



Platinum/nitrogen-doped carbon nanoparticles synthesized in nitrogen-doped carbon quantum dots aqueous solution for methanol electro-oxidation



Aofeng Zhang, Xingwei Li*, Ying He

Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, PR China

ARTICLE INFO

Article history:

Received 8 May 2016

Received in revised form 20 July 2016

Accepted 21 July 2016

Available online 25 July 2016

Keywords:

Nitrogen-doped carbon quantum dots

Platinum catalysts

Nanoparticles

Methanol electro-oxidation

ABSTRACT

Platinum-based catalysts are a key to develop direct methanol fuel cells, which are usually dispersed on carbon supports to enhance catalytic activity, stability and utilization. Here, platinum/nitrogen-doped carbon (Pt/N-C) nanoparticles are synthesized in nitrogen-doped carbon quantum dots (N-CQDs) aqueous solution, and catalytic performance of Pt/N-C catalysts is researched for methanol electro-oxidation. Compared with Pt catalysts supported on commercial carbon black Vulcan XC-72 (Pt/XC-72), the peak current densities of Pt/N-C catalysts are $0.59 \text{ mA cm}^{-2} \text{ Pt}$ and $385.2 \text{ A g}^{-1} \text{ Pt}$ in $0.5 \text{ M CH}_3\text{OH}$ and $0.5 \text{ M H}_2\text{SO}_4$, while those of Pt/XC-72 catalysts are $0.39 \text{ mA cm}^{-2} \text{ Pt}$ and $64.8 \text{ A g}^{-1} \text{ Pt}$. After polarizing 7200 s at a fixed potential of 0.15 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$), the catalytic activities of Pt/N-C are $0.14 \text{ mA cm}^{-2} \text{ Pt}$ and $86.5 \text{ A g}^{-1} \text{ Pt}$, and those of Pt/XC-72 are $0.02 \text{ mA cm}^{-2} \text{ Pt}$ and $2.6 \text{ A g}^{-1} \text{ Pt}$.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Direct methanol fuel cells (DMFCs) have been extensively studied as an ideal energy converter that directly converts chemical energy of methanol combustion to electrical energy [1–3]. Compared to other types of fuels, as a liquid fuel at ambient conditions, methanol is easily stored, transported, handled by the existing infrastructure, and with a high solubility in aqueous electrolytes. More importantly, methanol has a high energy density [3–5]. However, there are two key obstacles preventing DMFCs from successful commercialization: a high manufacturing cost and a sluggish kinetic rate of methanol electro-oxidation. In order to improve the poor kinetics of the methanol electro-oxidation reaction, appropriate anode catalysts have been regarded as a major contributor [3]. As has been demonstrated repeatedly, platinum-based catalysts play a key role in improving the poor kinetics of the methanol electro-oxidation reaction. Unfortunately, Pt catalysts are readily poisoned by intermediate carbonaceous species (mainly CO) during the methanol electro-oxidation reaction, consequently leading to a sharp decrease in electro-catalytic activity. In addition, rising Pt price, due to the scarcity of resources, also gives a high cost. It has been confirmed that the

control of distribution and morphology of Pt catalysts on supporting materials can offer effective assistance in improving catalytic activity and durability [6–9]. The excellent supporting materials should have the following characteristics: (1) a large specific surface area to achieve a high metal catalysts loading and a uniform dispersion; (2) a good stability under harsh electrochemical conditions; (3) a high electrical conductivity to promote electron transfer during the electrode reaction; (4) a strong interaction with metal catalysts to ensure the stability of the dispersed catalysts. So far, carbon materials have attracted immense and persistent attention, because they have extraordinary physical properties, abundance, processibility, environmental friendliness and relative stability in both acidic and basic media. And many studies suggest that carbon materials as catalyst supports, including carbon nanotubes [10,11], porous carbon [12,13], graphene [14] and graphene oxide [15], can improve performance of Pt-based catalysts. Currently, Vulcan XC-72 carbon black is the best commercial supporting material, but there are still some shortcomings, including low Pt loading, unsatisfactory catalytic activity and durability. Therefore, it is still a big challenge to develop new carbon supports and improve existing carbon materials.

