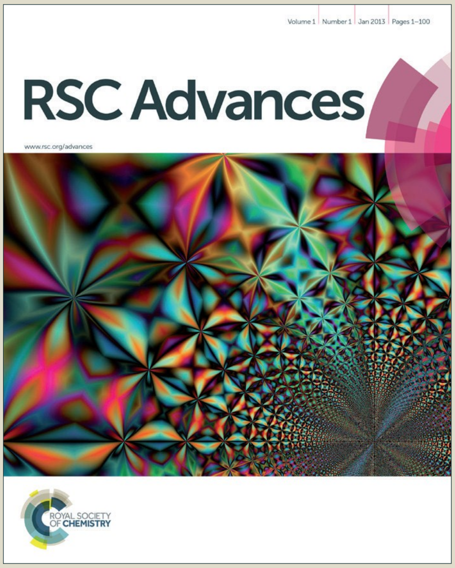
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Preparation and characterization of nano-sized PS@Pd core-shell architectures with one-pot method

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Nianchun Zhang,[a]* Bin Guo[b], Hong Liu[a], Ping Liu[a], Guihua Liu[c], Jinquan Cheng[c]

Monodispersed and nano-sized Pd (palladium) coated PS (polystyrene) core-shell architectures have been prepared successfully by a facile, green and fast one-pot method, in which an acrylic acid and vitamin C were used as a carboxyl-functioned of polymer beads and a reducing agent, respectively. The structures and morphologies of the PS@Pd core-shell architectures were characterized by X-ray diffraction (XRD), transmission (high resolution) electron microscopy (TEM, HRTEM), X-ray photoelectron spectroscopy (XPS) and so on. The results demonstrated that the Pd nanoparticles deposited on the surface of PS sphere beads, and the Pd nanoparticles were homogeneous and monodispersed. The results also indicated that the diameter of Pd shell was 5±1.2 nm and PS@Pd core-shell architectures were 80 ± 3.5 nm. So the one-pot preparation method would provide a development direction to fabricate all kinds of polymer@nonmetal core-shell architectures. And the PS@Pd showed improved electrocatalytic activity for formic acid oxidation in comparison with commercial Pd nanoparticles through controlling surface structures.

1.Introduction

Noble metal nanoparticles can be widely applied in optical, electronic, catalytic, conducting properties and antibacterial treatments because of their unusual properties and potentials.[1-2] And noble Pd (palladium) nanoparticles based catalysts are vital to fuel cells, sensors, the petroleum and automotive industries due to their high catalytic activity and stability.[3] Over the past decade, the design of novel Pd nanomaterials with unique properties had attracted great attention due to the potential for new applications and improving current applications.[4] The palladium as a relatively abundant resource has been intensively studied as the alternative electrocatalyst for its desirable activity toward the oxygen reduction reaction.[5-6] However, Pd is a precious metal of the platinum group metals, which most of the recent efforts have focused on decreasing Pd utilization through increasing the catalytic efficiency of its catalysts. It has also been found that Pd base composites could improve its catalytic activity.[7]

And the core-shell architectures would play a synergistic role to affect the thermodynamics and/or the kinetics.[8] The PS (polystyrene) is an effective template for the preparation of composite materials because of the ease of surface functionalization and size variations. And preparation of polymer@metal core-shell architectures is an ongoing challenge in new materials preparation. [9-10]

The most common methods for preparation polymer@metal core-shell structure are electroless plating, microwave absorbing coating and in-situ deposition.[11-13] There are few reports on Pd nanocomposites preparation with simple strategies, such as sequential condensation decarboxylation Heck, nitration and reduction of polystyrene nanospheres and polystyrene sphere as a template. [14-16] In the past, polymer@Pd had been prepared through using the supercritical carbon dioxide, sodium borohydride and hydrazine hydrate.[17] And all these chemicals pose potential environmental and biological risks. In the wake of increasing awareness about the environment has led researchers to focus on green prepared approaches. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy.[18] However, there were reports on the preparation of Pd nanparticles using environment-friendly the vitamin C as the reducing agent.

