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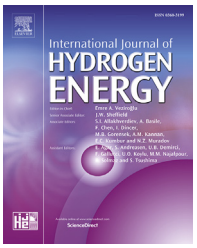

Reduced graphene oxide-poly-(2-(dimethylamino) ethyl methacrylate)-Pt/Ag nanoscrolls and its electrocatalytic performance for oxidation of methanol

Xiaoguang Jin, Xiaobei Wang, Yue Zhang, Hefang Wang, Yongfang Yang *

Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China

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ABSTRACT

The reduced graphene oxide-poly-(2-(dimethylamino)ethyl methacrylate)-Pt/Ag (RGO-PDMAEMA-Pt/Ag) nanoscrolls were prepared by rolling up the RGO-PDMAEMA-Pt/Ag sheets under freezing conditions. The compositions and structures of RGO-PDMAEMA-Pt/Ag sheets and nanoscrolls were characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). Because of the bimetallic synergetic effect and unique scrolled structure, RGO-PDMAEMA-Pt/Ag nanoscrolls show excellent catalytic performance and high electrochemical stability. The ECSA value of RGO-PDMAEMA-Pt/Ag nanoscrolls for Pt is 891 cm^2/mg, which is 1.28 times that of the RGO-PDMAEMA-Pt/Ag sheets (698 cm^2/mg). The ratio of the forward oxidation peak current to the reverse peak current is about 1.25. The electrochemical results indicate the RGO-PDMAEMA-Pt/Ag nanoscrolls are promising electrocatalysts for direct methanol fuel cell.

Introduction

Recently, direct methanol fuel cell (DMFC) has been popular because of its high energy utilization, high energy efficiency and less pollution. For DMFC, platinum (Pt) is one of the most widely used catalysts in methanol oxidation reactions [1,2]. However, the high cost and easy poisoning by carbon monoxide limit the application of Pt in catalytic field. To reduce the usage and the cost of Pt and improve its electrocatalytic performance, many attempts such as alloying with other electrochemically active and more plentiful metals [3,4], preparation of fine nanocatalysts [5,6] and high dispersion of Pt nanoparticles (NPs) on a support with high specific surface area [7], have been made. Over these years, Pt-based bimetallic catalysts have become one of the important classes of catalysts which can reduce the cost of electrical energy [8–10]. Pt-containing alloys such as PtNi [11], PtCo [12], PtSn [13], and PtCu [14] exhibit superior electrocatalytic activities, compared with monometallic counterparts. Among these metals, silver is regarded as one of the most popular transition alloy metals owing to its low cost and desired synergistic effect [15–18]. The bimetallic Pt-Ag alloy NPs attracted increasing attention owing to its improved activity in many reactions by forming new active sites and inducing synergistic effect. Yang et al. prepared the $PtAg_2$/C-D and $PtPd_3Ag_5$/C-D catalysts via a simple and effective chemical reduction to improve the electrocatalytic performance (about 3.35 times as high as that of Pt/C) [19].

* *Corresponding author.*
E-mail address: yyf@mail.nankai.edu.cn (Y. Yang).

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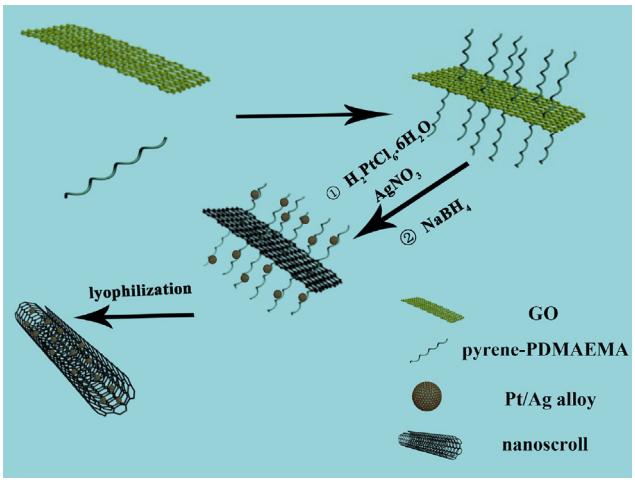
Before commercial viability of DMFC, another important issue to be solved is the long-term durability of electrocatalysts. During the long period of operation, the agglomeration of metal NPs leads to the reduction of catalytic performance. The agglomeration of metal NPs can be reduced by choosing a support which has strong interaction with metal. Therefore, it is necessary for DMFC to find a stable support in electrochemical and strong acid/alkaline environment to run long time.

