Materials Research Bulletin 102 (2018) 172–179

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Highly dispersive platinum nanoparticles supporting on polyaniline modified three dimensional graphene and catalyzing methanol oxidation

Yanli Wang[a,c], Zhongshui Li[a,b], Shuhong Xu[a], Yixin Xie[a], Shen Lin[a,b,*]

[a] College of Chemistry & Materials Science, Fujian Normal University, Fuzhou 350007, China
[b] Fujian Key Laboratory of Polymer Materials, Fujian Normal University, Fuzhou 350007, China
[c] College of Physics & Energy, Fujian Normal University, Fuzhou 350117, China

ARTICLE INFO

Keywords:
Platinum
Three dimensional graphene
Polyaniline
Methanol oxidation
Electrocatalysis

ABSTRACT

Direct methanol fuel cells have been attracting serious attention due to its high power density and low pollution, and huge effort has focused on its electrode catalysts. Here, a hydrothermal process was used to synthesize Pt/three dimensional graphene (polyaniline) catalyst (Pt/3D-GNs (PANI)), in which $PtCl_4^{2-}$ and graphene oxide (GO) were reduced synchronously. Especially, aniline was polymerized to form polyaniline (PANI) in situ, catalyzed by pre-generated Pt. After cooling by liquid nitrogen, graphene sheets (GNs) were converted into three dimensional (3D) corrugated graphene. The introduction of PANI promotes formation of 3D graphene structure and favors optimal distribution of Pt particles. Synergistic effect of 3D corrugated graphene structure, highly dispersive Pt nanopartilces and fast electron transfer of support makes Pt/3D-GNs (PANI) have superior electrocatalysis for methanol oxidation. Electrochemical tests show that Pt/3D-GNs (PANI) exhibits much higher electrocatalytic activity (1172 mA mg^{-1}), better stability and improved CO tolerance in comparison with commercial Pt/C.

1. Introduction

Direct methanol fuel cells (DMFCs) have been attracting more and more attention in recent decades, owing to its high energy conversion efficiency, ease of handling and processing, low operation temperatures and less pollutant emission [1–4]. Anodic catalyst is one of the key materials of DMFC, and its electrocatalytic activity plays an important role in the performance of fuel cell [5,6]. So an enormous effort has been dedicated to exploit novel catalyst systems with lower cost and longer durability. For example, Atar et al. [7] reported the synthesis of non-platinum Fe_3O_4@AuNPs/cys/rGO as an efficient electrocatalyst for methanol electro-oxidation. Colak et al. [8] reported a cost-effective Pt-PdNPs/NaPWO/GQDs catalyst, with large active surface area and high catalytic activity for methanol oxidation. Yu et al. [9] prepared a core-shell nanostructure AuPd@Pd NCs/N-RGOH catalyst, exhibiting enhanced catalytic activity and stability for methanol oxidation. Although non platinum-based catalysts exhibit valuable electrocatalytic activity for methanol oxidation in DMFCs, Pt-based catalysts still serve as the most popular and effective electrocatalysts for methanol oxidation because of its superior catalytic capacity [1–3,5]. However, its high cost, poor durability and vulnerability to CO_{ads} poisoning have limited their extensive use [3,5]. So the construction of Pt-based catalysts with desirable structure in combination with appropriate support materials to alleviate its drawbacks is much desired.

Three dimensional graphene sheets (3D-GNs) are a new type of graphene with ruffle and pore structure and can effectively tune itself electrical, mechanical and catalytic properties, so that it not only has the inherent physicochemical properties of graphene but also has greater surface area (rich porous micro/nano structure) and superior ability for electronic conduction and mass transfer, providing a unique pathway for rapid transfer and fast conduction of charge [10,11]. Generally, the composite materials formed by graphene and Pt can effectively reduce the oxidation potential of methanol and show high catalytic efficiency [12]. The continuous network structure of pores from 3D-GNs will provide a favorable reaction microenvironment for Pt active sites, so the combination of Pt and 3D graphene can prevent the agglomeration of composite and inhibit its fast decay of catalytic activity [13,14]. However, the surface inertia (hydrophobicity) of graphene sheet results in the weak interaction between Pt active sites and 3D graphene, obviously affecting the catalytic capacity of Pt based composites. Therefore, it is necessary to further modify the surface of 3D-GNs with some functional molecules, especially conductive polymers, such as polyaniline, polypyrrol and polythiophene [15,16]. It was reported that Selvaraj et al. [17] synthesized polypyrrole (PPy)

