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Facile Fabrication of Palladium Nanoparticles Immobilized on the Water-Stable Polyvinyl Alcohol/ Polyehyleneimine Nanofibers Via In-Situ Reduction and Their High Electrochemical Activity

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Facile Fabrication of Palladium Nanoparticles Immobilized on the Water-Stable Polyvinyl Alcohol/Polyehyleneimine Nanofibers Via *In-Situ* Reduction and Their High Electrochemical Activity

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A facile strategy for the fabrication of electrochemical biosensors by immobilizing well-dispersed palladium nanoparticles (PdNPs) on the water-stable polyvinyl alcohol/polyethyleneimine (PVA/PEI) nanofibers through the combination of electrospinning technique and the process of *in-situ* reduction has been demonstrated. The synthesized PdNPs/(PVA/PEI) nanocomposites were characterized by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The experimental results confirmed that the PdNPs immobilized on the electrospun PVA/PEI nanofibers with an average diameter of 3.4 nm were well-dispersed, which could be ascribed to the complexation between Pd(II) and the free amine groups of PEI. Further investigations suggested that the PdNPs/(PVA/PEI) nanocomposites with well-separated PdNPs and large surface area exhibited high performance as electrochemical biosensors to detect hydrogen peroxide (H₂O₂).

Keywords: Electrochemical activity, Electrospinning, H₂O₂, PdNPs/(PVA/PEI) nanocomposites

Introduction

With the progress of time and the improvement of living standards, the demands for more sensitive sensors for global environmental monitoring, food inspection, and medical diagnostics have become urgent, leading to an upsurge of interest in the exploration of efficient sensors (1). The past several decades have witnessed the significant development in preparing sensitive sensors for accurate detection of NH₃, HCHO, H₂O₂, and so on. Varied nanostructures, such as hierarchical mesoporous SnO₂ structures (2), PANI/PEO nanowires (3), and LiCl-doped TiO₂ nanofibers (4) have been employed as gas sensors or humidity sensors. Nanostructured materials have been widely used as sensing materials, which may be attributed to their high surfaceto-volume ratios, high porosity, and low cross-section areas. Consequently, better performances of electrochemical detectors, such as mass transport and electric charge transport, have been reported (1, 5-7).

In response to the extensive need for electrochemical detectors, tremendous efforts have been focused on the development of the nanostructured materials. Electrospinning is a noticeable technique that provides a relatively inexpensive strategy to acquire continuous fibrous mats with higher surface area to volume ratio through the action of an external electric field (8–13). The easily-acquired nanomaterials with remarkable specific surface area and high porosity make them potential candidates in the fields of drug delivery systems, enzyme immobilization, and electrochemical biosensors (14).

Noble metal nanoparticles have received immense attention due to their unique structure-dependent properties and potential applications in numerous areas, such as electronics, catalysis, and sensor-technology (15–17). Among the many investigated metal nanoparticles, PdNPs have proven to be of great importance in the fields of catalysis (18), hydrogen storage (19), and electrochemical biosensors (20, 21) because of their large surface area-to-volume ratio. However, the PdNPs are easy to aggregate, difficult to recycle, and quickly consumed. Therefore, it is necessary to load PdNPs on the surface of supporting nanomaterials with high surface area, desired recovery, low cost, and longevity (14, 20). PVA is a type of biocompatible synthetic polymer

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with high-temperature-resistance and mechanical-stability (10) and its nanofibrous mats can be conveniently obtained by electrospinning the aqueous solution (22). However, the prepared nanofibrous mats are rapidly dissolved in water, which limits their practical applications. PEI is a cationic branched weak polyelectrolyte with high concentration of secondary amine functional groups, making it an ideal polymeric ligand for complexing heavy metal ions (23, 24). Over the past several years, intensive research has been conducted to develop PVA/PEI nanofibrous mats that are cross-linked by glutaralde-hyde (GA) as supporting nanomaterials (25). Based on a previous study (26), we successfully prepared well-separated PdNPs functionalized PVA/PEI nanofibrous mats for electrochemical biosensors.

