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Amphoteric surfactant promoted three-dimensional assembly of graphene micro/nanoclusters to accomodate Pt nanoparticles for methanol oxidation

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ABSTRACT

An intelligent amphoteric surfactant (sodium lauryl aminopropionate) was introduced to the construction of 3D graphene micro/nanoclusters, which was used to the synthesis of platinum nanoparticles to obtain the Pt/3D graphene micro/nanocomposite. Owing to the unique pH induced charge transition and micellar arranging property of the amphoteric surfactant, a higher-order assembly of 3D porous graphene-based architectures from stacked graphene oxide layers can be readily achieved. More importantly, the as-made catalyst Pt/3D graphene exhibits unprecedented activity, excellent CO tolerance and good stability towards methanol oxidation which can be attributed to the large surface area, efficient mass transport within the composite and the uniform distribution of small Pt NPs. These outstanding electrochemical properties make Pt/3D graphene a promising catalyst applied in direct methanol fuel cells.

1. Introduction

Direct methanol fuel cell (DMFC), which provides a promising way to convert chemical energy directly into electrical energy, has attracted extensive attention as green power sources for vehicles and portable electronics due to its high energy conversion efficiency, low emission, and simplicity in device fabrication. However, the practical application of DMFC is still hindered by the high cost of Pt catalyst and the sluggish methanol oxidation reaction [1,2]. Recently, developing novel carbon materials to support catalyst has been demonstrated as one effective way to enhance the catalytic activity and reduce the usage of Pt-based catalysts. Such support materials can not only maximize the availability of surface area of the nanosized electrocatalyst for electron transfer but also provide better mass transport of reactants to the electrocatalyst. Graphene (GN), a two-dimensional carbon material with single (or a few) atomic layer, has attracted great attention for both fundamental science and applied research. The combination of the extremely high specific surface area (theoretical value of 2630 $m^2 g^{-1}$), particular electronic conductivity and unique graphitized basal plane structure [3–5] makes graphene a promising candidate as anode catalyst support in DMFC. However, the strong planar stacking of 2D graphene sheets by forming irreversible agglomerates leads to a drastic loss of electroactive sites during the electrode assembly. More recently, a novel 3D graphene nanostructures have been reported [6–8], which opens up a new promising way for the application of graphene based materials. Exhibiting an open-pore honeycomb structure, this 3D graphene has an exceptionally large void volume, high surface area, high corrosion resistance and high electrical conductivity. All these properties make it ideal as the catalyst support material for fuel cell applications. However, the traditional preparation strategy, such as CVD [6], silica templated method [7] and noble-metal promoted assembly [8] usually suffers from high cost and tanglesome processing. To explore a more efficient approach to controllably prepare 3D graphene based micro/nanomaterials with low cost is still challenging.

Herein, we demonstrate a promising strategy by employing an intelligent mediator sodium lauryl aminopropionate to produce graphene based micro/nanocomposites with higher-order 3D architectures such as sponge-like macroporous scaffolds. Sodium lauryl aminopropionate ($C_{12}H_{25}NHCH_2CH_2COO^-Na^+$) (SLA) is a kind of amphoteric surfactants. Amphoteric surfactants have both

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cationic and anionic centers attached to the same molecule which feature the intrinsic ability to change in charge from cationic to anionic going from low to high pH. In this report, the amphoteric property of this surfactant plays a significant role for assembling Pt/3D graphene networks. The overall synthetic procedure leading to this micro/nanocomposite is illustrated in Fig. 1. Firstly, graphite oxide (GO) negatively charged were synthesized by a modified Hummers method [9]. Afterwards, the amphoteric surfactant which is positively charged in aqueous solution was added into GO suspension, in which the lamellar spacing of GO could be expanded with the surfactant intercalation via electrostatic interplay. Then NaOH was introduced to the above suspension leading to charge change of the surfactant from cationic to anionic, through which the stacked layers could be further separated via electrostatic repulsion. With the above treatment, the stacked interaction would be largely relaxed which was favorable for exfoliation through ultrasonication to generate GO clusters. In particular, under certain conditions, the surfactant micelle would be formed surrounding the GO cluster through compatible hydrophilicity which rendered GO more disciplined structures. Finally, after a co-reduction process the desired micro/nanocomposite with 3D structures could be obtained. Our results found that Pt nanoparticles with well-defined morphology and small size supported on 3D graphene frameworks could be facilely obtained. Electrochemical characterization showed that compared with traditional Pt/2D graphene scaffold without the tuning of amphoteric surfactants, our as-made Pt/3D graphene catalysts exhibited much improved catalytic activity and stability for methanol oxidation, demonstrating their great potential as excellent electrocatalysts for methanol oxidation in direct methanol fuel cells.