In this work, we reported a facile, green and fast one-pot method for fabrication of PS@Pd core-shell architectures by using the acrylic acid as carboxyl-functioned and the vitamin C as reducing agent. With gentle heating, this system is a mild, renewable, inexpensive and nontoxic reducing agent. And the structure and morphology of PS@Pd core-shell architectures are also investigated.

2. Experimental

2.1 Materials

Styrene (St, 98%), polyvinylpyrrolidone (PVP, K30), acrylic acid (AA, 99.9%) and azodiisobutyronitrile (AIBN, 99.5%) were

---

[a] College of Material Science and Engineering, South China University of Technology, Guangzhou 510641, P. R. China
[b] Microelectronics, School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, P. R. China
[c] Shenzhen Center for Disease Control and prevention,Shenzhen 518020, P. R. Chnia
*Corresponding author, E-mail: cenczhang@scut.edu.cn

purchased from Aldrich-Sigma. Vitamin C was obtained from Tianjing product Inc. Others solvents and reagents were purchased from the Guangzhou chemical company. All chemicals were used as received without further purification.

2.2 Preparation of PS@Pd core-shell architectures

A typical procedure for preparing the PS@Pd core-shell architectures were as follows: Firstly, Prior to use, the styrene was treated with 10 wt(weight)% NaOH solution in a separatory funnel and rinsed the funnel three times in order to remove the antipolymerizer. The sealed purified sample was stored at 4℃ until required. Secondly, 0.1 g of PVP, 0.5 g of AIBN, 0.3 g AA, 80 mL of ethanol and 20 mL of H_2O were added to a 300 mL three-necked flask. The above mixture was stirred into the transparent homogeneous phase solution. Then 10 mL of styrene was added under a nitrogen atmosphere and rapid stirring. The above emulsion solution was heated to 70 ℃ and polymerized for 3 h. Thirdly, a fresh 10 mL of 0.1 mol/L palladium chloride solution was added to the above solution. And stirring was continued for another 30 min at room temperature. Finally, A 40 mL 0.1 mol/L of Vitamin C aqueous solution was dropwise added into the mix solution. And the mixture was kept at 50℃ for 2 h. Then obtained precipitates centrifuged at 8 000 rpm in 5°C for 15 min, washed several times with distilled water, and dried in vacuum at 60 °C for 2 h.

2.3 Electrode preparation

The nano-sized PS@Pd and commercial Pd nanoparticles were electrodeposited on the glassy carbon rod electrode in 0.2 mM $PdCl_2$ + 0.5 M H_2SO_4 solution at room temperature. Firstly, the glassy carbon rod electrode was subjected to a potential step from 1.20 V to −0.10 V and stayed for 20 ms to produce Pd nuclei; a square wave potential to the lower potential limit of 0.30 V and upper potential limit of 0.70 V at 100 Hz was then used for the growth of Pd nuclei to PS@Pd and commercial Pd nanoparticles.

2.4 Measurements

The crystallinity of the samples was determined with a MSAL-XD2 X-ray diffractometer (XRD) with Cu Kα radiation (40 KV, 20 MA, λ=1. 54051 Å). Fourier transform infra-red spectroscopy (FTIR) spectra were obtained with a spectrophotometer (EQUINOX-55, Thermo Electron Corporation). The high-resolution transmission electron microscopy (HRTEM) images, selected area electron diffraction (SAED) and energy-dispersive X-ray spectrometry (EDX) were taken with a JEM-2010F instrument, using an accelerating voltage of 200 KV. The particle size distribution was measured by dynamic light scattering (DLS, Malvern Instr., UK). The electrochemical properties of the catalysts were measured in a three-electrode cell at room temperature using a potentiostat (Eco Chemie, AUTOLAB).