In the present work, we acquired PVA/PEI nanofibers by the process of electrospinning and then cross-linked them with GA vapor to render the fibrous mats water-stable, followed by the immobilization of PdNPs on PVA/PEI nanofibers. Subsequently, the PdNPs/(PVA/PEI) nanocomposites were obtained through *in-situ* reduction of the Pd(II) complexed with the water-stable nanofibrous mats. TEM, FE-SEM, XRD, FT-IR, EDS, TGA, and XPS were employed to characterize the morphology and investigate the PdNPs/(PVA/PEI) nanocomposites. The electrochemical activity of the PdNPs/(PVA/PEI) nanocomposites were investigated by the detection of H₂O₂. The results suggested that the PdNPs immobilized on the PVA/PEI nanofibers were well-dispersed and the PdNPs/(PVA/PEI) nanocomposites exhibited high sensitivity as electrochemical biosensors for the detection of H₂O₂.

Experimental Section

Materials

Palladium chloride (PdCl₂, 99.9%) was obtained from Shanghai Civi Chemical Technology Co., Ltd. Sodium borohydride (NaBH₄) was bought from Tianjin Yongda Chemical Reagent Co., Ltd. Epigallocatechingallate (EGCG, 98%) was supplied by Xuancheng BaiCao Plant Industry and Trade Co., Ltd. Polyethylenimine (PEI, 50%, $M_{\rm w}$ = 70000) and Nafion aqueous solution (5 wt%) were acquired from Aladdin Chemistry Co., Ltd. Polyvinylacohol (PVA, 88% hydrolyzed, $M_w =$ 88000) was from Sigma Aldrich. Glutaraldehyde (GA, 25%) was purchased from Kermel, Tianjin Chemical Reagent Co., Ltd. Ethanol (C₂H₅OH) and phosphate buffer (PBS) was gained from Hangzhou Gaojing Fine Chemical Industry. Hydroquinone (HQ), horseradish peroxidase (HRP, RZ \sim 3, activity \geq 250 units mg⁻¹) and H₂O₂ (30 wt%) were obtained from Aladdin Chemistry Co., Ltd. All chemicals were analytical grade and used as received without further purification. Deionized water used in all experiments was purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA).

Methods

Synthesis of Well-Separated PdNPs in the Aqueous Solution

The well-separated PdNPs in the aqueous solution were synthesized as follows: i) 2 mL of 4 g/L EGCG was slowly added into

5 mL of 4 mM PdCl₂ solution under continued stirring at room temperature over a period of 5 min; ii) after thorough mixing, $0.04 \text{ mol/L NaBH}_4$ with a volume of 10 mL was dripped into the aforementioned solution; iii) entire solution was maintined under mechanical stirring for an hour; and iv) the PdNPs were obtained and kept for further observations.

Preparation of PdNP/(PVA/PEI) Nanocomposites

In a typical synthesis, the electrospun PVA/PEI nanofibers were prepared as follows: 14 g PVA (12 wt%) and 1.12 g PEI (50 wt%) were mixed together under appropriate stirring for 12 h to acquire homogeneous solution. The obtained mixture was electrospun under a fixed voltage of 18.6 kV; the products were collected for 6 h on a piece of aluminum foil at a distance of 15 cm, and the velocity of flow was set at 0.3 mL/h. The freshly prepared nanofibrous mats were detached from the aluminum foil and cross-linked by GA vapor at 60°C for 24 h. Three pieces of the cross-linked PVA/PEI nanofibrous mats (C0) with a weight of 10 mg were immersed into 2.5 mL, 7.5 mL, and 12.5 mL of PdCl₂ solution (4 mM), respectively, and labeled C1, C2, and C3, respectively. After the absorption equilibrium, the mats were removed and washed with deionized water to remove excess Pd(II). Then, the PdNPs/(PVA/PEI) nanocomposites were synthesized by reducing the Pd(II) that are absorbed on the PVA/PEI nanofibers into PdNPs with NaBH₄.

