Journal of Power Sources 275 (2015) 734–741

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Design and synthesis of palladium/graphitic carbon nitride/carbon black hybrids as high-performance catalysts for formic acid and methanol electrooxidation

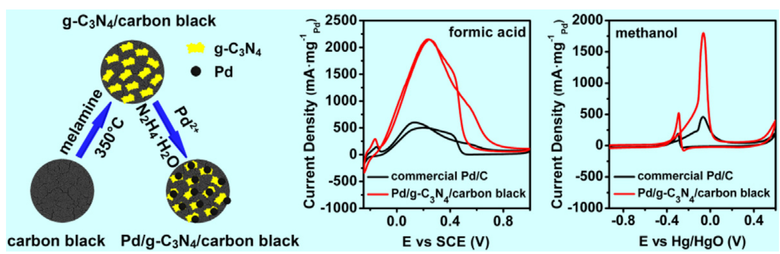
Huayu Qian [1], Huajie Huang [1], Xin Wang*

Key Laboratory for Soft Chemistry and Functional Materials of Ministry Education, Nanjing University of Science and Technology, 210094 Nanjing, China

HIGHLIGHTS

- A Pd/g-C_3N_4/carbon black hybrid is designed and synthesized.
- The hybrid shows excellent catalytic activity for formic acid and methanol electrooxidation.
- The catalyst also exhibits unusual poison tolerance and reliable stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 August 2014
Received in revised form
12 October 2014
Accepted 20 October 2014
Available online 12 November 2014

Keywords:
Carbon black
Graphitic carbon nitride
Palladium
Direct formic acid fuel cells
Direct methanol fuel cells

ABSTRACT

Here we report a facile two-step method to synthesize high-performance palladium/graphitic carbon nitride/carbon black (Pd/g-C_3N_4/carbon black) hybrids for electrooxidizing formic acid and methanol. The coating of g-C_3N_4 on carbon black surface is realized by a low-temperature heating treatment, followed by the uniform deposition of palladium nanoparticles (Pd NPs) via a wet chemistry route. Owning to the significant synergistic effects of the individual components, the preferred Pd/g-C_3N_4/carbon black electrocatalyst exhibits exceptional forward peak current densities as high as 2155 and 1720 mA mg^{-1}_{Pd} for formic acid oxidation in acid media and methanol oxidation in alkaline media, respectively, far outperforming the commercial Pd-C catalyst. The catalyst also shows reliable stability, demonstrating that the newly-designed hybrids have great promise in constructing high-performance portable fuel cell systems.

1. Introduction

As environmentally friendly power sources, fuel cells are one of the most promising sources for portable, transportation and stationary applications [1]. Among the various types of fuel cells, direct methanol fuel cells (DMFCs) and direct formic acid fuel cells (DFAFCs) have attracted great attention owing to their high-energy conversion efficiency, low working temperature, low pollutant emission and ease of handling and processing of the liquid fuels [2].

Platinum is the most efficient and commonly used electrocatalyst for accelerating chemical reactions in both DMFCs and DFAFCs. However, Pt-based catalysts suffer from a number of problems such as the high cost and the poor poison tolerance, hampering the widespread application of fuel cells. Accordingly, a great deal of efforts has been aimed at developing more abundant non-platinum catalysts that can offer acceptable performance [3]. Among the studied non-Pt catalysts, Pd-based anode catalysts have received increasing attention because of their lower cost, superior

* Corresponding author.
E-mail address: wangx@njust.edu.cn (X. Wang).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jpowsour.2014.10.109
0378-7753/

activity and greater resistance to CO in comparison with Pt-based catalysts [4–6].

On the other hand, it is known that the metal nanoparticles can be well dispersed on carbon supports with high electrical conductivity and high stability [7], such as carbon black [8], carbon nanofibers [9], fullerenes [10], carbon nanotubes [11], graphene [6,12] and so on. Of those carbon materials, Vulcan XC-72R carbon black is the most popular electrocatalyst support owing to its low cost, high availability, large surface area, high electrical conductivity and suitable pore structure [7]. Nevertheless, carbon black presents some disadvantages when used as catalyst support for fuel cells, for example, porous electrically conductive carbon blacks do not have enough corrosion resistance [13]. Surface modification is a general approach to mitigation of corrosion, such as functionalization by sulfonates, carboxylates, tertiary amines, and steric polymers/oligomers [14,15]. Another way to modify pure carbons is to dope the respective materials with heteroatoms and a suitable doping may lead to a remarkably enhanced performance [16]. Increasing evidences show that the electrochemical property of carbon materials is sensitive to the doped heteroatoms [17]. In particular, the doped nitrogen atoms have an obvious effect on the surface chemical activity and could change surface properties such as polarity, basicity, adsorption ability and heterogeneity [18].

