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Ionic liquids-noncovalently functionalized multi-walled carbon nanotubes decorated with palladium nanoparticles: A promising electrocatalyst for ethanol electrooxidation

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ABSTRACT

A new palladium-based electrocatalyst (Pd/PDIL-MWCNTs) with ionic liquids molecules derived from 3,4,9,10-perylene tetracarboxylic acid (PDIL) noncovalently functionalized multi-walled carbon nanotubes (PDIL-MWCNTs) decorated with palladium nanoparticles is fabricated through a facile and surfactant-free synthetic technique. Due to the introduction of PDIL molecules, the Pd/PDIL-MWCNTs remarkably possesses smaller mean nanoparticles (NPs) size, better distribution of Pd NPs and larger electrochemical active surface area than the Pd NPs immobilized on the MWCNTs and the harsh acid treated MWCNTs (AO-MWCNTs). Furthermore, the Pd/PDIL-MWCNTs exhibits the enhanced electrocatalytic activity and improved stability for ethanol electrooxidation compared with Pd/MWCNTs and Pd/AO-MWCNTs, owing to the role of PDIL functional molecules. Additionally, a possible synergistic mechanism of PDIL-MWCNTs and Pd NPs for ethanol electrooxidation is also proposed on the basis of the previous literatures and the experimental results. The results indicate that the PDIL-MWCNTs is a promising support for electrocatalyst and the Pd/PDIL-MWCNTs catalyst may be a well candidate for direct ethanol alkaline fuel cells.

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Introduction

Direct ethanol fuel cells (DEFCs), a new promising kind of sustainable biomass-derived energy technology, has drawn

increasing attention due to ethanol has advantages of non-toxicity, low permeability and high theoretical mass energy density (8 Kw h kg^{-1}) compared with other fuel types [1–4]. In addition, ethanol can be easily produced in large quantities by the fermentation of biomass [5]. Especially in an alkaline

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medium, the electrode ethanol electrooxidation kinetics in this medium is higher than in the acid medium [2]. Therefore, designing and synthesizing an efficient anode catalyst with a high ability to break the C–C bond of the ethanol molecule at low overpotential and a high tolerance to the partially oxidized products is crucial for direct ethanol alkaline fuel cells (DEAFCs) technologies. For decades, Pt-based catalysts have been extensively investigated and proved as good electrocatalysts for DEAFCs [6,7]. However, the widely application of Pt-based catalysts as anodes in DEAFCs is limited by the high cost, limited resource, susceptible for deactivation and vulnerability toward poisoning by intermediate products for Pt [8]. Nowadays, Pd is considered to be a promising alternative to Pt on ethanol electrooxidation in alkaline medium since it is much cheaper, more abundance, and possesses higher electrocatalytic activity and greater resistance to intermediate products than Pt-based catalysts [9–14]. Although Pd has shown marked superiority compared to Pt, more efforts still needed to further improve its electrocatalytic performance so as to meet the application requirements of DEAFCs [15].

