



Efficient anchorage of highly dispersed and ultrafine palladium nanoparticles on the water-soluble phosphonate functionalized multiwall carbon nanotubes

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ABSTRACT

A facile noncovalent approach is proposed to graft phosphonate groups onto the surface of the multiwall carbon nanotubes (MWCNTs) by π - π stacking interaction between naphthalen-1-ylmethylphosphonic acid (NYPA) and MWCNTs. Noncovalently attachment of phosphonate groups on the MWCNTs surface is confirmed by Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and zeta potential analysis. The water-soluble phosphonate functionalized MWCNTs are further deposited with Pd nanoparticles (Pd-NPs) as electrocatalyst for formic acid oxidation. The morphology and structure of Pd-MWCNTs nanocomposites are characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and XPS measurements. It is observed that Pd-NPs are highly dispersed and effectively anchored on the side walls of the phosphonate functionalized MWCNTs. The Pd-MWCNTs nanocomposites exhibit better electrocatalytic activity and long-term stability for formic acid electrooxidation than the un-phosphonated counterpart.

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1. Introduction

The unique one-dimensional geometric structure, high electric conductivity, large surface area, good chemical and thermal stability, and excellent mechanical properties of carbon nanotubes (CNTs) make these excellent candidates for basic scientific study of material science [1–16]. However, the insolubility and the bundling of CNTs in aqueous solution, originated from their inert graphitic nature, strong hydrophobicity and strong intertube van der Waals interactions [17], impede seriously their applications in a number of important areas, such as nanoscale electronics [17,18], quantum devices [19], sensors [18], reinforcement for materials [20], support for catalysts [21], energy storage [3], and so on. Over the past decades, enormous efforts have been devoted to addressing the insolubility problem. One of the most commonly used strategies to render CNTs soluble in aqueous media is through their surface functionalization to form the kinetically stable suspension [4,19].

Chemical modification of side walls, defect sites, and open ends has been used to impart solubility to CNTs. It is well known that the oxidatively shortened CNTs are inherently soluble in water owing to ionic defects at side walls and tube ends [22]. Tube ends and side walls of the oxidative CNTs can be further functionalized by water-solubilizing agents via covalent approach. Unfortunately, the covalent chemistry dramatically alters the atomic and electronic

structures of CNTs, causing the loss of the electrical properties and the degradation of their mechanical strength and chemical stability [22]. Functionalization of the CNTs can also be achieved by noncovalent (supramolecular) approach, which generally retains the electronic structure of the CNTs. In the approach, the bundled nanotubes are individually dispersed via physical adsorption, using suitable solubilizers (such as surfactant or biological polymers) to overcome the hydrophobic interactions between CNTs by means of the electrostatic repulsion force between solubilizer molecules, and/or the hydrophilic property of solubilizer molecules [23]. Another strategy of CNTs solubilization is to anchor ionic charges on the CNTs surface via suitable linker groups. Herein, several aromatic organic compounds, such as derivatives of pyrene, porphyrin and phthalocyanine, can adsorb on the CNTs surface via π - π stacking. In a polar medium, the major contributions to π - π stacking result from electrostatic interactions, van der Waals interactions, and/or hydrophobic interactions between CNTs surface and aromatic compounds [20,22]. The straightforward preparation has also the advantage of maintaining the structure of the CNTs [23], similar to noncovalent (supramolecular) attachment method.

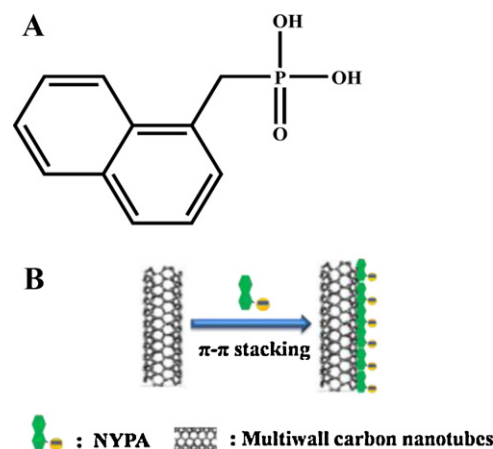
Phosphonates and organophosphates are structurally similar. The organophosphate has four oxygens with an alkyl group connected via a phosphoester bond, while the phosphonates have three oxygens with a carbon attached directly to phosphorus. The lack of the hydrolyzable C–O–P linkage makes the phosphonate compounds more stable in aqueous solution than the organophosphate compounds [24]. The phosphonic acid groups ($-\text{PO}_3\text{H}_2$) terminated functional interface has been applied in various fields such

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as ZrP materials [25], gold surface modification [26,27], metal ion recognition [28], biomimetic membrane [29,30], electrochemical sensor [24,31–33] oriented nucleation of minerals [34], and enzyme immobilization [29,35–37], owing to its excellent biocompatibility, strong coordination ability and adjustable interfacial charge density, etc. Up to now, the carboxylated CNTs and the sulfonated CNTs have been extensively studied and used in various fields. Surprisingly, little attention has been given to the phosphonate functionalized CNTs. To the best of our knowledge, the phosphonate functionalized CNTs have thus far been reported in only two cases. In both cases, the phosphonate functionalized CNTs were synthesized by covalent functionalization method. Namely, the phosphonate functionalized CNTs were prepared by reacting fluorinated CNTs (CNTs-F) with the 3-aminopropyl-phosphonic acid [38], or by reacting the carboxylated CNTs (CNTs-COOH) with 2-aminoethyl phosphonic acid [39,40]. Since phosphonic acid ($-\text{PO}_3\text{H}_2$) group is a dibasic acid, the electrostatic repulsion between $-\text{PO}_3^{2-}$ species is expected to be much stronger than that between $-\text{COO}^-$ or $-\text{SO}_3^-$ groups according to Coulomb's law [29]. Moreover, $-\text{PO}_3\text{H}_2$ groups are extremely hydrophilic [41]. Such a strong electrostatic repulsion together with the excellent hydrophilic property of the $-\text{PO}_3^{2-}$ groups should facilitate the solubility of the CNTs [29]. However, phosphonate functionalized CNTs prepared by Pillai are insoluble in water [40], which may be attributed to the low functionalization degree due to the limitation of covalent modification.

