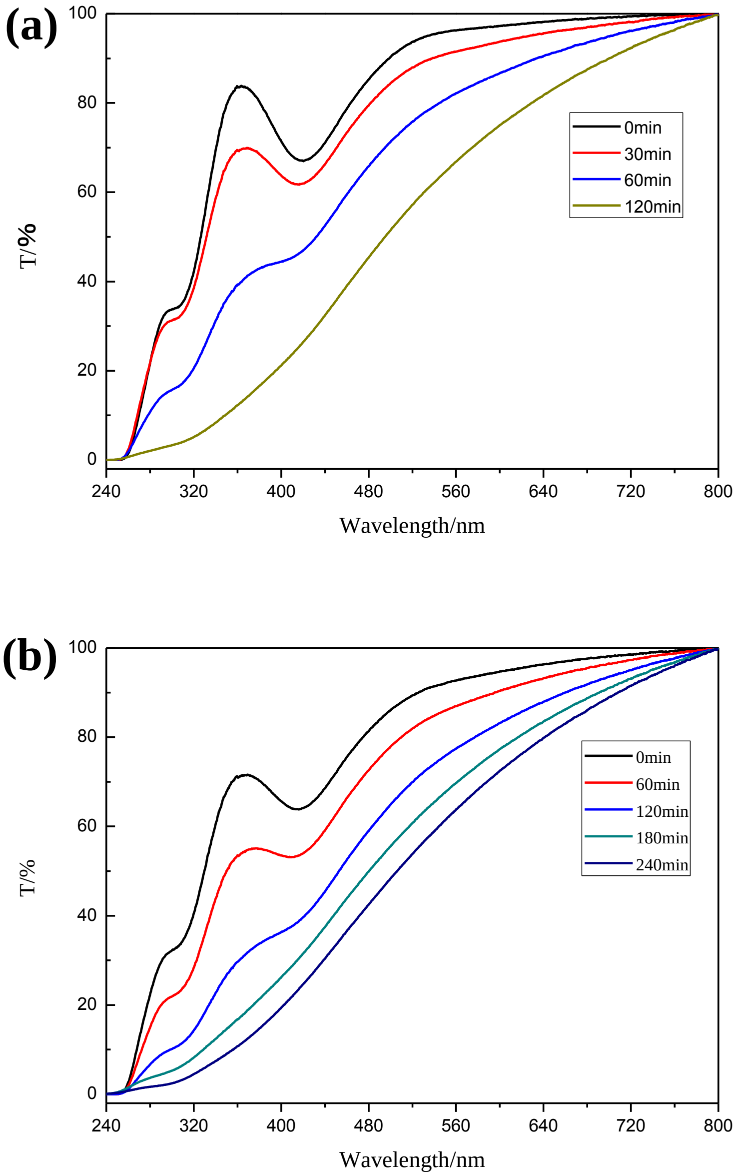


Fig. 1. UV–vis spectrum of PdNPs: (a) PdNPs-MW; (b) PdNPs-C.

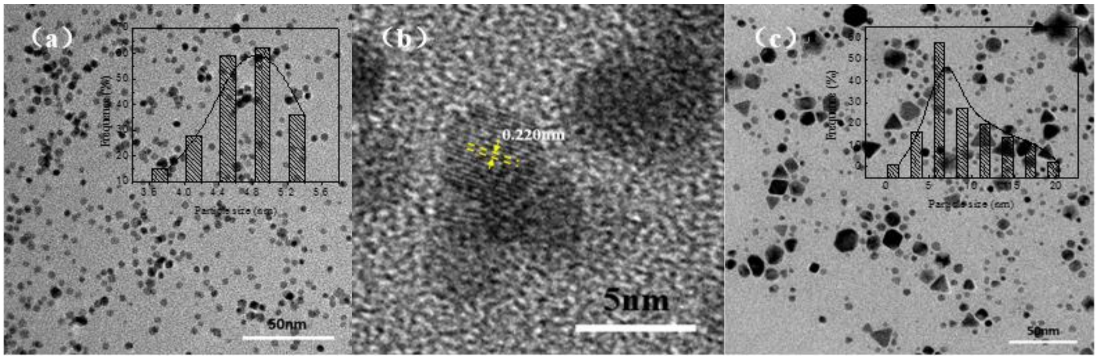


Fig. 2. TEM images of PdNPs: (a) PdNPs-MW; (b) a close vision of PdNPs-MW; and (c) PdNPs-C.

