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Phase-transfer synthesis of amorphous palladium nanoparticle-functionalized 3D helical carbon nanofibers and its highly catalytic performance towards hydrazine oxidation

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ABSTRACT

Amorphous palladium nanoparticles functionalized helical carbon nanofibers (ApPd–HCNFs) were synthesized using a phase-transfer method. Palladium nanoparticles (Pd-NP) were first prepared using *n*dodecyl sulfide as reducing agent and stabilizing ligands in ethanol. The Pd-NPs were then modified with benzyl mercaptan and transferred into a toluene solution with HCNFs which were decorated with amorphous palladium. The materials were characterized with high-resolution transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy and cyclic voltammetry showing that amorphous palladium nanoparticles were uniformly anchored at the HCNFs surface and that the ApPd–HCNFs exhibit high electrocatalytic activity towards hydrazine oxidation.

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1. Introduction

Direct fuel cells have attracted considerable attention as advanced power sources for portable applications due to advantages such as, high efficiency, low environmental impacts, and easy storage of raw materials [1–3]. Although hydrazine exhibits some drawbacks regarding toxicity it also has significant advantages over traditional organic fuels such as methanol, ethanol and formic acid, since it easily can be used in neutral aqueous solutions and since the electrochemical oxidation process of hydrazine does not produce any poisoning decomposition species such as carbon monoxide and sulfur composites [4,5], which might seriously affect the efficiency of the expensive anode catalysts in fuel cell systems.

Noble metals, such as Pt and Rh show good electrocatalytic activity towards hydrazine [6,7]. However, these noble metals are extremely rare in the Earth's crust (5 and 1 ppb in weight, respectively) and hence quite expensive, limiting their industrial and practical applications in commercial fuel cell systems. Compared to traditional bulk material, nanoscale materials can evidently minimize the needed amount of precious catalyst material but also they possess some unique physical and chemical properties [8] such as a significantly enhanced electrocatalytic activity towards hydrazine oxidation [9–11]. However, small Pd nanoparticles with high surface energy quite easily accumulate to form large and irregular Pd particles, seriously limiting their catalytic

performance. To prevent this mechanism different kinds of support materials have been used to immobilize noble metal particles to retain their electrocatalytic activity [12–14]. Carbon nanomaterials are especially attractive as support due to their excellent conductivity, good chemical inertness and large surface area for the immobilization of metal particles [15–20].

Compared to other methods for preparing noble metal/carbon nanocomposites such as electroless deposition [21], microemulsion [22], and chemical reduction [23], phase transfer synthesis is a more simple, rapid and straightforward method for the preparation of noble metal nanoparticles. This method not only avoids the accumulation of noble metal nanoparticles in the polarized water phase but also easily allows control of size, monodispersity and surface chemical properties of the nanoparticle in the organic phase [24]. Chen et al. reported an efficient anchorage of Pd nanoparticles on carbon nanotubes using phase transfer method and applied it as catalyst for hydrazine oxidation [25], and this has also been demonstrated for synthesizing high quality gold/carbon nanotube hybrids in toluene and water phases [26].

In this Letter, we prepared amorphous Pd nanoparticle-functionalized helical carbon nanofibers (ApPd–HCNFs) using a novel phase transfer method. Pd nanoparticles were first prepared in ethanol containing *n*-dodecyl sulfide as reduction reagent and stabilizing ligands. Then the as-prepared nanoparticles were modified with benzyl mercaptan and transferred into the toluene phase. The benzyl ring functionalized Pd nanoparticles were easily fixed on the helical carbon nanofiber surface via the π – π interaction between benzyl ring groups and graphite surface of HCNFs. We show



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that the as-prepared material significantly decreases the oxidation potential of hydrazine and thereby increases the oxidation current in neutral buffer solution. The excellent electrocatalytic activity towards hydrazine oxidation shows that the ApPd–HCNF composite has potential as high performance catalyst in a direct hydrazine fuel cell.

2. Experimental

Sodium tetrachloropalladate (99.998%), benzyl mercaptan (99%), *n*-dodecyl sulfide (99%) and Nafion solution (5%) were purchased from Ion Power Inc. Hydrazine hydrate (80% in water) is from Merck Corporation in Germany. Ethanol was supplied by Eka Chemicals AB in Sweden. Other chemicals are analytical grade.