Electrochemical Evaluation of PdNP/(PVA/PEI) Nanocomposites

The electrochemical experiments were conducted with a CHI660E workstation (Shanghai Chenhua, Shanghai, China). The whole process was carried out using a conventional threeelectrode system in 0.1 mol/L PBS (pH = 6.8). Herein, a saturated Ag/AgCl electrode and a platinum foil electrode were selected as the reference electrode and the auxiliary electrode, respectively. The PdNP/(PVA/PEI) nanocomposites (C1 and C3) and PVA/PEI nanofibrous mats (C0) were immersed in 2.5 mg/mL HRP solution (2 mL) at 4°C overnight in a humidity chamber. Then, the HRP modified nanocomposites were obtained. The HRP/(PdNPs/[PVA/PEI])/GCE and HRP/(PVA/PEI)/GCE were both employed as the working electrodes. Prior to the surface coating, the GC electrode was polished carefully with 1.0, 0.3, and 0.05 µm alumina powder and rinsed with deionized water, followed by sonication in acetone, ethanol, and distilled water, respectively. Afterward, the electrode was allowed to dry under nitrogen. Then, $2 \mu L$ of Nafion (0.2%) and HRP/(PdNP/[PVA/PEI]) and HRP/ (PVA/PEI) nanocomposites were placed on the surface of the GC electrode, successively. Eventually, the electrodes were dried with an infrared lamp for further electrochemical experiments. The PBS was purged with nitrogen for 1 h prior to each experiment to maintain the solution from oxygen exposure.

Instrumentation

The obtained PdNPs in aqueous solution and the PdNP/(PVA/PEI) nanocomposites were both placed on the ultra-thin carbon-coated copper grid and dried under infrared



Fig. 1. (a) and (c) TEM images of the PdNPs and (b) the corresponding particle size distribution of PdNPs. (d) The HRTEM image of the PdNPs.

lamp for ten minutes, respectively, and the samples were performed on a JSM-2100 transmission electron microscopy (TEM, JEOL, Japan) at an accelerating voltage of 200 kV. The surface morphologies of the PdNP/(PVA/PEI) nanocomposites were characterized by a field emission scanning electron microscope (FE-SEM, JEOL ULTRA-55) with an energy dispersive spectrometer (EDS). The composition and crystal phase of the obtained samples were checked by a X-ray diffractometer (XRD, Thermo ARL X'TRA) using a Cu Ka radiation source at 35 kV, with a scan rate of $0.02^{\circ} 2\theta \text{ s}^{-1}$ in the 2θ range $10-80^{\circ}$. The Fourier transform infrared spectroscopy (FT-IR) spectra of PVA/PEI nanofibers and PdNP/(PVA/PEI) nanocomposites were recorded on a Thermo Scientific Nicolet 5700 FTIR spectrometer in the wavenumber of 500-4000 cm⁻¹ under ambient conditions. The X-ray photoelectron spectra (XPS) of the PVA/PEI nanofibers and PdNP/(PVA/PEI) nanocomposites were recorded by using an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with Aluminum (mono) Ka source (1486.6 eV). The high-resolution survey (pass energy = 48 eV) was performed at spectral regions relating to carbon, oxygen, nitrogen, and palladium. The aluminum Ka source was operated at 15 kV and 10 mA. The thermal properties of PVA/PEI nanofibers and PdNP/(PVA/PEI) nanocomposites were carried out on a Perkin-Elmer Pyris 1 Thermogravimetric Analyzer (TGA) with a heating rate of 5° C/min between 30° C and 800°C in a nitrogen atmosphere. The sizes of PdNPs and the fiber diameters of PdNP/(PVA/PEI) nanocomposites were both measured with Image-Pro Plus 6.2 software, and at least 100 randomly selected nanoparticles or nanocomposites in different FE-SEM or TEM images were analyzed for each sample in order to acquire the average diameter or size distribution histograms.