2.5 Electrocatalytic activity test

The Ag/AgCl (in saturated KCl) was used as a reference electrode. The glassy carbon electrode as a working electrode was polished with Al_2O_3 paste and then washed in deionized water. The catalyst ink was prepared with ultrasonic dispersing catalyst powders in an appropriate amount of Millipore water. Prior to electrocatalytic activity test for methanol oxidation, the glassy carbon rod electrode loaded with PS@Pd commercial Pd nanoparticles was electrochemical cleaned by continuous potential cycling between -0.20 and 1.20 V at 50 mV s^{-1} until a stable cyclic voltammograms (CVs) curve was obtained**.** The CVs of the electrocatalysts for formic acid electrooxidation were obtained from −0.2 to +1.2 V in 0.5 M H_2SO_4 +0.5 M methanol.

3. Results and discussion

3.1 Characterization of morphology and structure

Fig. 1a displays the XRD patterns of the PS@Pd core-shell structure. The data for the core-shell architectures peaks at the peaks at 40.1°, 46.7°, 68.1°, 82.1° and 86.6 correspond to the (111), (200), (220) and (311) crystal planes of Pd, respectively. And it indicates that the prepared Pd in this study possesses a face-centered cube structure. And the curved peak observed with of 20° indicates that PS did not form a regular crystal structure. It can be seen from Fig. 1b that observed strong FTIR absorption bands at 3012, 2885, 1460, 1400 and 690 cm^{-1} agree with PS standard absorption bands. And the absorption bands centered at 3400 cm^{-1} are attributed to $–COO^{-}$. After coating with these Pd nanoparticles, the band of at 3012 and 2885 cm^{-1} gradually weaken, which belong to the asymmetric and symmetric stretching vibrations of $–CH_2$. And the intensity peak at 690 cm^{-1} may result from the deformation vibration of C–H of the benzene ring has been reduced significantly. The results also show that the PS and Pd had formed composite materials.

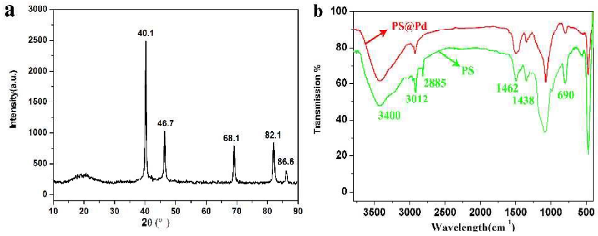


Fig. 1. (a) XRD patterns of PS@Pd, (b) FTIR spectrum of PS and PS@Pd.

Fig. 2a shows TEM images of PS@Pd core-shell architectures and the morphology of the PS@Pd are almost spherical uniform. The size of PS@Pd core-shell architectures are 80 ± 3.5 nm. And it also displays that the homogeneous and monodispersed Pd nanoparticles deposited on the PS beads matrix. Fig. 2b shows a magnified TEM image of the PS@Pd core-shell architectures and it can be seen that the details of Pd shell nanoparticles. The electrostatic interactions of the negatively charged $PS–COO^{-}$ can accelerate Pd nanoparticles deposition, which could be proved by the result that the Pd nanoparticles were almost completely adsorbed onto the PS surface.**[19]** The hydrodynamic diameter distribution of the PS@Pd is shown in Fig. 2c, and the nanoparticles are smaller with a narrower distribution. It also shows that the PS@Pd core-shell architectures are monodispersed with a polydispersity index of 0.024 and an average diameter of 80 nm.

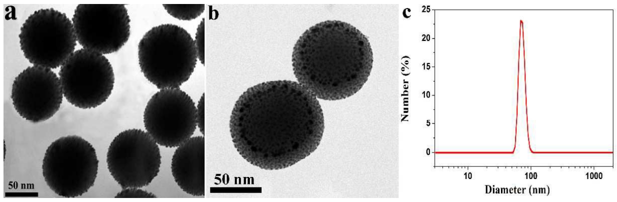


Fig. 2. TEM images of (a) PS@Pd, (b) magnified TEM image of PS@Pd, and (c) size distribution of PS@Pd.

