Hollow mesoporous carbon nitride nanosphere/three-dimensional graphene composite as high efficient electrocatalyst for oxygen reduction reaction
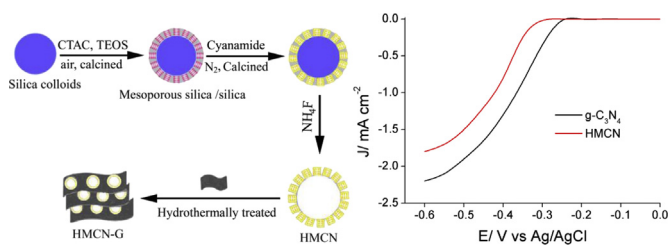
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HIGHLIGHTS

- Hollow mesoporous g-C_3N_4 nanosphere (HMCN) is fabricated by hard template strategy.
- HMCN/3D graphene composite is prepared and used as an electrocatalyst for ORR.
- The composite exhibits excellent catalytic performance for ORR.
- Hollow structure and graphene plays essential role to enhance catalytic activity.

GRAPHICAL ABSTRACT

ABSTRACT

Hollow mesoporous carbon nitride nanosphere (HMCN) is firstly prepared *via* an etching route using hollow mesoporous silica as a sacrificial template. The *as*-obtained HMCN is a uniform spherical particle with a diameter of ~300 nm , and possesses a high specific surface area up to 439 m^2 g^{-1}. Hollow mesoporous carbon nitride nanosphere/three-dimensional (3D) graphene composite (HMCN-G) is subsequently fabricated *via* a hydrothermal treatment of HMCN with graphene oxide. As an electrocatalyst for oxygen reduction reaction (ORR), the HMCN-G shows significantly enhanced electrocatalytic activity compared to bulk graphitic carbon nitride (g-C_3N_4) and HMCN in terms of the electron-transfer number, current density and onset potential. Increased density of catalytically active sites and improved accessibility to electrolyte enabled by the hollow and mesoporous architecture of HMCN, and high conductivity induced from graphene are considered to contribute to the remarkable electrocatalytic performance of the HMCN-G. Furthermore, HMCN-G exhibits superior methanol tolerance to Pt/C catalyst, suggesting that it is a promising metal-free electrocatalyst for polymer electrolyte membrane fuel cell (PEMFC).

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1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) has been considered as one of the most promising energy conversion system.

Currently, the greatest limitation of PEMFC as a clean and green energy sources is the sluggish kinetics of the cathodic oxygen reduction reaction (ORR) [1–3]. Although Pt-based catalysts have been deemed as effective ORR electrocatalysts, large scale application has been precluded due to its prohibitive costs and vulnerability of carbon monoxide poisoning as a result of fuel cross over to the cathode side [4–8]. To fundamentally get rid of the dependence on noble metal catalysts, alkaline fuel cell (AFC) equipped with

metal-free electrocatalysts for cathodic ORR has been developed recently [9–11]. The state-of-the-art nitrogen-doped carbon materials are generally accepted as promising noble metal-free catalyst because of their excellent electrocatalytic activity, low costs, long durability and environmental friendliness [11–15]. Among these materials, graphitic carbon nitride (g-C$_3$N$_4$) is especially appreciable because it contains more pyridinic nitrogen which has been proven to play essential role in AFC [2,16–18]. However, the extensive application of g-C$_3$N$_4$ is still confronted with two critical problems. The first is the low electrical conductivity of g-C$_3$N$_4$, which impedes the electron transportation during the ORR process, thus degrades the electrocatalytic activity [19,20]. Although several routes including P-doped and protonation have been proposed to enhance the electrical conductivity of g-C$_3$N$_4$ [21,22], these modifications decrease the quantity of pyridinic nitrogen, thereby plague the electrocatalytic performance. To date, compositing carbon materials with g-C$_3$N$_4$ has been regarded as an effective strategy to enhance the electrical conductivity of g-C$_3$N$_4$ [23–25]. Various routes, such as mechanical mixing of g-C$_3$N$_4$ with carbon black [23], immobilization of g-C$_3$N$_4$ onto mesoporous carbon [24], coating macroprous g-C$_3$N$_4$ with carbon have been proposed [25]. Although the modified composites show improved performance toward ORR in comparison with the pristine g-C$_3$N$_4$, neither their cathodic reaction current nor electron-transfer number is comparable to Pt-based catalysts. The second problem is the low specific surface area (SSA) of bulk g-C$_3$N$_4$. Basically, g-C$_3$N$_4$ conventionally fabricated by calcining some nitrogen precursors such as urea, cyanamide and melamine at high temperature just owns a low SSA of several square meters per gram [23,26] because of the π–π conjugation interaction and van der Waals force between the nanosheets. Although etching method utilizing porous silica as a sacrificial template can increase the SSA of g-C$_3$N$_4$ up to over 400 m^2 g^{-1} [27], the irregular morphology and large bulk size hamper the integrating of g-C$_3$N$_4$ into other conductive materials including active carbon, carbon nanotube and graphene.