Various types of carbon supports such as carbon Vulcan [20,21], graphene [22] and multiwall carbon nanotubes (MWNTs) [23] are often used to disperse Pt NPs to improve the electrocatalytic activity. As a new carbon nanomaterial, graphene nanoscrolls (GNSs), formed by rolling up the two-dimensional graphene sheets, possess the similar properties with the graphene sheets such as high thermal conductivity, excellent electrical conductivity and strong mechanical properties [24–26]. Besides, GNSs, with the open ends, adjustable interlayer galleries and diameter by intercalation or doping, became the optional candidate as the support to load metal NPs. Liu et al. synthesized Pt/reduced graphene oxide nanoscroll (Pt/RGOS) by oxygen implosion in situ rolling up of Pt/RGO sheets and found the Pt/RGOSs possessed significantly higher electrocatalytic activity and stability than Pt/RGO [27]. However, nanoscrolls prepared by rolling up the graphene sheets on which the bimetallic Pt-Ag alloy NPs dispersed have not been reported.

In the previous work, we reported a general method to prepare GO-PDA-Au nanoscrolls by rolling up the GO-PDA-Au sheets through lyophilization method [28]. In this study, to reduce the agglomeration of alloy metal NPs, PDMAEMA chains with pyrene terminal groups were introduced to GO sheets via π-π stacking interaction. PDMAEMA chains can act as a stabilizer to disperse metal NPs for its abundant nitrogen atoms which can interact with various metal ions such as Pt, Ag, Pd et al. During the formation of alloy NPs, GO sheets were reduced. The Pt/Ag alloy NPs were uniformly loaded on the surface of RGO-PDMAEMA sheets and were rolled up to form RGO-PDMAEMA-Pt/Ag nanoscrolls by a lyophilization method [29,30]. RGO-PDMAEMA-Pt/Ag nanoscrolls would have the excellent electrocatalytic activity owing to the synergistic effect of Pt/Ag bimetallic alloy and the long stability caused by the introduction of PDMAEMA to GO sheets which effectively avoid the aggregation and falling of Pt/Ag NPs and the unique scrolled structure which reduce the opportunity for metal poisoning. The structure and composition of bimetallic alloy on the GO-PDMAEMA sheets were characterized by XRD, XPS and the electrocatalytic activity of methanol oxidation were compared between RGO-PDMAEMA-Pt/Ag sheets and nanoscrolls. The RGO-PDMAEMA-Pt/Ag nanoscrolls will broaden application of graphene-based materials in eletrocatalytic field. The schematic illustration of the procedure for the preparation of RGO-PDMAEMA-Pt/Ag nanoscrolls is as follows in Scheme 1.



Scheme 1 – The schematic illustration of the procedure for the preparation of RGO-PDMAEMA-Pt/Ag nanoscrolls.

Experimental section

Materials

The GO sheets with the average sheets size of 10–20 μm were purchased from Zhejiang carbon Valley Mstar Technology Ltd. 2-(Dimethylamino) ethyl methacrylate (DMAEMA, 99%) was provided by Acros and was distilled under reduced pressure. Copper bromide (CuBr, 99.5%, from Guo Yao Chemical Company) was washed with glacial acetic acid and dried under vacuum. N,N,N′,N′,N″-Pentamethyldiethylenetriamine (PMDETA, 99%), 1-pyrenemethanol (98%) and 2-bromo-2-methylpropionyl bromide (98%) were purchased from Aldrich and were used without any further treatment. Triethylamine (AR grade) and THF (AR grade) were bought from Tianjin Chemical Reagent Company and distilled before use. Silver nitrate (AR grade, from Tianjin Yingda Rare Metal Chemical Reagents Company) and chloroplatinic acid (AR grade, from Shanghai Jiuding Chemical Reagents Company) were used directly.

Characterization

The structure of pyrene-Br and pyrene-PDMAEMA were characterized by nuclear magnetic resonance spectrometer (NMR 400 MHz). The apparent molecular weight and molecular weight distribution of pyrene-PDMAEMA were determined with gel permeation chromatography (GPC) equipped with a Hitachi L-2130 high-performance liquid chromatography (HPLC) pump. The structure of GO sheets and GO-PDMAEMA sheets were characterized by Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700 FTIR Spectrometric Analyzer) and thermogravimetric analysis (TGA) (Perkin–Elmer Thermal Analysis SDT/Q600), respectively. The structure of GO sheets, GO-PDMAEMA sheets and RGO-PDMAEMA-Pt/Ag sheets were characterized by X-ray diffraction (XRD) (a D8 Focus diffractometer with Cu Kα radiation), a UV-1800 PC and X-ray photoelectron spectroscopy (XPS) spectra (Kratos Axis Ultra DLD spectrometer employing a monochromated Al Kα X-ray source). The morphologies of the samples were observed by the field-emission transmission electron microscope (FEI-TEM, Tecnai G2 F20) and scanning electronic microscopy (SEM, Nova Nano SEM 450). The thickness of GO sheets and GO-PDMAEMA sheets were characterized by Atomic force microscopy (AFM) (Nanoscope IV atomic force microscope, Digital Instruments). All the products were measured by a Raman spectrometer (Renishaw inVia) with a 532 nm laser excitation source.

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