Results and Discussion

Fig. 1 illustrates the morphology and particle size distribution of the obtained PdNPs in the aqueous solution. As observed in the figure, the synthesized PdNPs were well-separated, which is attributed to the fact that EGCG served as both dispersant and stabilizer during the process of synthesizing well-dispersed PdNPs (16). It is evident that the PdNPs exhibited a relatively narrow size distribution, and the average diameter of the PdNPs was in the range 4.7–6.9 nm. The indicated lattice spacing of 0.226 nm, as shown in Fig. 1(d), along a certain direction can be assigned to the interplanar spacing of Pd (111), which also echoed the later XRD analysis.

The morphologies and microstructures of the as-prepared PdNP/(PVA/PEI) nanocomposites were investigated via TEM combined with selected area electron diffraction (SAED), which are shown in Fig. 2. In our present work, the PVA/PEI nanofibrous mats, which provide many "sites" for Pd(II), were immersed into different volumes of PdCl₂ solution, followed by the reduction of NaBH₄ after the end of the absorption process. Apparently, compared with that of the PdNPs in the aqueous, the mean diameter PdNPs immobilized on the PVA/PEI nanofibers was much smaller, ranging from 2.3 nm to 4.5 nm. On the other hand, it is clearly seen that some of the PdNPs were aggregated, which may be assigned to the following reasons. First, the Pd (II), which was not absorbed on the PVA/PEI nanofibrous mats in the aqueous, was reduced and then attached to the surface of the nanocomposites; and secondly, the small particle diameter of the PdNPs leads to higher surface energy, which is also of great significance to the aggregations (25, 27, 28). In the meantime, the SAED investigation also indicated the polycrystalline structure of the



Fig. 2. The TEM images of the PdNPs/(PVA/PEI) nanocomposites (a), (b), (c) and (e); and (d) the corresponding particle size distribution of PdNPs. (f) The SAED pattern of PdNPs.

synthesized PdNPs immobilized on the PVA/PEI nanofibrous mats (29, 30).

In order to observe the macroscopic morphology of the acquired PdNP/(PVA/PEI) nanocomposites, the FE-SEM images were taken. As presented in Fig. 3, there is a three-dimensional network structure consisting of a large quantity of randomly deposited nanofibers and the average diameter of the PdNP/(PVA/PEI) nanocomposites was approximately 588 ± 130 nm. Evidently, with the increase of the contents of Pd(II), the quantity of PdNPs which were immobilized on the PVA/PEI nanofibers was increased. Additionally, the PdNPs were well-dispersed and did not exhibit obvious aggregation, which could be ascribed to the effective "sites" provided by PVA/PEI nanofibers. From the EDS spectrum, as demonstrated in Fig. 3(e), the existence of the Pd element further demonstrates the successful immobilization of PdNPs on the nanofibers.

The typical X-ray diffraction (XRD) patterns of PVA/PEI nanofibers, together with those of the PdNP/(PVA/PEI) nanocomposites that possessed different levels of PdNPs, are shown in Fig. 4. Fig. 4 shows the broad diffraction pattern detected at 20 between 17° and 23° , which is caused by the scattering from the PVA/PEI nanofibers (18). As depicted in Fig. 4, there were more diffraction peaks detected in the nanocomposites with the increase of the content of PdNPs. Characteristic Pd

peaks at 40.1° , 46.3° , and 67.5° corresponds to the (111), (200), and (220) plane of a typical Pd crystal structure, respectively (31, 32). According to the standard pattern of Pd (JCPDS NO. 05-0681), all of the peaks can be indexed to the face-centered cubic (fcc) of Pd, suggesting a good crystallinity of the supported PdNPs in the nanocomposites (33–35).

The FT-IR analysis was used to verify the chemical changes during the reaction process. As illustrated in Fig. 5, the broad absorption band around 3338 cm^{-1} in curve (a) shifts to 3363 cm⁻¹, implying the involvement of O-H groups and N-H groups during the formation process of PdNPs, which is presumably attributed to the interaction between the hydroxyl/amino groups of the PVA/PEI nanofibers and the obtained PdNPs. The peak at 1720 cm⁻¹ and 1440 cm⁻¹ are ascribed to the C=O and -CH₂- of GA, respectively, and the intensity in curve (b) is relatively lower than that of in curve (a), which may be caused by the immersion of PdCl₂ solution, leading to the dissolution of partial GA. The absorption peaks centered at 850 cm^{-1} . which are assigned to the stretch vibrations of C-O in curve (a) become weaker in curve (b), confirming the variation of O-H groups in the reduction of Pd ions (36, 37). The peaks at 1096 cm⁻¹ and 1599 cm⁻¹ are indicative of the ether linkages and aldimine generated between GA/PVA and GA/PEI after cross-linking (26).