Considering the immobilization of the catalyst nanoparticles (NPs) on a suitable support is an ideal goal for maximizing the utilization rate of catalyst, it is one of the key factors for improving the catalytic activity to choose a suitable support [16]. Consequently, the seeking and developing novel catalyst supports is an effective approach to enhance electrocatalytic activity. Currently, carbonaceous supports, such as Vulcan XC-72 carbon black, ordered mesoporous carbons (OMCs), carbon nanofibers (CNFs), multi-walled carbon nanotubes (MWCNTs), graphene and so on, are commonly used as supports for DEAFCs [10,11,17–22]. Due to its high specific surface area, electrical conductivity and good thermal stability, MWCNTs is an ideal catalyst support system [23–27]. Unfortunately, pristine MWCNTs used in such applications are hindered by their agglomeration, poor dispersibility and insufficient binding sites for anchoring the precursors of NPs. In order to solve these problems, surface functionalization of MWCNTs is usually carried out by chemical oxidation, covalent or noncovalent functionalization [28]. As one of the most common strategies, the aggressive oxidation treatment with HNO_3 or $\text{HNO}_3\text{--H}_2\text{SO}_4$ mixture can introduce carboxyl groups onto the MWCNTs surface which can improve the hydrophilicity of MWCNTs and anchor the NPs by coordination or electrostatic interaction. However, such harsh acid oxidation inevitably causes some structural damage of MWCNTs and leads to the loss of their electronic conductivity and corrosion resistance [29]. Compared to covalent methods, the noncovalent strategies through supermolecular interactions such as $\pi\text{--}\pi$ stacking is easy to operate and can preserve the intact electronic structure of MWCNTs [28]. Furthermore, MWCNTs will be endowed with other properties when it is combined with functionalized molecules through noncovalent methods [29]. Ionic liquids (ILs) are finding increasing applications in various diverse fields because of its high ionic conductivity, wide temperature liquid range, environment friendly green nature, wide electrochemical stability window and good thermal stability [30–32]. As our reports, ILs grafted onto the supports not only is beneficial for preparing the small mean NPs size, narrow size distribution and well distribution of NPs but also

can remarkably enhance the conductivity and catalytic activity [10,33]. In addition, the ionic liquids derived from 3,4,9,10-perylene tetracarboxylic acid (PDIL) promotes the ethanol electrooxidation [34]. Furthermore, the PDIL have the advantages compared with other surfactants. A great amount of surfactants are used to prepare NPs and a lot of post-processing is needed to remove the excess surfactant preventing the catalyst surface is covered. However, the PDIL do not need to be removed. Additionally, the PDIL molecules produced a large number of imidazole groups with charge served as surfactants or protective agents through electrostatic interaction and coordination to prevent the agglomeration and loss of NPs during the reaction process.

On the base of the excellent properties of Pd NPs, MWCNTs and ILs, a new electrocatalyst (Pd/PDIL-MWCNTs) with ionic liquids functional derived from 3,4,9,10-perylene tetracarboxylic acid (PDIL) noncovalently functionalized multi-walled carbon nanotubes decorated with palladium nanoparticles was fabricated through a facile and surfactant-free synthetic technique, aiming to design and develop efficient ethanol electrooxidation anode catalysts for DEAFCs. The morphology, structure, component and dispersibility in water of as-prepared catalyst were investigated by systematic characterization. Furthermore, the Pd/PDIL-MWCNTs was applied in DEAFCs and the electrocatalytic activity and durability was studied under half-cell conditions. In addition, a possible synergistic mechanism of PDIL-MWCNTs and Pd NPs for ethanol electrooxidation was also proposed on the basis of the previous literatures and the experimental results.

Experimental sections

Materials

High-purity multi-walled carbon nanotubes (MWCNTs) were supplied by Chengdu Organic Chemicals Co. Ltd, Chinese Academy of Sciences (Chengdu, PR China). All analytically pure reagents were used as received without any further purification. Water used in the experiments was deionized and doubly distilled.

Synthesis of PDIL and preparation of PDIL-MWCNTs and AO-MWCNTs

The PDIL was synthesized according to our previous reported literature [33].

The pristine MWCNTs (50 mg) was ultrasonicated in deionized water (50 mL) containing of PDIL (25 mg) for 12 h. After that, the mixture was filtered through membrane and washed repeatedly with absolute ethyl alcohol and distilled water for several times. The final products were dried in vacuum oven at 60 °C overnight.

The acid oxidized MWCNTs (AO-MWCNTs) were obtained by refluxing pristine MWCNTs (100 mg) in a mixture of concentrated sulfuric acid and nitric acid (3:1, 60 mL and 20 mL, respectively) under at 80 °C for 60 min. Then resulting mixture was diluted with distilled water and filtered repeatedly until the pH of the filtrate was neutral. The sample was then dried at 60 °C overnight under vacuum.

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