



Full Length Article

Fabrication of graphene-fullerene hybrid by self-assembly and its application as support material for methanol electrocatalytic oxidation reaction



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ABSTRACT

Graphene-fullerene hybrids were facilely fabricated by self-assembly of graphene oxide (GO) and multi-substituted fulleropyrrolidines (PyrC₆₀). The hybrids (GO-PyrC₆₀) were applied as support materials to deposit Pd nanoparticle catalyst by a simple hydrothermal co-reduction approach. The as-prepared electrocatalysts (Pd/RGO-PyrC₆₀) were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), respectively. The RGO-PyrC₆₀ hybrid supported Pd catalyst with the optimal ratio of RGO to PyrC₆₀, exhibited much enhanced electrocatalytic activity and stability toward methanol oxidation reaction (MOR) compared to the RGO alone supported Pd as well as commercial Pd/C. The introduction of fulleropyrrolidine as spacer between graphene layers could increase the electrocatalytic activity and improve the long-term stability. This strategy may contribute to developing graphene-fullerene hybrids as effective support materials for advanced electrocatalysts.

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1. Introduction

As a new power source technology, direct methanol fuel cells (DMFCs) has attracted increasing current attention and achieved great progress toward practical applications [1–3]. However, the slow anode methanol oxidation reaction (MOR) and high cost of catalysts still limited the commercialization of DMFCs [4]. Tailoring the composition of metal catalyst and the structure of support material has become to be important strategies to improve the performance of DMFCs [4–9]. At present, Pt-based anode electrocatalyst is the most popular for MOR, but that usually faced the problems such as high cost, poor durability and low resistance to CO poisoning [10–13]. Based on the more abundant resources and stable catalytic performance, Pd-containing electrocatalysts have been recently employed as a promising alternative to the precious Pt for MOR [14–22].

It was well-known that tailoring the structure of the support material, such as spatial structure, surface functional groups, large surface area as well as electrical and mechanical properties, has

significant effect on the activity and durability of the catalysts [23,24]. Carbon materials such as carbon black, carbon nanotubes (CNTs), graphene and fullerene (C₆₀), have been extensively used as support materials in DMFCs because of their extraordinary physical properties, abundance, processibility, environmental friendliness and relative corrosion stability in both acidic and basic media [24]. Among these carbon materials, graphene has attracted particular attention due to its large surface area, high electrical conductivity and low cost [25]. Generally, the graphene materials could be simply prepared from chemical reduction of graphene oxide (GO) in aqueous solutions, but the strong agglomerations of graphene layers during the reduction procedure would seriously decline the electrochemical conductivity and surface area of the as-prepared reduced graphene oxide (RGO) material [26–29]. To overcome this problem, many efforts have been devoted to fabricate the graphene hybrid materials to decrease the tendency of stacking and improve the performance of graphene-based support materials [30–42]. Consequently, various hybrids of graphene with CNTs [33–39], graphitic carbon nitride [40,41], and cationic fullerenes [42] have been successfully fabricated and used as effective electrode materials. For example, Yamaguchi et al. synthesized the hybrids of graphene with exfoliated CNTs and found that the addition of CNTs spacer significantly enhanced the surface area

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of carbon material, and the hybrid-supported PtPd catalyst showed an enlarged electrochemical active surface (ECSA) as well as mass activity toward the MOR [35]. Pyo et al. reported a self-assembled composite obtained from anionic GO and cationic fullerene via electrostatic interaction, and the hybrid composite showed an enhanced capacitance performance [42].

C₆₀ has been widely investigated as an efficient electron-acceptor in various optoelectronic devices [43,44], but less studied as support material in DMFCs [45–48]. One main reason is the poor solubility of pristine C₆₀ in most solvents. Functionalization of C₆₀ by introducing substituents on the cage surface is an efficient strategy to improve its solubility. We have recently reported the synthesis of serious functionalized C₆₀ and their potential applications on electrode materials for MOR and biosensor [49–53]. In the present work, multi-substituted fulleropyrrolidines (PyrC₆₀) was synthesized and used as a novel carbon spacer to fabricate the self-assembled graphene-fullerene hybrid (RGO-PyrC₆₀) via hydrogen bonding interactions between abundant carboxylic acid groups in GO and pyrrolidine nitrogen in fullerene. The hybrids were employed as support materials to deposit Pd nanoparticles to prepare electrocatalysts (Pd/RGO-PyrC₆₀) by a simple hydrothermal co-reduction approach. The RGO-PyrC₆₀ hybrid supported Pd catalyst with the optimal ratio of RGO to PyrC₆₀, exhibits much enhanced electrocatalytic activity and stability for MOR compared to the RGO alone supported Pd, demonstrating that graphene-fullerene hybrids is promising support materials for DMFCs applications.