---

* Corresponding author at: College of Chemistry & Materials Science, Fujian Normal University, Fuzhou 350007, China.
E-mail addresses: 1060337271@qq.com (Y. Wang), zsli@fjnu.edu.cn (Z. Li), 932814695@qq.com (S. Xu), 2560578971@qq.com (Y. Xie), shenlin@fjnu.edu.cn (S. Lin).

https://doi.org/10.1016/j.materresbull.2018.02.028
Received 11 October 2017; Received in revised form 8 February 2018; Accepted 14 February 2018

modified multiwalled carbon nanotubes (MWCNTs) to support Pt-Ru nanoparticles, and obtained Pt-Ru/PPy-CNT catalysts exhibited excellent catalytic activity and stability towards methanol oxidation. And Zhao et al [18] prepared a new bimetallic Pt–Fe/PPy–carbon catalyst by in situ interfacial polymerization combined with metallic co-precipitation, showing high electrochemical activity for methanol oxidation.

As for conductive polymers, polyaniline (PANI) is one of the most promising conducting polymers due to its low cost, facile synthesis, and high pseudocapacitance [19]. It contains alternating single and double bonds, forming a large conjugated π electron system. The flow of π electrons can produce good conductivity, to endow PANI with many unique advantages in the application of electrode catalysis [20–24], such as good electrochemical activity and high oxidation corrosion resistance, characteristics of proton and electron conduction, strong electronic effects between metal nanoparticles and π electron conjugated structure of conducting polymer [25,26]. All of the advantages make it much suitable as a functional molecule to modify the inertia surface of graphene sheets and provide superior conductivity and high specific surface area as an appropriate catalyst support [27]. However, the introduction of PANI into graphene is generally via oxidant polymerization or interfacial polymerization in situ [27–29], in which additional reagents such as ammonium peroxydisulfate and iron trichloride are needed. These reagents can bring about residuals into PANI, damaging its advantages in synthesizing high catalytic capacity Pt-based catalysts. So how to realize the combination of PANI with graphene in situ without additional agent is also desired.

In this work, a novel polymerization method was developed to introduce PANI into graphene without additional oxidizing agents, in which the polymerization of PANI was realized in situ by the aid of the pre-generated Pt particles as a catalyst under hydrothermal conditions. In brief, the precursors of Pt and GNs were reduced synchronously in one pot hydrothermal process, and pre-generated Pt particles catalyze aniline polymerization reaction. Furthermore, the morphology of graphene was changed from planar to three-dimensional structure to obtain 3D corrugated Pt/3D-GNs (PANI) composite by rapid cooling the reaction products in liquid nitrogen. The as-synthesized Pt/3D-GNs (PANI) composite shows superior electrocatalytic performances during catalyzing DMFCs anodic reaction in comparison with the counterpart Pt/3D-GNs and the commercial available Pt/C catalyst (Pt/C-JM).

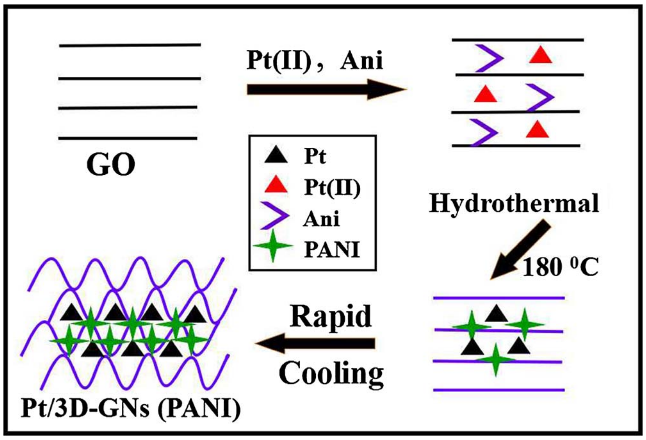
2. Experimental

2.1. Materials

Graphite powder (325 mesh, 99.9995%) was purchased from Alfa Aesar. K_2PtCl_4 (solid, 99.9%), P_2O_5 (solid, 99%), $KMnO_4$ (solid, 99%), $K_2S_2O_4$ (solid, 99%), $(NH_4)_2S_2O_4$ (solid, 99.9%), H_2O_2 (aq, 30%), H_2SO_4 (liquid, 98%), $HClO_4$ (liquid, 72%), $C_6H_5NH_2$ (liquid, 99.9%), C_2H_5OH (liquid, 99.9%), and CH_3OH(liquid, 99.9%) were all purchased from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China) and used without purification. The water used in all experiments was deionized to a resistivity of 18 MΩ cm.