High quality helical carbon nanofibers were synthesized according to our latest report using Pd_2C_{60} as catalyst [27]. The Pd nanoparticles synthesis is similar to our former report and can be described as follows [28,29]: (i) 21 mg palladium acetate and 170 mg n-dodecyl sulfide were carefully dissolved in 50 mL ethanol solution. The yellow and transparent solution was heated to 333 K and kept for about 1 h; (ii) then 25 mL of toluene containing 0.25 mL phenyl mercaptan were added into the above-mentioned mixture and kept stirring for 1 h; (iii) a large volume (about 5-fold) water was added into the mixture to remove the miscible ethanol from toluene, and Pd nanoparticles were successfully transferred into the toluene solution from the water phase containing ethanol; (iv) the black up-layer solution (toluene phase) was transferred into another beaker using a separating funnel and then 33 mg HCNFs were added and stirred at 700 rpm overnight. Due to the π - π interaction between Pd nanoparticles and HCNFs the benzyl mercaptan-functionalized Pd nanoparticles were attached at the HCNF surface; (v) the as-prepared suspension was carefully filtered and washed three times with ethanol and water, respectively, and then dried at 80 °C in air overnight. The as prepared composite was labeled as ApPd-HCNFs. The detailed synthesis process is listed as in Scheme 1. The preparation of Pd–HCNFs composite synthesized without using the phase transfer step is the same as that of ApPd–HCNFs but by ignoring step (ii) in Scheme 1. This material is labeled as Pd–HCNFs.

The morphology and structure of ApPd–HCNFs was carried on a transmission electron microscopy (TEM, JEOL-1230) with an acceleration voltage of 80 kV. The high-resolution TEM images were obtained with a JEOL-2100F at 200 keV. X-ray diffraction was performed on a Siemen's D5000 using Cu K α (α = 1.5406) radiation. X-ray photoelectron spectrum of the products was carried on an AXIS Ultra DLD (Kratos Analytical Ltd., UK).

The electrocatalytic performance of the as-prepared catalysts was measured on Autolab PGSTAT30 with a three-electrode cell at room temperature (22 ± 1 °C). As counter and reference electrodes a Pt wire and a saturated calomel electrode were used and as working electrode a glassy carbon electrode coated with the catalvst was used. The working electrode was prepared as follows: (i) a glassy carbon electrode was first polished with 0.05 µm aluminum oxide paste on a chamois and then washed in acetone, ethanol and water under a ultrasonication for 5 min, successively; (ii) 2.5 µL ApPd-HCNF (or HCNFs or Pd-HCNFs) suspension mixed with DMF (2 mg/mL) was carefully dropped onto the upward surface of the electrode and dried at room temperature; (iii) 5 µL of Nafion solution (0.05%) was covered on the surface of the catalyst-covered electrode and dried in air without any heating process. Phosphate buffer solution (concentration: 0.1 M, pH = 6.8) was used as the supporting electrolyte during the electrochemical measurement. The electrolyte solution was bubbled with argon for at least 30 min to completely remove dissolved oxygen before electrochemical measurement.

3. Results and discussion

The TEM image of the HCNFs is shown in Figure 1A. The morphology of HCNFs is a classic helix structure with a diameter about

Scheme 1. Preparation procedure for ApPd-HCNFs.





Figure 1. Bright-field TEM images of HCNFs (A) and ApPd–HCNFs (B); (C and D) are HR TEM of ApPd–HCNFs. Inset of (B) is the TEM image of Pd–HCNFs that synthesized without using phase transfer method. Inset of (D) shows a zoom of the area indicated by the red dotted square. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

80-100 nm, which is in good agreement with our former reports [27,30]. The unique helical structure of the HCNFs makes them to excellent candidates as catalyst support like coiled and bamboolike carbon nanotubes [31–34]. Figure 1B presents a TEM image of ApPd-HCNF nanocomposites. Pd nanoparticles are uniformly attached at the surface of HCNFs without a significant accumulation. Also, although the TEM grids were prepared by ultrasonication of the samples no palladium nanoparticles can be found on the carbon film indicating a strong interaction between the nanoparticles and the nanofiber surface. The TEM image of the sample prepared without phase transfer method, shows that by this method only very few Pd particles were fixed on the HCNFs surface, and that these were consistently smaller with a diameter about 1-2 nm (Figure 1B inset). This observation points to the fact that when not using the phase transfer method the larger Pd nanoparticles are not attached at the HCNF surface during the synthesis process and therefore lost in the filtration process. Further magnification of ApPd–HCNFs in the high-resolution TEM image (Figure 1C) shows that the Pd nanoparticles have an unusual form compared to our earlier reports [28-30]. The Pd nanoparticles (Pd-NPs) in this Letter are more oval in shape and seem to be much more rigidly attached to the HCNF surface so that the interaction between the HCNF surface and the Pd-NP hinders the Pd-NPs to form standard spherical shapes. The form of these Pd-NPs rather resembles freshly splashed mud at a brick wall. The Pd-NPs are homogenously distributed at the HCNF surface with a diameter range from 3 to 15 nm. The average size obtained by measuring 170 randomly selected Pd-NP in TEM micrographs show an average diameter of 8.2 ± 2.2 nm. Further magnification of the selected area (Figure 1D) shows that these nanoparticles are not crystalline but have completely amorphous structure in contrast to earlier reports using phase transfer methods with other types of short linker molecules [28,29]. A possible explanation for the amorphous character of the Pd-NPs is that long-chain *n*-dodecyl sulfide attaches so strongly at the surface of Pd nanoclusters that it effectively hinders the 'free' reorganization of the Pd-atoms into ordered crystalline structures.

