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Multiwall-carbon nanotube modified by N-doped carbon quantum dots as Pt catalyst support for methanol electrooxidation

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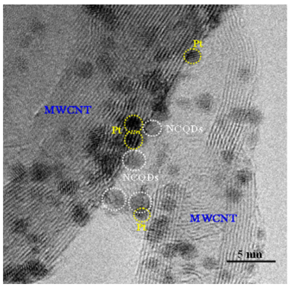
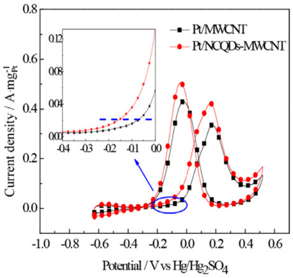
HIGHLIGHTS

- The modification of NCQDs is an innovative approach to change the properties of MWCNT.
- NCQDs-MWCNT support has been successfully synthesized by a facile hydrothermal treatment.
- NCQDs can improve the dispersion of MWCNT and Pt nanoparticles.
- The electrochemical performance of Pt/NCQDs-MWCNT catalyst is superior to that of Pt/MWCNT.

GRAPHICAL ABSTRACT





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ABSTRACT

The modification of N-doped carbon quantum dots (NCQDs) is an innovative approach to change the properties of multiwall-carbon nanotube (MWCNT). Here we report a facile hydrothermal treatment to synthesize NCQDs-MWCNT support, which acts as an improved catalyst support of Pt-based anode catalyst for direct methanol fuel cells. The structural properties of homemade catalysts are characterized by X-ray diffraction, Energy dispersive analysis of X-ray, transmission electron microscopy and X-ray photoelectron spectroscopy. The results indicate that Pt nanoparticles are well dispersed onto NCQDs-MWCNT and have a synergetic interaction with NCQDs. The results of electrochemical measurements reveal that Pt/NCQDs-MWCNT catalyst exhibits 1.3 times higher activity for methanol electrooxidation than that of Pt/MWCNT. The enhanced performance of Pt/NCQDs-MWCNT is attributed to the fact that NCQDs improve the dispersion of MWCNT and more uniform Pt nanoparticles are stabilized on NCQDs-MWCNT. NCQDs play a critical role in electrocatalytic performance for methanol electrooxidation.

1. Introduction

Direct methanol fuel cells (DMFCs) are promising power conversion devices for stationary and mobile applications in view of their high energy efficiency and environmental friendly [1–3]. Although the DMFCs have rapid development in recent decades, high cost of noble metal, poor methanol oxidation activity and short-life durability for catalysts are major issues for the wide commercialization of DMFCs [4,5]. These problems have become the critical challenges for successful introduction of DMFCs into the market. The catalyst support plays a significant role in the activity and durability of catalyst due to its structure, surface properties and

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interaction with the catalyst. Therefore, the exploration of advanced catalyst support is a promising approach to improve the electrocatalytic performance [6–8].

In general, the conventional carbon black (Vulcan XC-72) is the most widely used support for the dispersion of Pt nanoparticles. Nevertheless, Vulcan XC-72 corrosion leads to the decrease of catalytic activity during the long term working of DMFCs [9,10]. In order to enhance the catalyst stability, such as carbon nanotube (CNT) [11–13] and graphene [14,15] are widely researched. Owing to large surface area, high chemical stability and good electric conductivity, CNT has been an attractive catalyst support. However, CNT is chemically inert and generally do not provide enough surface groups for Pt deposition [16]. Thus, it needs to modify the surface of CNT for the sake of improving the dispersibility.

Carbon quantum dots (CQDs), a new form of nanostructured carbon, which have attracted much attention in recent years because of their chemical and physical properties. Heteroatom doping into CQDs has been becoming a more powerful way to improve the properties of CQDs and broaden their applications in analysis and electrocatalysis [17,18], such as N-doped CQDs (NCQDs) [19] and S-doped CQDs (SCQDs) [20], etc. The particle size of NCQDs is generally below 10 nm and its surface is functionalized by polar organic groups such as carboxylate, and/or hydroxyl groups and/or animo groups [21–23]. Furthermore, NCQDs can provide a promising way to tailor the transport properties of catalyst support for electronic applications [24]. The electronic structures of the host can be greatly modified by NCQDs, the oxygen-containing groups on NCQDs have been proposed to improve hydrophilicity in solution [25,26]. Therefore, NCQDs by virtue of their unique structural properties and good water-soluble have been applied to aspects of catalysis and electrochemistry [27].