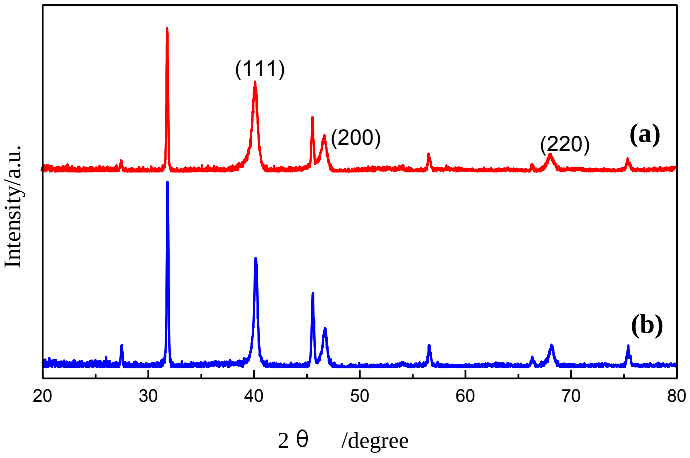


Fig. 3. XRD patterns of PdNPs: (a) PdNPs-MW; (b) PdNPs-C.

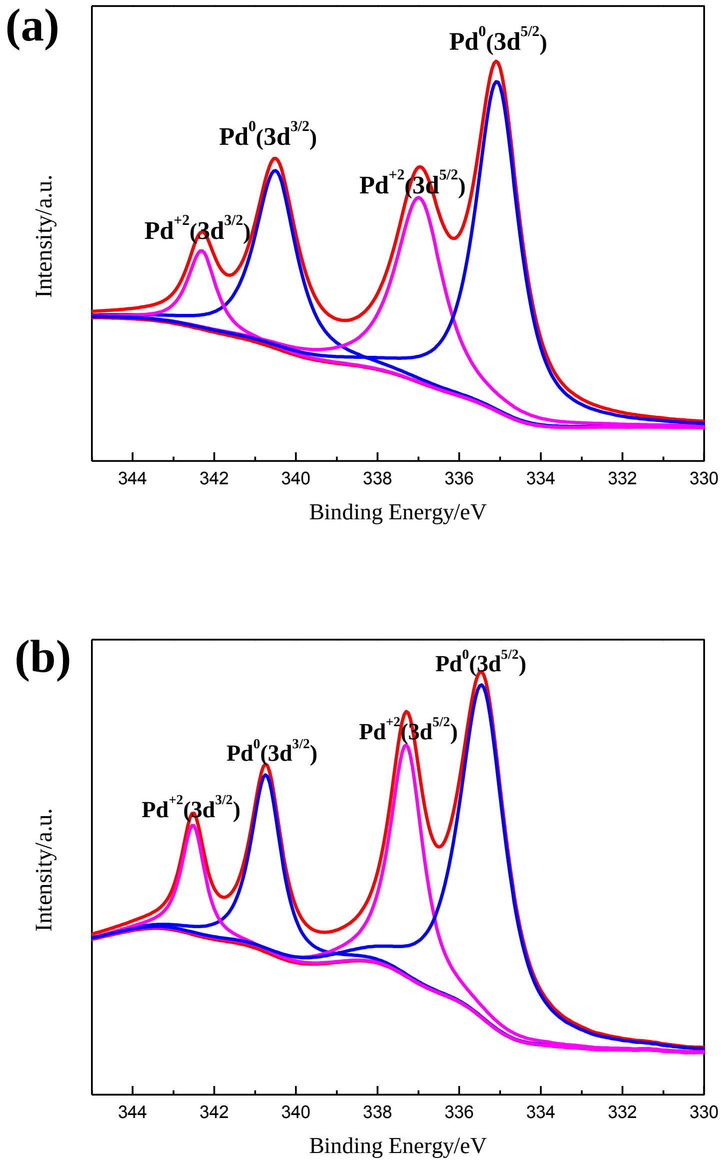


Fig. 4. XPS spectra of PdNPs: (a) PdNPs-MW; (b) PdNPs-C.