2.2. Synthesis of Pt/3D-GNs (PANI), Pt//3D-GNs and GNs (PANI)

Graphene oxide (GO) were synthesized using a modified Hummers' method [30,31], and the detailed procedures were described previously [32–34]. The synthetic route of Pt//3D-GNs (PANI) was illustrated in Scheme 1. In a typical procedure, 50 mg of GO were dispersed in 25 mL of distilled water by sonication for 1 h. 10 uL aniline (Ani) was dissolved into 20 ml 1 M H_2SO_4 stirring for 30 min, then 5 mL of K_2PtCl_4 (1 g/100 mL) was added and sonicated for 30 min. After that, the mixture was put into the GO solution and further sonicated for 1 h to ensure sufficient mixing. Then the mixed suspension was transferred into a Teflon-lined stainless steel autoclave and reacted at 180 °C for 24 h under autogenous pressure. When hydrothermal synthesis is completed, autoclave was placed in liquid nitrogen for 1h to freeze rapidly. Afterwards, the product returned to room temperature, and the black suspension was purified through repeated centrifugation (at 10, 000 rpm for 20 min) and washing cycles to neutral pH. Finally, the black precipitate was lyophilized for 72 h and Pt/GNs (PANI) was obtained. For comparison, Pt/3D-GNs and GNs (PANI) were synthesized by similar procedure, with the absence of Ani and K_2PtCl_4, respectively. Their Pt actual contents were determined by ICP-AES (inductively coupled plasma-atomic emission spectroscopy), and it is shown that the mass loading of Pt/3D-GNs (PANI) and Pt/3D-GNs was 29.1% and 28.6%, respectively.



Scheme 1. The synthetic route of Pt/3D-GNs (PANI) composites.

2.3. Characterization

Infra-red (IR) spectra were recorded on a 380 FT-IR spectrophotometer (Nicolet). The microscopic feature and morphology of composites were characterized by a field emission scanning electron microanalyzer (FE-SEM, SU8010, HITACHI, Japan) and high-resolution transmission electron microscope (HRTEM, TECNAI G2, FEI, USA, 200 kv). The surface chemical state and bonding of composites were recorded by X-ray photoelectron spectrometer (XPS, VG ESCALAB 250, Thermo Scientific, USA) with monochromatic Al Ka radiation (1486.6 eV). Powder X-ray diffraction (XRD) patterns were determined at a scanning rate of 5° min^{-1} in the range of 10–90° (2θ) on a Philips X' pert Pro diffractometer (USA), using Cu Ka radiation. Raman spectra were investigated by a Renishaw-invia Raman micro-spectrometer equipped with a 514 nm diode laser excitation on a 300 lines mm^{-1} grating. The amount of actual Pt loading was analyzed by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICAP6300, Thermo Scientific, USA).

2.4. Electrochemical measurements

All electrochemical experiments were performed with a standard three-electrode cell using a CHI 660C electrochemical workstation (ChenHua, Shanghai, China) at room temperature. A saturated calomel electrode (SCE), a platinum electrode and the modified glassy carbon electrode were used as reference electrodes, counter electrode and working electrode, respectively. The working electrode was prepared as described previously, in brief, it was modified by pipetting 5 μL catalyst ink onto the surface of pre-polished GCE electrode (3.0 mm in diameter) [35]. Cyclic voltammetry (CV) was tested in 1 M NaOH + 1 M CH_3OH or 1 M $HClO_4$ solution at 100 mV s^{-1}. The CO stripping voltammograms were recorded by oxidation of preadsorbed CO in 1 M $HClO_4$ solution at 100 mV s^{-1}. CO gas was purged into 1 M $HClO_4$ solution at a constant potential of 0.1 V for 30 min to ensure the complete adsorption of CO onto the samples' surface. And the excess CO gas in the electrolyte was