Last few years, carbon quantum dots (CQDs), as a new member of the carbon family, have been used in many fields due to good water solubility, biocompatibility, low cytotoxicity, excellent conductivity and optical properties [16–20]. It is particularly

* Corresponding author.

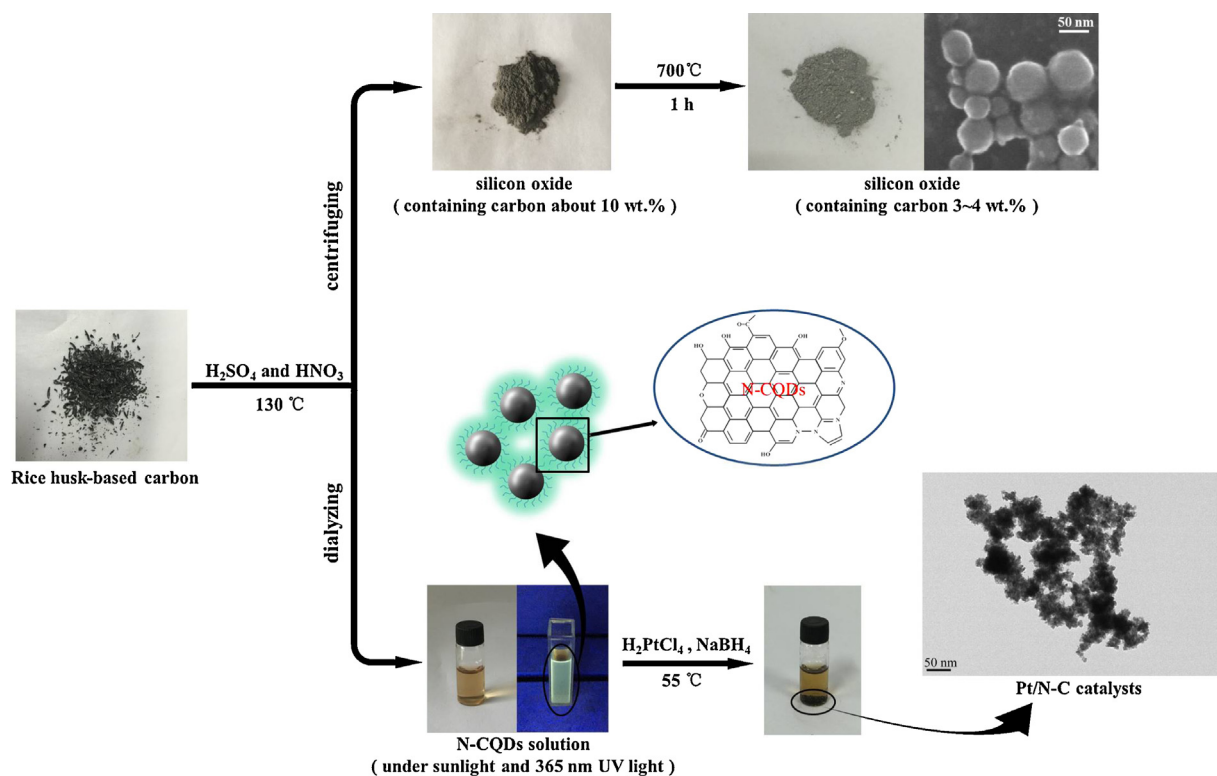
E-mail addresses: lixingwei_nj@yahoo.com, lixw_nj@126.com (X. Li).