2. Experimental

2.1. Materials

Graphite was provided by Qingdao Fujin graphite Co., Ltd. (Qingdao, China). Sodium lauryl aminopropionate ($C_{12}H_{25}NHCH_2CH_2COO^-Na^+$) was purchased from Beijing Huamei Co. Ltd. (Beijing, China). Ethylene glycol, $H_2PtCl_6{\cdot}6H_2O$, NaOH, H_2SO_4 and methanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the reagents were of analytical grade and used without further purification. Doubly distilled water was employed throughout the experiment.

2.2. Apparatus

SEM and TEM images were taken by JEOL JSM-7001F and JEOL JEM-2100, respectively. Cyclic voltammetric (CV) and amperometric measurements were carried out on a CHI 660C electrochemical workstation (Shanghai, China) with a conventional three-electrode system. Raman spectroscopy (Renishaw Microscope, Lab RAMHR800; laser excitation at 532 nm). The N_2 adsorption-desorption analysis was measured on a Micromeritics ASAP 2010 instrument. The catalyst composition was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, P-4010). pH measurements were performed using a Metrohm pH-meter, Model 713, with a glass electrode (Metrohm, Swiss). The composite films coated glassy carbon electrode was used as working electrode, while a saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrode, respectively. All the potentials reported in this work were with respect to the SCE reference electrode.

2.3. Preparation of Pt/3D graphene (Pt/3D GN) micro/nanocomposite

Graphene oxide (GO) were synthesized by a modified Hummers method [9]. As shown in Fig. 1, to fabricate the composite catalyst, firstly, 50 mg GO was dissolved in 50 mL of a mixed solution of ethylene glycol and water with a volume ratio of 1:1 under stirring to form the GO suspension whose pH was measured to be 4.2. Then 10 mL 5 wt% aqueous SLA was added dropwise under vigorous stirring. The pH of the resulting solution was adjusted to 11.0 by 0.01 M NaOH, followed by ultrasonication of the solution for 2 h. Then 2 mL 38 mM H_2PtCl_6 was added dropwise under vigorous stirring. The above mixture was then transferred to a stainless-steel autoclave, which was then heated at 160 °C for 7 h to prepare 3D porous Pt/graphene structures. The resulting black precipitate was filtered, washed several times with ethanol-water solution, and collected after vacuum drying at 60 °C for 24 h to obtain the Pt/3D GN micro/nanocomposite. As controls, Pt/GN was also synthesized by the same procedures without adding the surfactant. ICP-AES analyses showed that the Pt loading of Pt/3D GN and Pt/GN was 28.3% and 25.9%, respectively.

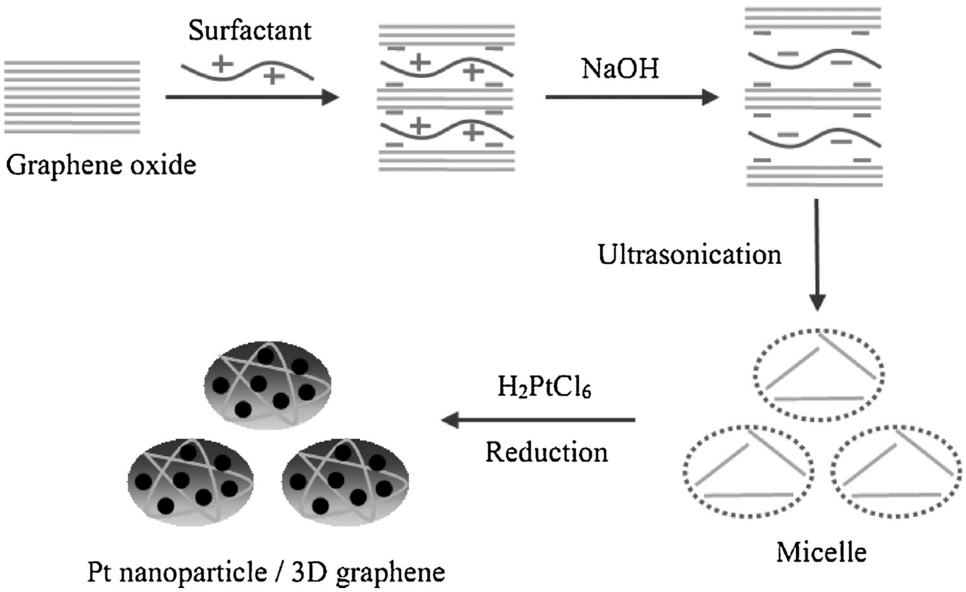

Fig. 1. The scheme of fabricating Pt/3D porous graphene micro/nanostructures.