Fig. 3a displays HRTEM image analysis of the PS@Pd core-shell architectures, and Pd nanoparticles shell are 5 ± 1.2 nm. And the lattice fringes are shown in Fig. 3b. The distance between the adjacent fringes in the particle's shell is 0.225 nm, which fits well with the distance between the (111) planes of the face centered cubic Pd. The point pattern of the corresponding SAED (Fig. 3c) further confirms the single crystalline nature of the Pd. The EDX (Fig. 3d) analysis of the PS@Pd nanoparticles shows that the contents of the constituent weight are 82.7% (C) and 14.8% (Pd). The other peaks such as Cu and O are attributed to the copper grid.

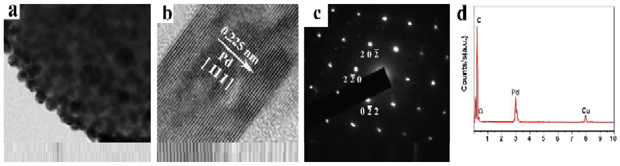


Fig. 3. (a) HRTEM image of PS@Pd, (b) lattice fringes HRTEM image of PS@Pd (c) SAED analysis of PS@Pd, and (d) EDX analysis of PS@Pd.

As can be seen from Fig. 4a, the peaks of Pd and C elements are obviously found in the survey scan the XPS spectrum of PS@Pd core-shell architectures. The XPS analysis shows that the constituent weights are 83.1 wt% C and 15.1 wt% Pd in the PS@Pd. The amount of Pd is 15.1 wt% calculated from the XPS, and the weight percentages of Pd investigated with the XPS and EDX (14.8 wt%) show similar results from the different characterization methods. In order to investigate the chemical state of Pd nanoparticles, the high resolution XPS spectrum of Pd 3d is recorded. Fig. 4b shows that the Pd 3d spectrum of two individual peaks which can be attributed to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies. The values of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ were 335.3 and 340.6 eV, respectively, which can be attributed to the metallic Pd (0) state.[20] During this procedure, Pd^{2+} ions are adsorbed onto the surfaces of the PS bead which functionalized a negatively charged $-COO^-$ groups due to electrostatic attraction. And all of the Pd^{2+} ions are completely reduced Pd^0 by using the vitamin C as reducing agent.

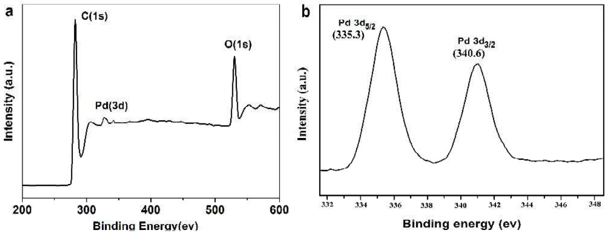


Fig. 4. XPS spectrum of (a) PS@Pd core-shell architectures and (b) Pd3d.

3.2 The mechanism for formation the PS@Pd core-shell architectures

The formation of PS@Pd core-shell architectures is schematically represented in Fig. 5, which schematically displays an overall procedure for preparation of the core-shell architectures. From the above results, the Pd nanoparticles could deposit on the negatively charged PS. The surface electric charged polystyrene beads are prepared by grafting with –COOH groups. When the PS–COOH groups are deprotonated, it can obtain charged $PS–COO^-$. The $PS–COO^-$ has negative charges on the surface of water, which will facilitate $[Pd]^{2+}$ to attract $PS–COO^-$ by the electrostatic attraction.

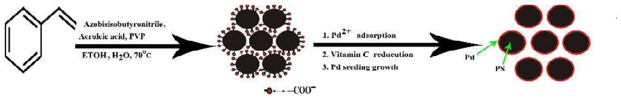


Fig. 5. schematic representation of the formation of PS@Pd.

The mechanism for the formation the PS@Pd core-shell architectures is as follows. Firstly, the positive charges Pd^{2+} ions is attracted to the negatively charged $[PS–COO]^-$ surface by the electrostatic attraction. The L-ascorbic acid serves as a stable electron donor in interactions, and is converted into the radical ion called the semidehydroascorbic acid and dehydroascorbic acid.[21] And then the obtained Pd seeding is used as the nucleation center for forming the silver nanoparticles afterwards. The more the Pd^{2+} ions are attracted onto PS, the more the number of Pd nanoparticles deposit on the surfaces of PS particles.