worth mentioning that CQDs can be easily modified and doped by a simple chemical method due to their unique chemical structure thereby obtaining desired properties. Recently, ultra-small size of CQDs with an outstanding stability and a good electrical conductivity makes them interesting contenders as electrocatalysts supports for oxygen reduction. For example, He G. Q. et al. [21] prepared graphene quantum dots (GQDs) from carbon fibers, and obtained Pt catalysts supported on GQDs (Pt/G). For oxygen reduction in acid electrolyte solutions, Pt/G catalysts exhibited an enhanced electrocatalytic performance with a more positive onset potential, higher specific activity as well as stability, as compared to commercial Pt/C. In another work, the silver nanoclusters supported on CQDs were synthesized through a facile and green approach with only glucose and AgNO_3 as precursors and without any other protecting ligand and reducing agent [22]. Silver nanoclusters also showed remarkable electrocatalytic performance towards oxygen reduction reaction. Moreover, Kang and co-workers [23] synthesized carbon quantum dot/NiFe layered double-hydroxide composite as a highly efficient electrocatalyst for oxygen evolution reaction (OER).

The structure of carbon materials can also be changed via hetero atoms doping, thus effectively controlling its intrinsic properties, including electronic property, surface structure and chemical state [24–27]. Currently, nitrogen-doped carbon materials are of concern. Nitrogen-doped carbon materials have been proposed as supports for the metal-based catalysts. Such as, Zhang L. M. et al. [28] synthesized a novel nitrogen-doped carbon material with honeycomb-like mesoporous structure via carbonization of polyaniline under template and acted as a support for Pt catalysts. Authors think that an improved performance of Pt catalysts should be attributed to N species introduced to the support and optimal proportion of pyridinic N, pyrrolic N and graphitic N. Some studies also have shown that nitrogen-doped carbon quantum dots (N-CQDs) with abundant structural defects can promote charges

transfer from catalysts to reactants as well as to improve the dispersal of Pt catalysts, because amounts of defects at surface and edge can generate more active sites [21,29–31]. Several methods have been used to synthesize N-doped carbon quantum dots. For instance, N. Parvin et al. [32] reported the synthesis of a highly fluorescence nitrogen-doped carbon quantum dots bioimaging probe. N-doped carbon quantum dots (N-CQDs) were synthesized by the hydrothermal treatment of agarose and ethylenediamine. In this work, mono-dispersed N-CQDs averaging 4.5 nm in diameter were achieved in a quantum yield of 74.16%. Li Y. et al. [33] developed a simple electrochemical strategy for generating nitrogen-doped graphene quantum dots (N-GQDs) by using N-containing tetrabutylammonium perchlorate (TBAP) in acetonitrile to introduce N atoms into the resultant graphene quantum dots in situ. In another study, Shen J. H. et al. [34] presented a simple hydrothermal treatment of melamine and glutaraldehyde to synthesize carbon-nitrogen quantum dots (N-CQDs). The resulting carbon-nitrogen quantum dots have a uniform morphology, with a size of ca. 5 nm, plentiful oxygen and nitrogen functional groups, and a high N/C atomic ratio of ca. 20.7%. Furthermore, Te-Fu Yeh et al. [35] reported N-doped graphene oxide quantum dots as photocatalysts for water-splitting under visible light illumination, which N-doped graphene oxide quantum dots were synthesized by treating graphene oxide in NH_3 at 500 °C, and then subjecting the NH_3 -treated graphene oxide to oxidation using a modified version of Hummers' method. Natural nitrogen-containing biomass materials are usually selected as raw materials for synthesizing N-doped carbon quantum dots, such as, Zhu C. Z. et al. [36] developed a simple, low cost and green strategy toward water-soluble, N-doped fluorescent carbon nanodots by the hydrothermal treatment of soy milk. In addition, there were also fruit juice [37], animal hair [38] and plant fiber [39].

In this study, rice husk-based carbon is used as a nitrogen-containing carbon. Firstly, N-doped carbon quantum dots



Scheme 1. Schematic illustration of the preparation process for Pt/N-C catalysts.

Download English Version:

<https://daneshyari.com/en/article/6605656>

Download Persian Version:

<https://daneshyari.com/article/6605656>

[Daneshyari.com](https://daneshyari.com)