Fig. 3. The FE-SEM images of the PdNPs/(PVA/PEI) nanocomposites (a) and (c) are corresponding to C3; (d) and (f) are corresponding to C1; (b) the corresponding fiber diameter distribution of PdNPs/(PVA/PEI) nanocomposites; and (e) EDS spectrum of the PdNPs/(PVA/PEI) nanocomposites (C1).



Fig. 4. XRD patterns of (a) PVA/PEI nanofibers (C0); (b)–(d) PdNPs/(PVA/PEI) nanocomposites (corresponding to C1, C2, and C3, respectively).



Fig. 5. The FT-IR spectra of (a) PVA/PEI nanofibers and (b) PdNPs/(PVA/PEI) nanocomposites.



Fig. 6. XPS spectra of (b, d, f) PVA/PEI nanofibers and (a, c, e, g) PdNPs/(PVA/PEI) nanocomposites.

The surface elemental composition was acquired by X-Ray photoelectron spectroscopy (XPS) measurements. As observed in Fig. 6(a), the splitting pattern of the Pd 3d band of the resulting PdNP/(PVA/PEI) nanocomposites consists of two doublets: the more intensive doublet with the binding energy at 335.4 eV and 340.5 eV are ascribed to the Pd 3d_{5/2} and Pd 3d_{3/2} for metallic Pd, whereas the other doublet with binding energy at 337.8 eV and

343.1 eV belongs to the oxidation state of Pd (38–40). The clear difference in the intensity of these two doublets indicated that a small portion of PdNPs was oxidized into PdO, which might be due to that the external PdNPs were easily oxidized to the form of Pd oxide under ambient conditions (41, 42). The XPS spectra in the C 1s binding energy range were also obtained on PVA/PEI nanofibers and PdNP/(PVA/PEI) nanocomposites. In Fig. 6(b),

the deconvoluted XPS peaks of C 1s centered at the binding energies of 284.8, 286.3, and 287.6 eV correspond to sp_2 -hybridized C-C & C-H, C-OH, and C=O groups, respectively (38, 43, 44). However, the peaks of sp_2 -hybridized for C-OH were divided into two peaks, suggesting the hydroxyl groups were changed during the formation process of PdNPs. The binding energy shift of O 1s from 532.6 eV [in Fig. 6(d)] to 532.2 eV and 532.7 eV [in Fig. 6(e)] was due to the strong coordination between the surface hydroxyl group and PdNPs (45). The binding energy between 398.6 eV and 399.1eV belong to the N 1s peak for the tertiary amine moieties, and the binding energy at 400.0 eV is attributed to the primary amine groups (46).

Additionally, the N 1s at a higher binding energy of 402.1 eV originated from quaternary ammonium bonds (47, 48), as demonstrated in Fig. 6(f). However, as seen in Fig. 6(g), many intermediate values appeared, implying the formation of different chemical states of nitrogen in PEI and the strong interaction between PdNPs and PEI during the reduction of Pd(II) (46, 48, 49).

TGA was employed to characterize the thermal stability of the nanofibrous mats and the loading capacity of PdNPs immobilized on the PVA/PEI nanofibers. As shown in Fig. 7, the PVA/PEI nanofibers exhibit two main degradation stages (A1A2 and A2A3), whereas the PVA/PEI nanofibers with PdNPs show a single-step sharp degradation curve (B1B2) (36). In the case of



Fig. 7. TGA curves of the PVA/PEI nanofibers [curve (a)] and PdNPs/(PVA/PEI) nanocomposites [curve (b)].