Hollow nano-materials have attracted tremendous attention because of their large variety of application in chemistry, biotechnology and material science [28–30] in the past decades. The hollow nanospheres possess the advantage of encapsulation property, controllable permeability, and surface functionality. Moreover, hollow nanospheres can provide a fast pathway for the ionic and electronic transport in energy storage and conversion devices [31,32]. Although carbon nitride with various morphologies including two-dimensional (2D) planar sheet [33], porous [34,35] and nanodots [36] have been extensively demonstrated, the preparation of hollow carbon nitride nanosphere is still a challenge so far.

Recently, graphene has been fascinated enormously as a new-generation material because of its unique 2D planar structure, exceptional chemical and physical properties, and wide potential applications in nanoelectronics [37], energy storage and conversion [38,39], chemical and biological sensors [40,41]. However, the π–π conjugation interaction between 2D planar graphene sheet enables it prone to aggregate severely [42]. Very recently, three-dimensional (3D) graphene, a framework of interconnecting 2D graphene sheets, has been constructed to address the restacking issue of 2D graphene. The 3D architecture provides graphene materials with high specific surface areas, fast mass and electron transport kinetics, thus it has been used in the fields of pollutant adsorption, energy strorage, conversion and sensing platform [43–45].

In this work, we present a method to fabricate hollow mesoporous carbon nitride nanosphere/3D graphene (HMCN-G) composite. HMCN is firstly prepared by etching method using hollow mesopore silica nanosphere as a sacrificial template, and is

subsequently encapsuled in 3D graphene network. The composite is proven to be a high efficient ORR electrocatalyst for AFC due to its increased catalytical active sites and improved electrical conductivity.

2. Experimental section

2.1. Chemicals and reagents

Graphite powder (99.95%, 8000 mesh), Pt/C catalyst, melamine, cyanamide and cetyl trimethyl ammonium chloride (CTAC) are purchased from Shanghai Aladdin Chemistry Co. Ltd (China). Tetraethoxysilane (TEOS) is purchased from Sinoreagent (China). All other chemicals are of analytical grade and used as received.

2.2. Preparation of graphene oxide (GO)

GO is prepared from nature graphite flakes by using an improved Hummers' method [46]. Typically, graphite flakes (1.0 g) and KMnO$_4$ (6.0 g) are added into a mixture of 120 mL concentrated H$_2$SO$_4$ and 13.3 mL H$_3$PO$_4$, producing a slight exotherm to 35 °C. The mixture is then heated to 40–55 °C and stirred for 12 h. The mixture is cooled to room temperature and poured into ice water (150 mL) with 30% H$_2$O$_2$ (10 mL). The mixture is sifted through a polyester fibre cloth. The filtrate is centrifuged (4000 rpm for 4 h), and the supernatant is decanted away. The remaining solid material is then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol. The solution is centrifuged (4000 rpm for 4 h) and the supernatant is decanted away. The solid is vacuum-dried overnight at room temperature.

2.3. Preparation of solid silica@mesoporous silica core–shell nanosphere

The solid silica@mesoporous silica core–shell nanosphere template is prepared by a cationic surfactant assisted selective etching route [47]. Solid SiO$_2$ nanosphere is prepared following a modified Stober method in the first. Typically, 6 mL of TEOS are rapidly added into a mixture of ethanol (74 mL), deionized water (10 mL), and ammonium aqueous solution (25–28%, 3.15 mL). The mixture is then stirred at room temperature for 1 h, resulting in the formation of a white silica colloidal suspension. The silica particles are centrifugally separated from the suspension and washed with deionized water and ethanol. 50 mg of the *as*-prepared solid SiO$_2$ nanosphere is homogeneously dispersed in 10 mL of deionized water by ultrasonication for 15 min. The suspension is then added into a solution containing CTAC (75 mg), deionized water (15 mL), ethanol (15 mL), and ammonia solution (0.275 mL). After the mixture is stirred at room temperature for 0.5 h, 0.125 mL of TEOS is added quickly. After 6 h, the products are collected by centrifugation, and extensively washed with deionized water and ethanol. Calcination is used to remove CTAC from the *as*-prepared products. The resulting products are heated to 550 °C in air at a rate of 1.5 °C min^{-1}, dwelling for 6 h.

2.4. Preparation of HMCN and bulk g-C$_3$N$_4$

HMCN is prepared by etching method using above solid silica@mesoporous silica core–shell nanosphere as the sacrificial template. Typically, 50 mg solid silica@mesoporous silica core–shell nanospheres are dipped into 4 mL 50% (wt.) cyanamide solution. After 24 h, the mixture is centrifuged and decaned away the supernatant. The remained solids are washed by water quicky to remove the cyanamide on the surface. The solids are calcined at 550 °C for 5 h under N$_2$ atmosphere. The obtained gray powder are