



Facile synthesis of holey graphene-supported Pt catalysts for direct methanol electro-oxidation



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ABSTRACT

A simple synthetic method was developed to produce holey graphene with in-plane nanopores by a fast thermal expansion of graphene oxide (GO) in air and further thermal reduction in N₂ flow at 900 °C. The as-synthesized holey graphene nanosheets (HGN) shows meso-macroporous structure and higher surface area than chemically reduced graphene oxide (CRGO) by using hydrazine hydrate. The catalysts of HGN-900 supported Pt nanoparticles (Pt/HGN-900) were further prepared through *in-situ* chemical co-reduction and applied in the electro-oxidation of methanol. The electrocatalytic performance of catalysts was investigated by cyclic voltammetry (CV) and chronoamperometry (CA) analysis. The results indicate that the catalytic activity of Pt/HGN-10min-900 (377.5 mA mg⁻¹_{Pt}) is about 1.83 and 2.77 times higher than that of Pt/CRGO-900 (206.1 mA mg⁻¹_{Pt}) and Pt/XC-72 (136.2 mA mg⁻¹_{Pt}) catalysts in 0.5 mol L⁻¹ H₂SO₄ and 1.0 mol L⁻¹ CH₃OH, and Pt/HGN-900 catalysts show higher stable current density compared to that of Pt/XC-72 and Pt/CRGO-900 catalysts.

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1. Introduction

Nowadays, a great deal of research on graphene has focused on energy-storage devices (e.g. direct methanol fuel cells [1,2], supercapacitors [3,4], Li-ion battery [5,6], solar cells [7,8]) owing to its excellent electrical conductivity and high theoretical surface area. However, the layered structure of graphene tends to aggregate by the stacking of graphene nanosheets during the charge/discharge process, which decreases the accessible surface area and limits the kinetics between neighboring layers of graphene and therefore leads to poor performance [9]. It is reported that holey graphene, a graphene structure with abundant in-plane nanopores throughout ranging from several angstroms to the nano-scale, can provide more edges on nanosheets to enhance ion intercalation and overcome the inherent impermeability of graphene, which has attracted much interest [10–12].

The most cost-effective route to introduce nanopores in the graphene planes is the chemical oxidation method, which can be accomplished by the oxidation of carbon atoms with catalysts or oxidants. A highly interconnected 3D N-doped holey reduced graphene oxide framework [13] was successfully synthesized with

hydrofluoric acid (HF, 40%) as an oxidant. Bai group [14] reported a holey graphene achieved through a mild defect-etching reaction between graphene oxide and hydrogen peroxide. Zhao et al. [15] fabricated a holey graphene paper for the use in Li-ion batteries by a mechanical cavitation-chemical oxidation of concentrated HNO₃. However, these approaches usually need to introduce hazardous oxidants, and require complicated and time-consuming processing. Most recently, Han et al. [12] demonstrated a single-step synthetic method to generate holey graphene using air as the oxidant and applied the holey graphene in ultracapacitor, which showed a remarkably improved volumetric capacitance. Peng group [9] also demonstrated an ultra-rapid heating method in air to prepare holey graphene nanosheets (HGNSs), and the supercapacitor made of the HGNSs electrode exhibited excellent electrochemical properties.

Herein, we use a modified method of fast thermal expansion in air to create in-plane nanopores on graphene oxide nanosheets and further high-temperature thermal reduction in N₂ flow to produce highly conductive holey graphene. The as-synthesized holey graphene nanosheets (HGN) were used as a substrate to grow Pt nanoparticles for the electro-oxidation of methanol application. To the best of our knowledge, the application of holey graphene in methanol electro-oxidation is rare [16]. Compared to chemically reduced graphene oxide (CRGO) without nanopores, HGN provides significant accessible surface area. Furthermore, the abundant in-

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plane nanopores on HGN not only provide even more edges and active sites for the deposition of Pt nanoparticles, but also provide cross-plate ion diffusion channels for medium solution or the electrolyte and conductive pathway for electron in the direction vertical to graphene surface, resulted in an elevated electrocatalytic performance.

2. Experimental section

2.1. Synthesis of HGN-900 and CRGO-900

Graphene oxide (GO) was synthesized from natural graphite powder according to the modified Hummers method [17,18]. The as-synthesized GO product was stored in the form of bulk film.