Concentrated efforts have been focused on the detection of H₂O₂, considering its extensive applications in various fields such as biological, chemical, environmental, clinical, food, and industrial analysis (5, 25). The majority of the research methods for measuring H2O2 have been investigated, such as colorimetric, chromatographic, and photometric methods, which are time-consuming and low-efficient. Therefore, exploring a highefficiency analytic technique is of vital significance. Among these, the electrochemical method is attracting increasing attention because of its high sensitivity, simplicity, and precision (52). The horseradish peroxidase (HRP), which is an important peroxidase that can catalyze the oxidation of substrates when activated by hydrogen peroxide or other peroxides, could be attached tightly onto the negatively charged PdNPs through electrostatic attraction (10, 27). Herein, taking advantages of the porous structures of PVA/PEI nanofibers and the well-dispersed PdNPs, we selected these prepared HRP/(PdNP/(PVA/PEI) nanocomposites as substrate materials in electrochemical biosensors, and the HRP/(PVA/PEI nanofibers) were used as a control. Furthermore, hydroquinone (HQ) was employed to detect H_2O_2 as an excellent electron mediator (25).

As shown in Fig. 8(a), (b), and (c), well-defined cyclic voltammograms (CVs) of the HRP/(PVA/PEI nanofibers)/GCE and HRP/(PdNP/[PVA/PEI] nanocomposites)/GCE are observed. In the presence of 0.5 μ M, 1 μ M, and 10 μ M H₂O₂, the redox peak potential obtained at the HRP/(PdNP/(PVA/PEI) nanocomposites/GCE (C1) was (-0.18 and 0.42 V), suggesting the strong reactions among HRP, H₂O₂, and HQ. Whereas, for the HRP/(PVA/PEI nanofibers)/GCE (C0), with the inexistence of PdNPs, the change of the cathodic peak current and the anodic peak current are both extremely remarkable, indicating that the PdNPs play a key role in the electron transfer between the redox-active site of H₂O₂ and GCE. However, with an evident increase of the PdNPs, there was a minimal obvious difference for the electrochemical activity toward the HQ, indicating that the fabricated HRP biosensor allowed the highly sensitive detection of H_2O_2 . Only the mass concentrations of



Fig. 8. Cyclic voltammograms of (C0) HRP/(PVA/PEI nanofibers)/GCE, (C1) HRP/(PdNPs/(PVA/PEI) nanocomposites)/GCE (2.5 mL PdCl₂), and (C3) HRP/(PdNPs/(PVA/PEI) nanocomposites)/GCE (12.5 mL PdCl₂). The functionalized GCE in (a), (b) and (c) were immersed in 10.0 mM HQ in 0.1 M PBS (pH = 6.8) containing 0.5 μ M, 1 μ M, and 10 μ M H₂O₂, respectively (scan rate, 50 mV s⁻¹).

PdNPs immobilized on the PVA/PEI nanofibrous mats were kept in a suitable range, which may be as a result of the active sites being blocked due to the agglomeration of PdNPs (20). Taking into consideration the sensitive response to H_2O_2 of the asprepared HRP/(PdNP/(PVA/PEI) nanocomposites, it is believed that the highly porous fibrous structure of the PdNP/(PVA/PEI) nanocomposites were a facile substrate material for the development of enzyme-based electrochemical biosensors for H_2O_2 detection (53, 54).

Conclusions

In summary, the PdNP/(PVA/PEI) nanocomposites, which took advantage of the large surface area of PVA/PEI nanofibers and the high catalytic activity of PdNPs, were successfully fabricated by employing the electrospinning technique and the *in-situ* reduction. Further research demonstrated that the PdNP/(PVA/PEI) nanocomposites showed high performance as electrochemical biosensors for the detection of H_2O_2 , and the electron transfer between the redox-active site of H_2O_2 and GCE were greatly enhanced. We hope that this approach to fabricating the PdNP/(PVA/PEI) nanocomposites and the resulting sensing behaviors will aid in the design of nanosensors functionalized by noble metal nanoparticles and has clear implications for the future environmental pollution monitoring devices.

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