2. Experimental section

2.1. Materials

Graphite powder (99.9%) and fullerene (C₆₀) (99.5%) were purchased from XFNANO (Nanjing, China). Nafion (5%) was purchased from Alfa. Palladium chloride (PdCl₂), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂, 30%), concentrated sulfuric acid (98%, H₂SO₄), hydrazine hydrate and concentrated nitric acid (HNO₃, 65%) were obtained from Sinopharm Chemical Reagent Corp. (Shanghai, China). Commercial 20 wt% Pd/C catalyst was supplied by Alfa Aesar. All chemicals were of analytical grade and used as received. Multi-substituted *N*-methylfulleropyrrolidines (PyrC₆₀) was similarly synthesized according to the reported procedures [54,55] and characterized by MALDI-TOF-MS, a series of peaks appeared at *m/z* 890.49, 949.62, 1006.71, 1063.79, 1119.87, corresponding to 3–7 substituted fulleropyrrolidine derivatives, respectively. Graphene oxide (GO) was prepared by following the available Hummers method [56–58].

2.2. Preparation of GO-PyrC₆₀

The hybrids of GO-PyrC₆₀ were prepared by spontaneous self-assembly of GO and PyrC₆₀ in water/ethanol mixed solvents. In a typical procedure, GO (10 mg) and PyrC₆₀ (10 mg) were ultrasonically dissolved into 20 mL water and ethanol, respectively. Then 10 mL GO solution was mixed with 1.7 mL, 2.5 mL, 5 mL, 10 mL PyrC₆₀ solution to control the mass ratio of GO to PyrC₆₀ as 6:1, 4:1, 2:1, 1:1, respectively, and precipitates immediately formed. The mixture was stand for 30 min at room temperature and used for further characterization as well as decoration of Pd catalyst.

2.3. Preparation of Pd/RGO-PyrC₆₀

The Pd/RGO-PyrC₆₀ catalyst was prepared by hydrothermal co-reduction approach, where both GO and Pd²⁺ were reduced simultaneously by chemical reductant. Typically, the above as-

prepared GO-PyrC₆₀ hybrids solution was transferred into a Teflon autoclave; then an appropriate PdCl₂ (0.01 M) solution was added to form 20 wt% Pd/GO-PyrC₆₀; finally 40 μL hydrazine hydrate was added and heated at 95 °C for 4 h. The Pd/RGO-PyrC₆₀ catalysts were obtained by centrifugation, washing with deionized water and ethanol, and drying under vacuum at 50 °C overnight. Pd supported on RGO was similarly prepared for comparison of their electrocatalytic performance on MOR.

2.4. Characterization

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were carried out on a Rigaku D/max 2550 with Cu-Kα radiation and PHI 5400, respectively. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed on JEM-2100F (JEOL, Japan) and S-4800 (Hitachi, Japan), respectively. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was measured on Prodigy (Leeman, USA). Mass spectra were recorded on a MALDI-TOF-MS spectrometer (AB Sciex 4700, USA).

2.5. Electrochemical measurements

All electrochemical measurements were performed on an electrochemical workstation (CHI660D, Chenhua, Shanghai) with a standard three electrodes system at room temperature. A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The glass carbon electrode (GCE, 3.0 mm diameter) was successively polished using 0.05 μm alumina slurry, rinsed thoroughly with 1:1 HNO₃, ethanol and water each for 5 min, and dried at ambient temperature. Then 5 μL of catalyst ink (2 mg mL⁻¹ ethanol suspension) was transferred onto the cleaned GCE surface, sequentially coated with 5 μL Nafion solution (0.5% in ethanol) and dried at room temperature. The as-prepared working electrode was then electrochemically activated by potentially cycling between -0.2 and 1.0 V (vs. SCE) in 1.0 M H₂SO₄ solution with a scan rate of 50 mV s⁻¹. The electrocatalytic activity for methanol oxidation reaction was investigated by cyclic voltammetry (CV) in 1.0 M NaOH solution containing 1.0 M MeOH between -1.0 and 0.2 V (vs. SCE) with a scan rate of 50 mV s⁻¹. The stability was examined by chronoamperometry (CA) at a potential of -0.2 V (vs. SCE) for 6000 s. The durability of the catalysts was tested in 1.0 M NaOH solution containing 1.0 M MeOH by potentially cycling from -1.0 to 0.2 V (vs. SCE) for 1000 cycles.

3. Results and discussion

3.1. Self-assembly of GO and fulleropyrrolidine

The hybrids of GO-PyrC₆₀ were facily fabricated by spontaneous self-assembly of GO and PyrC₆₀ in water/ethanol mixed solvents. Upon addition of the transparent reddish solution of PyrC₆₀ into the yellowish solution of GO, a flocculent precipitate was immediately produced (insets in Fig. 1). Due to the addition of pure ethanol or water solvent into the individual GO or PyrC₆₀ solution did not induce any precipitate, the flocculent precipitate that formed in the mixed solutions must result from the interaction between GO and PyrC₆₀. It was noted that the addition of small amount of PyrC₆₀ (GO/PyrC₆₀ = 6:1) induced an appearance of substantial precipitate that floated on the top solution, and the supernatant color remained a little yellowish due to the soluble residue of individual GO component. With increasing the amount of PyrC₆₀ (GO/PyrC₆₀ = 4:1), the compact precipitate formed and completely floated on the top solution, and the supernatant color became almost colorless. Further increasing the amount of PyrC₆₀ (GO/

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