3.3 Cyclic voltammogram of PS@Pd core-shell architectures

The cyclic voltammograms of PS@Pd (black line) architectures and commercial Pd catalyst (red line) recorded in 0.5 M H_2SO_4 solution. The CVs of PS@Pd and commercial Pd catalysts for methanol oxidation are shown in Fig. 6.

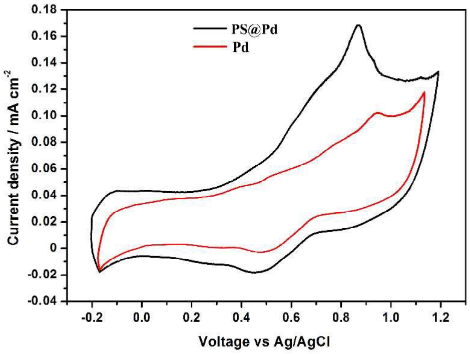


Fig. 6. CVs of commercial Pd and PS@Pd for methanol oxidation in 0.5 M H_2SO_4 with a scan rate of 50 mV s^{-1}.

In comparison of the CVs, the sphere PS@Pd core-shell architectures catalysts shows more negative peak potential (0.820 V) for oxidation than 0.960V of commercial Pd. It also shows that the structure controlled Pd can be a promising catalyst for formic acid electrooxidation.[22] Thus, by combing electrochemical data and structural analysis, it is concluded that the core-shell PS@Pd can be a promising candidate for the formic acid oxidation in comparison with commercial Pd.

4. Conclusions

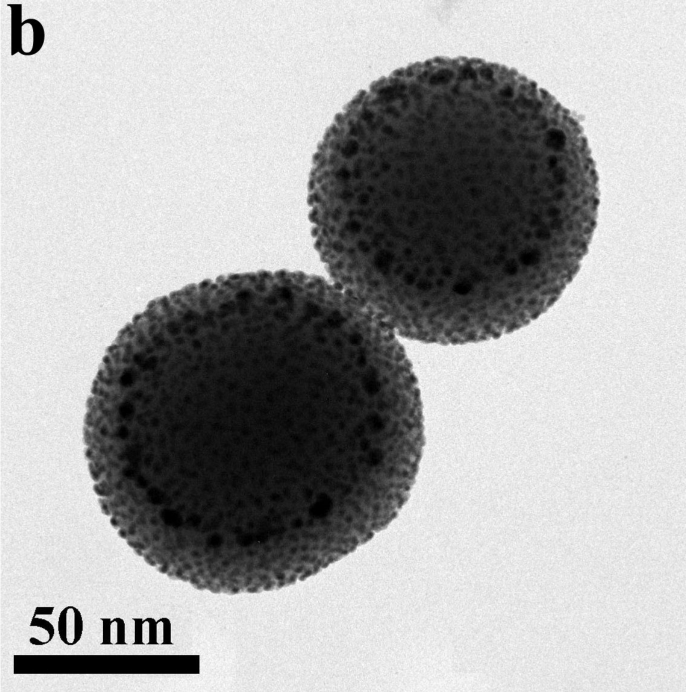
In summary, the PS@Pd core-shell architectures have been successfully prepared through a facile, green and fast one-pot method. And the preparation method was an efficient, simplified and environmentally benign. The experimental results indicate that the carboxyl functionalized and vitamin C played an important role in the formation of the core-shell architectures. The core-shell architectures had a spherical structure in a size 80 ± 3.5 nm and the diameter of Pd shell was 5±1.2 nm. And the Pd nanoparticles shell were homogeneous and monodispersed. The PS@Pd core-shell architectures showed improved electrocatalytic activity for formic acid oxidation in comparison with commercial Pd. Therefore, the unique PS@Pd core-shell materials are also expected to find potential applications in many areas such as electrocatalyst, fuel cells and sensors.