Herein, in this work, we have designed an innovative support that multiwall-carbon nanotube (MWCNT) combined with NCQDs by one simple hydrothermal treatment and then synthesized Pt/NCQDs-MWCNT anode catalyst through microwave-assisted polyol process (MAPP). The results indicate that Pt catalyst supported on NCQDs-MWCNT presents the higher electrochemical activity for methanol electrooxidation. The effects of NCQDs on the catalytic performance of Pt catalyst are also investigated in detail.

2. Experimental

2.1. Materials

Ethylenediamine tetraaceticacid disodium salt (EDTA) was purchased from Aladdin, Shanghai, China. MWCNT (with pristine specific surface areas is between 180 $m^2 g^{-1}$ and 200 $m^2 g^{-1}$ and diameter size is between 10 nm and 20 nm) was obtained from Chengdu Institute of Organic Chemistry, China. Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Shanghai, China. 5 wt.% Nafion solution was purchased from Dupont. Except where specified, all chemicals were of analytical grade and used as received.

2.2. Experimental

2.2.1. Synthesis of NCQDs-MWCNT support

The NCQDs-MWCNT composite support was synthesized from the untreated MWCNT and EDTA by a facile one-step hydrothermal treatment. First, 20 mg of MWCNT and 3.0 g EDTA was dispersed in 30 mL of deionized water followed an ultrasonic treatment for 3 h. After that, the mixture was placed in a contraposition polyphenyl lined stainless-steel autoclave and heated at 200 °C for 12 h. After cooling down to room temperature, the slurry was taken out from the autoclave, washed with ultrapure water (Millipore, 18.2 MΩ cm) several times. The obtained NCQDs-MWCNT support was dried for 6 h at 80 °C.

2.2.2. Preparation of Pt/NCQDs-MWCNT and Pt/MWCNT catalysts

Pt/NCQDs-MWCNT catalyst was synthesized by microwave-assisted ethylene glycol process (MAPP) [28]. To produce 20 wt.% of Pt loading catalyst, 20 mg NCQDs-MWCNT support was dispersed into the mixed solution of 60 mL containing ethylene glycol (EG) and isopropyl alcohol (v/v = 4:1) in a 150 mL beaker under ultrasonic treatment for 1 h to form uniform slurry. After the suspension was stirred for 3 h, and then adding a calculated amount of H_2PtCl_6-EG solution with agitation for 3 h. The pH value of mixture was adjusted to 12.0 with NaOH-EG (1 mol L^{-1}) solution and suspension was heated for 55 s under the argon saturated by microwave oven. The HNO_3 aqueous solution was added into mixture when the solution was cooled down to room temperature to adjust pH value of the solution to about 2–3. The suspension was stirred for 12 h by mechanical agitation and the product was washed several times with deionized water and dried under vacuum at 80 °C for 5 h. The 20 wt.% Pt/MWCNT catalyst was synthesized by the same procedures for preparing the Pt/NCQDs-MWCNT.

2.3. Catalyst characterization

2.3.1. X-ray diffraction (XRD)

Crystal structure in catalyst was obtained by XRD analysis with the D/max-RB diffractometer (made in Japan) using a Cu Ka X-ray source operating at 45 kV and 100 mA, scanning between 10° and 90° at a rate of 40° min^{-1}.

2.3.2. Transmission electron microscopy (TEM)

TEM images of all samples were characterized by using a TECNAI G2F30 field emission transmission electron microscope with a spatial resolution of 0.17 nm.

2.3.3. Ultraviolet–visible spectroscopy (UV–vis)

The UV–vis absorption spectra of NCQDs were recorded by a Perkin–Elmer Lambda 20 spectrometer with 1 × 1 cm quartz cuvette along the 1 cm length.

2.3.4. Fluorescence spectrometer

Fluorescence experiments of NCQDs were performed by a Hitachi FL-4500 fluorescence spectrometer.

2.3.5. X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out on PHI model 5700 instrument from Physical Electronics Corporation to determine the surface properties of the catalysts. The Al Kα X-ray source was operated at 250 W and the take-off angle of the sample to analyzer was 45°. Survey spectra were collected at a pass energy (PE) of 187.85 eV over a binding energy range from 0 eV to 1300 eV. High binding energy resolution multiplex data for the individual elements were collected at a PE of 29.55 eV. During all XPS experiments, the pressure inside the vacuum system was maintained at 1×10^{-9} Pa.

2.3.6. Energy dispersive analysis of X-ray (EDX)

All energy dispersive X-ray detector spectrum (EDX) measurements were performed with a scanning electron microscope (SEM, Hitachi Ltd. S-4700).

2.4. Electrochemical measurement

Electrochemical measurements were performed with CHI 650E