Graphitic carbon nitride (g-C_3N_4) is the most stable allotrope of carbon nitride and has attracted intensive interest for its promising applications ranging from photocatalysis, heterogeneous catalysis, to fuel cells [19,20]. However, the electrochemical performance of g-C_3N_4 is not satisfactory owing to its low electrical conductivity [21]. To overcome this shortcoming, it is of interest to explore the possibility of the combination of g-C_3N_4 with well-conductive carbon black to obtain novel support material presumably endowed with exceptional properties for electrochemical catalysis.

In this study, a Pd/g-C_3N_4/carbon black catalyst has been successfully synthesized through a two-step approach. As illustrated in Scheme 1, melamine and carbon black were first mixed together via a facile ultrasonic process. After heating treatment at 350 °C in N_2 atmosphere for 1 h, the protonated melamine could polymerize to form *s*-triazine ring-based structure and bond with oxygen-containing groups on the surface of carbon black, forming g-C_3N_4/carbon black hybrid supports. The use of a relatively low-temperature heat-treatment has the advantages of avoiding evaporation, sublimation and decomposition of melamine. Subsequently, Pd NPs were anchored on the surfaces of the as-prepared g-C_3N_4/carbon black via a wet chemistry method. Given its unique structural characteristics, the resulting Pd/g-C_3N_4/black catalyst shows excellent electrocatalytic performance for both formic acid and methanol electrooxidation, including high electrocatalytic activity and reliable stability.

2. Experimental

2.1. Materials

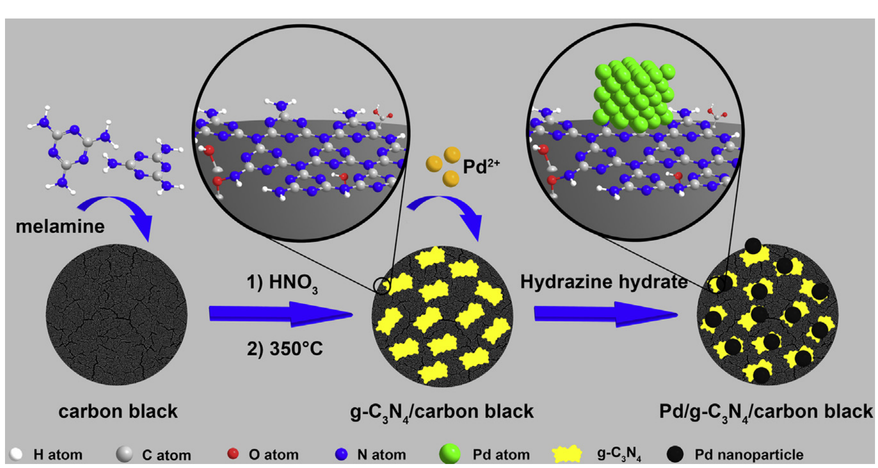
Vulcan XC-72R carbon black was purchased from Cabot Corporation. $Pd(NO_3)_2$ (≥99.99%) solution (0.94 M) was purchased from Shanghai July Chemical Co., Ltd. (Shanghai, China). Hydrazine hydrate (85%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion 117 (5%) solution was purchased from Dupont. Commercial Pd-C was purchased from Alfa Aesar (palladium, 20% on activated carbon powder, standard, reduced, nominally 50% water wet). All other chemicals employed were of analytical grade and used as received. All aqueous solutions were prepared using deionized water.

2.2. Synthesis of g-C_3N_4/carbon black

Typically, 1500 mg of Vulcan XC-72R was mixed with 150 mL of nitric acid (68%), and stirred for 1 h under room temperature. The mixture was transferred into a 200 mL Teflon-lined stainless steel autoclave and heated to 120 °C. After 12 h of solvothermal treatment, the resulting acid-treated Vulcan XC-72R was isolated by centrifugation, washed and dried at 60 °C. Afterwards, g-C_3N_4/carbon black with different dosages of melamine were synthesized. The typical experiment procedure for the synthesis of g-C_3N_4/carbon black (the weight percentage of melamine in the raw materials is 50%) is as follows: 100 mg of as-obtained acid-treated Vulcan XC-72R and 100 mg of melamine were dispersed in 4.4 mL ethylene glycol by sonication for 1 h. Then 14 mL of 0.1 M HNO_3 solution was added into the mixture drop by drop with vigorous stirring. The as-generated products were centrifuged, washed with absolute ethanol and dried at 60 °C. Subsequently, the dry samples were annealed at 350 °C in N_2 atmosphere for 1 h with a heating rate of 5 °C per minute and the product was labelled as gCN-CB-50. The other g-C_3N_4/carbon black catalysts were denoted as gCN-CB-x, where x is the weight percentage of melamine in the raw materials.

2.3. Synthesis of Pd/g-C_3N_4/black electrocatalysts

In a typical synthesis route, 10 mg of gCN-CB-50 was dispersed in 20 mL ethylene glycol to obtain uniform dispersion with



Scheme 1. Illustration of the synthesis of a Pd/g-C_3N_4/carbon black hybrid by our two-step wet chemistry method.