Acknowledgements

This project is supported by China Postdoctoral Science Foundation funded project (No.2014M562182) and the Fundamental Research Funds for the Central Universities (No. 2014ZM0058).

Notes and references

1 S. Ikurumi, S. Okada, K. Nakatsuka, T. Kamegawa, K. Mori and H. Yamashita, *J. Phys. Chem. C*, 2014, **118**, 575-581.
2 R. Wu, Y. P. Zhang, R. J. Hong, S. Q. Lai, C. Ye and J. Q. Hu, *Mater. Lett.,* 2012, **89**, 236-239.
3 Y. Shao, J. Liu, Y. Wang and Y. Lin, *J. Mater. Chem.*, 2009, **19**, 46-59.
4 X. Zhao, S. Chen, Z. C. Fang, J. Ding, W. Sang, Y. C. Wang, J. Zhao, Z. M. Peng and J. Zeng, *J. Am. Chem. Soc.*, 2015, 137, 2804-2807.
5 Z. Y. Zhang, T. Sun, C. Chen, F. Xiao, Z. Gong and S. Wang, *ACS Appl. Mater. Interfaces*, 2014, 6, 21035-21040.
6 M. Shao, P. Liu, J. Zhang and R. Adzic, *J. Phys. Chem. B,* 2007, **111**, 6772-6775.
7 Y. Suo, L. Zhuang and J. Lu, *Angew. Chem. Int. Ed.*, 2007, **46**, 2862-2864.
8 M. M. Zhang, T. H. Ngo, N. I. Rabiah, T. P. Otanicar, P.E. Phelan, R. Swaminathan and L. L. Dai, *Langmuir,* 2014, **30**, 75-82.
9 N. C. Zhang, X. Yu and J. Q. Hu, *Mater. Lett.*, 2014, 125, 120-123.
10 C. Rungsima, S. Wirasak and C. Arkadiusz, *RSC. Adv.*, 2014; 4, 30648-30653.
11 H. Y. Hsueh, Y. C. Huang, R. M. Ho, C. H. Lai, T. Makida and H. Hasegawa, *Adv. Mater.*, 2011, **23**, 3041-3046.
12 D. H. Nam, S. J. Lim, M. J. Kim and H. S. Kwon, *RSC Adv.*, 2014, **4**, 10212-10215.
13. Y. Jung, N. Singh and K. S. Choi, *Angew. Chem. Int. Edit.*, 2009, **48**, 8331-8334.
14 A. K. Shil and P. Das. *RSC Adv.*, 2015, **5**, 24859-24863.
15 G. J. Lan, X. M. Zhang, X.M. Zhang, M.R. Li, Y. Li and Q. H Yang. *RSC Adv.*, 2015, **5**, 35730-35736.
16 Z. Yan, Y. Gu, W. Wei, Z. Jiang, J. Xie and P. K. Shen. *Fuel Cells*, 2015, **15**, 256-261.
17 K. H. Tian, C. Y. Liu, H. J. Yang and X. Y. Ren, *Colloid Surface A,* 2012, **397**, 12-15.
18 M. R. Shantamal and J. S. Arora, *RSC Adv.*, 2014, **4**, 20323-20333.
19 J. Zhi, D. P. Song, Z. W. Li, X. Leia and A. G. Hu, *Chem Commun.,* 2011, **47**, 10707-10709.
20 Y. Sohn, D. Pradhan and K. T. Leung, *ACS Nano*, 2010, **4**, 5111-5120.
21 N. C. Zhang, X. Yu, J. Q. Hu, F. Xue and E. Y. Ding, *RSC Adv.*, 2013, **33**, 13740-13747.
22 Y. W Lee, J. K. Oh, H. S. Kim, J. K. Lee, S. B. Han, W. J. Choi and K. W. Park. *J. Power Sources* 2010,195, 5896-5901.



The TEM images for PS@Pd core-shell architectures are depicted in Fig. 2 (b). The nano size Pd nanoparticles are deposited on the surface of polystyrene spheres.