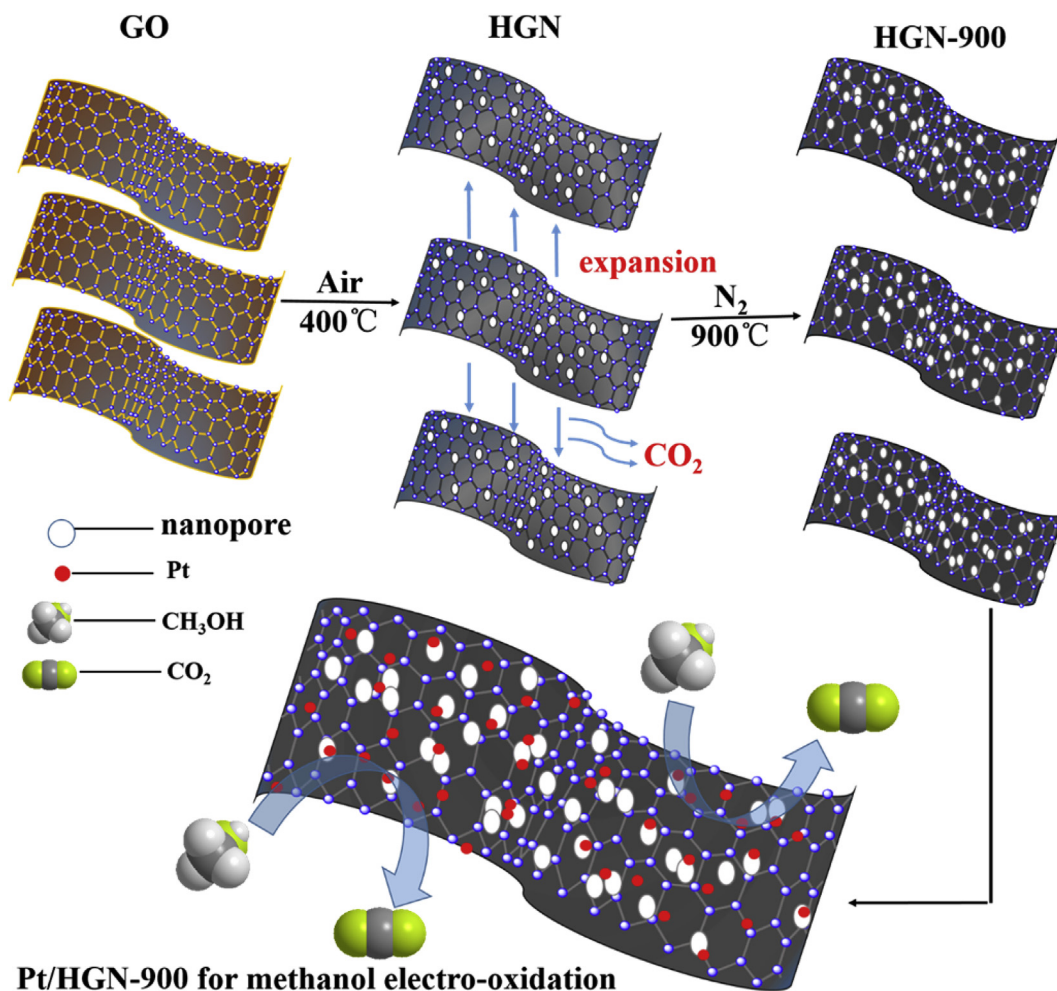
In a typical preparation of HGN-900, the as-synthesized GO film was cut into chips and dispersed in ethanol under stirring for several hours, then naturally dried in air and also cut into small chips for using later. Next, a porcelain crucible containing the GO chips was quickly put into a muffle furnace under 400 °C in air atmosphere. Waiting for 1–2 min, a slight ‘popping’ was heard. Then, the black and fluffy powder can be collected after annealing for a given period of time (10 min and 1 h, respectively) in air atmosphere, which denoted as HGN-10min and HGN-1h, respectively. Finally, HGN-10min and HGN-1h were annealed at 900 °C under N₂ atmosphere for 2 h to further reduce the products with a heating rate of 2 °C min⁻¹. The synthesized materials were denoted

as HGN-10min-900 and HGN-1h-900, respectively. A schematic for the process is illustrated in Scheme 1. HGN-900 stands for the HGN-10min-900 and HGN-1h-900 in Scheme 1.

In control experiments, the chemically reduced graphene oxide (CRGO) was synthesized by chemical reduction with hydrazine hydrate solution. 5 mL of ammonia was mixed with approximately 100 mL of GO solution (1 mg mL⁻¹) under stirring for 1 h at room temperature. Then 2 mL of hydrazine hydrate solution was added into the mixture and stirred at 90 °C under reflux condensation for 12 h. After natural cooling, the mixture was thoroughly washed with deionized water by vacuum suction filter to ensure it was neutral, finally dried in an oven at 60 °C for 12 h. In a similar way, CRGO was further reduced at 900 °C for 2 h under N₂ atmosphere, which was denoted as CRGO-900.

2.2. Synthesis of Pt/HGN-900, Pt/CRGO-900 and Pt/XC-72

The Pt nanoparticles were deposited on the substrates via an *in situ* chemical co-reduction according to the reference with some modification [19,20]. Typically, 50 mg HGN-10min-900 and HGN-1h-900 were ultrasonicated in 1:1 ethylene glycol/water solution (v/v) for 30 min, following by the addition of 1 mL of 0.0772 mol L⁻¹ H₂PtCl₆ solution. The suspension was stirred magnetically for 30 min before 5 mL of NaBH₄ solution (3 mg mL⁻¹) was added. Next, the mixture was magnetically stirred for 2 h at 52 °C. Then, the resulting slurry was filtered, washed and dried at



Scheme 1. Illustration of the synthesis process of Pt/HGN-900 and the electrochemical measurement.

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