Palladium (Pd) is an important noble metal that is widely recognized in heterogeneous catalysis, electroanalysis and hydrogen storage [42–49]. In order to disperse Pd nanoparticles (Pd-NPs) and to improve their catalytic efficiency, the CNTs are generally used as supporting materials due to their fascinating structures and electrical/mechanical properties [50–52]. For synthesis of Pd/CNTs nanocomposites, it is necessary to functionalize the graphitic surfaces of the CNTs since the pristine surface of the CNTs is chemically inert and hydrophobic. The most commonly used method is to oxidize CNTs by various oxidizing agents to introduce hydrophilic O-containing groups on the CNTs surface [3], which can effectively anchor and deposit Pd-NPs. It is worth noting that the CNTs are not ideal structures, but rather contain defects formed during synthesis. Typically around 1–3% of the carbon atoms of a nanotube are located at a defect site [53]. A frequently encountered type of defect is the so-called Stone–Wales defect, which is comprised of two pairs of five-membered and seven-membered rings [19,51]. Moreover, the ends of the CNTs are composed of five-membered rings. The previous reports have indicated five-membered and seven-membered rings at CNTs are more reactive than fullerenes at side walls of the CNTs [19,54]. Thus, functionalization of the side walls comprising the regular graphene framework is more difficult to accomplish. Indeed, O-containing surface groups are typically concentrated around the ends and the defects of the CNTs rather than side walls of the CNTs during oxidation treatment of the CNTs. Consequently, metal or metal oxides NPs are selectively immobilized at the ends and the defects of the CNTs during the synthesis of NPs/CNTs nanocomposites [55,56].

Direct formic acid fuel cells (DFAFCs) have attracted more and more attention as a new generation of environment-friendly portable power source with high operating power density [57,58]. The success of DFAFCs largely depends on the design and the preparation of the high performance anode catalyst [58–66]. Recent investigations have suggested that Pd catalysts, an inexpensive non-Pt catalyst, possess far better electrocatalytic activity for formic acid oxidation than Pt catalysts. In the present work, the water-soluble phosphonate functionalized multiwall carbon nanotubes (MWCNTs) were for the first time synthesized by π - π stacking interaction between naphthalen-1-ylmethylphosphonic acid (NYPA, shown in Scheme 1A) and MWCNTs. The resulting



Scheme 1. (A) Structure of naphthalen-1-ylmethylphosphonic acid (NYPA); (B) Schematic noncovalent functionalization of MWCNTs with NYPA.

phosphonate functionalized MWCNTs were further deposited with Pd-NPs as electrocatalyst for formic acid oxidation. Structural characterizations revealed that the well-dispersed Pd-NPs with an average size of 3 nm were loaded on the phosphonate functionalized MWCNTs surface. Electrochemical measurements displayed that the Pd-MWCNTs nanocomposites had the excellent electrocatalytic performance for formic acid oxidation.

2. Experimental

2.1. Reagents and chemicals

Crude multiwall carbon nanotubes (MWCNTs) (>95% purity; outer diameter 35–60 nm; inner diameter 25–40 nm; length 5–10 μm ; surface area: $180.6\text{ m}^2\text{ g}^{-1}$) used in this study were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, which were prepared by a catalytic decomposition method of hydrocarbons. The synthetic naphthalen-1-ylmethylphosphonic acid (NYPA) was gifted by Dr. Pengfei Wang at Nanjing University. Palladium chloride (PdCl_2) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and used without further purification. All the aqueous solutions were prepared with Millipore water having a resistivity of $18.2\text{ M}\Omega$.

2.2. Purification of the MWCNTs

Crude MWCNTs were purified by oxidation method [21]. Briefly, MWCNTs were pretreated carefully with concentrated HCl (12 M) for 2 h and concentrated HNO_3 (14 M) for 2 h at 50°C , consecutively. After filtration and dryness, ICP analysis showed metal (Fe, Co, Ni and La) loadings of the MWCNTs was lower than 1.5 mg g^{-1} , indicating the metal particles contained in the MWCNTs as the synthesis catalyst during production were removed. Meanwhile, XPS measurement indicated the oxidation method resulted in the generation of the oxygenous functional groups on the MWCNTs surface (Fig. S1). Theoretically, the produced oxygenous functional groups affected the surface modification of MWCNTs via π - π stacking method due to the space hindrance effect. Thus, possible surface functional groups like $-\text{OH}$ and $-\text{COOH}$ on the pretreated MWCNTs surface were removed by heat treatment at 500°C for 3 h in N_2 [22]. After the heat treatment, the reversible redox peaks of the oxidative MWCNTs [67] disappeared (Fig. S2), confirming the surface of MWCNTs had been cleaned successfully.

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