To complement the structural analysis of the Pd-NPs the samples were characterized by X-ray diffraction. The X-ray diffraction pattern shown in Figure 2 displays five sharp at 2θ = 39.04°, 45.35°,

66.09°, 79.53° and 83.84° These are assigned to the (111), (200), (220), (311) and (222) crystalline planes of the face centered cubic structure of Pd, respectively. However all these peaks have been shown in earlier reports to originate from the intrinsic Pdnanoparticle that are used in the synthesis of the helical fibers [30] and that is visible for example in Figure 1B (highlighted by an arrow). This is further supported by an estimation of the particles size from the Scherrer's fomula [35], which reveals a size of 35.6 nm for the crystalline Pd nanoparticles which is in good agreement with the size of the encapsulated Pd particles but quite different from the statistical result (10 nm) of TEM analysis of the externally anchored Pd-NPs. From our earlier studies we also know that it is relatively easy to distinguish between diffraction peaks from externally anchored small Pd-NPs and encapsulated larger Pd particles since the smaller particles normally show a different lattice constant leading to broadened (due to the smaller size)



Figure 2. XRD pattern of the Pd/HCNFs.

and shifted (due to the difference in lattice constant) side peaks. The lack of separated side peaks in the XRD spectrum gives further support to the amorphous character of the Pd-NPs.

To prove the formation mechanism of the Pd/HCNFs, energydispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS) were further used for the characterization of the asprepared materials. The EDX spectrum of the ApPd–HCNFs shown in Figure S1 (Supporting information) confirms the presence of C, S, O and Pd in the Pd/HCNF composite. Si, Cu and Cr are originating from the copper grid and the electron microscopy setup. The atomic ratio of Pd to S on the functionalized materials is about 3.9, which is significantly lower than that of Pd–HCNFs synthesized using a self-assembly method [28], indicating that the surface of the Ap-NPs in this Letter have a much higher coverage of sulfur. This supports our proposed model for explaining their amorphous character observed by TEM and XRD.

The XPS spectrum of Pd/HCNFs in Figure 3A, shows the O1s peak at 531.6 eV, the C1s peak at 284.3 eV, as well as peaks of S 2p and Pd 3d. Further analysis of the XPS data shows that the C1s peak can be deconvoluted into five peaks at 284.3, 285.6, 286.9, 287.9 and 290.5 eV (I–V) in Figure 3B. As well known, the peaks at 286.9, 287.9 and 290.5 eV (C1s III–V) are mainly attributed to the carbon atoms bound to oxygen atoms in the HCNFs (C–OH, C=O and COOH) and π – π transition loss [36,37]. The C1s (II) peak at 285.6 eV is assigned to the defect carbon atoms in the graphite structure while the main peak at 284.3 eV originates from the sp² hybridized graphite carbon C=C bond [38]. The shift of the C1s peak of HCNFs from 284.8 to 284.3 eV confirms the bonding of benzyl mercaptan on the HCNFs achieved through the typical π – π interaction [33,39].

The Pd 3d spectrum in Figure 3C shows a doublet structure, Pd $3d_{5/2,3/2}$ which contains three pairs of peaks: the first pair is

assigned to Pd 3d_{5/2} and Pd 3d_{3/2} at 335.6 and 340.9 eV, respectively, which is in good agreement with the reported values (335.5 and 341.1 eV) of bulk Pd(0) [40]. The second pair of peaks appears at 336.8 and 342.2 eV, respectively, and can be assigned to Pd(II)-type species such as oxides and sulfides [41]. The third pair of peaks 338.3 and 343.6 eV are attributed to Pd(IV) [42]. Figure 3D shows the high resolution core level spectra of S 2p. Three pairs of doublet peaks for S $2p_{3/2}$ and S $2p_{1/2}$ can be deconvoluted by a typical 2:1 peak area ratio with a 1.2 eV peak separation. The peak at 162.5 eV is unequivocally attributed to Pd-S bonds fixed on the Pd nanoparticles at the HCNFs surface [43]. The peak at 167.9 V can also be assigned to oxidized sulfur (-SO₃-) groups originating from the air exposure of the as-prepared materials during storage [44] while peak at 164.6 eV most probably represents sulfur-containing molecules (*n*-dodecvl sulfide and benzvl mercaptan) adsorbed on the nanocomposite [45]. The EDX and XPS results give strong support that the synthesis of the Pd nanoparticles and their anchoring onto the HCNFs occur by the proposed self-assembly process.

It is well known that sulfur compounds can have a negative effect on the electrocatalytic oxidation of small organic molecules such as methanol and ethanol, except for Pd nanocrystals with low loading of short chain sulfur compounds which in some cases have been shown to exhibit very high electrocatalytic activity to methanol, ethanol and formic acid in alkaline solutions [28,29]. We have tested our materials catalytic activity to several different organic solvents and find that the ApPd–HCNFs have very low electrocatalytic activity to ethanol, methanol and formic acid. In sharp contrast to this we find that our material exhibits very high activity to the oxidation of hydrazine which has received considerable attention for use in direct fuel cells applied to high-value systems such as satellites and submarines.



Figure 3. (A) XPS spectra of ApPd-HCNFs and XPS patterns of C1s (B), Pd3d (C) and S2p (D) of Pd/HCNFs.

The electrocatalytic activity of the ApPd–HCNF nanocomposite towards hydrazine oxidation was tested in 0.1 M phosphate buffer solution (PBS, pH = 6.8). Figure 4 shows the cyclic voltammetric (CV) curves of different electrodes in argon-saturated 0.1 M PBS solution containing 0.01 M hydrazine. The curve in Figure 4 shows a weak electrocatalytic oxidation for the bare glassy carbon electrode with no peaks of hydrazine oxidation in the potential window from -0.2 to 0.6 V. This is attributed to the slow heterogeneous electron-transfer process of hydrazine at traditional bulk carbon materials. The HCNF-modified electrode (Figure 4, curve b) shows a limited improvement towards hydrazine oxidation compared to the bare GC electrode. This is ascribed to a number of defects at the HCNFs surface. For the electrode modified with Pd-HCNFs synthesized without the phase transfer method a weak and broad oxidation peak (the peak potential is at 0.474 V with a current density about 1.88 mA/cm²) for the oxidation of hydrazine can be seen (Figure 4, curve c). However, at the electrode modified with ApPd-HCNFs that was synthesized with the phase transfer method (Figure 4, curve d), the oxidation peak potential of hydrazine significantly decreases to 0.068 V and shows a very high current density of 15.6 mA/cm² (8 times higher than Pd-HCNFs synthesized without phase transfer method), showing that the ApPd-HCNF composite can effectively catalyze the electro-oxidation of hydrazine. The above experimental data shows that amorphous ApPd-NPs on the HCNFs surface have a particularly good electrocatalytic activity towards oxidation of hydrazine, which is in accordance with the previous literature [25]. Additionally, the current density of hydrazine for our material is higher than for Pd/TiO₂ and Pd/MWCNT composites in the latest reports [46–48] at a very low potential, indicating that the proposed materials can be potentially used as electrocatalyst in fuel cells and as sensor platforms.

Helical carbon nanofibers functionalized with amorphous palladium nanoparticles were synthesized using a phase-transfer route. TEM images and XPS data show that amorphous palladium nanoparticles with diameter 3–15 nm were homogenously distributed and very strongly anchored at the HCNF surface. We show that the ApPd–HCNFs are highly efficient as electrocatalyst for hydrazine oxidation, showing a high potential for applications in direct fuel cell, as well as in advanced sensor platforms.



Figure 4. Cyclic voltammograms of hydrazine oxidation on pristine HCNFs (b, red line), Pd–HCNFs without using phase transfer method (c, green line) and ApPd–HCNFs using phase transfer method (d, blue line) and bare GC (a, black line) electrodes in 10 mM hydrazine + 0.1 M PBS solution (pH = 6.8) in room temperature. Scanning rate: 50 mV/s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2012.05.042.

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