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Hollow carbon hemisphere with controlled morphology as support material for platinum nanoparticle catalyst towards the methanol electro-oxidation

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ABSTRACT

Morphology controlled hollow carbon hemisphere (HCHS) has been prepared using polystyrene (PS) spheres as templates. The obtained HCHS can be tailored from hollow carbon sphere (HCS) to bowl-like hemispheres by adjusting the ratio of precursor to templates, and mainly in amorphous structure with a BET surface area of 507 m^2/g. The HCHS was then applied for the support material of the platinum (Pt) nanoparticle catalyst (Pt/HCHS). The nanoparticles can be highly dispersed with a narrow particle size distribution and an average diameter of 3.9 nm. The electrochemical analysis indicated that the Pt/HCHS exhibits enhanced catalytic activity towards the methanol electro-oxidation in terms of the onset potential, current density and stability in alkaline solution compared with carbon black supported Pt catalyst (Pt/CB), suggesting that the HCHS with unique hollow structure has great potential as a support material for the electrocatalysts.

1. Introduction

In the past two decades, the different structured or shaped carbon materials, such as carbon nanotubes [1], diamond-like carbon [2], glass-like carbon [3], porous carbon [4], carbon nanowires [5], and hollow carbon spheres [6,7], have been synthesized and extensively studied. They are utilized as the electrode materials in a wide range of electrochemical systems including fuel cell [8], supercapacitors [9], lithium ion battery [10], etc. due to their high electrical conductivity, well developed porosity, relatively low cost and high tolerance in harsh chemical conditions [11]. Especially, almost all the mentioned carbon materials have been investigated as support materials for the electrocatalysts in the fuel cell application, although much effort has also been devoted to applying non-carbon materials as alternatives to carbon materials [12,13]. In order to achieve a higher efficiency of the electrocatalysts, noble metal nanoparticles have to be well dispersed on the carbon materials. Therefore, it is desirable that the carbon material provides a suitable specific area and surface chemistry as well as a good electrical conductivity [14]. This directly drives the research interests to the design and synthesis of new carbon materials.

Hollow carbon sphere (HCS) is one of the most promising carbon support materials for the catalysts applied on electrodes because of their high surface area [14,15]. Various approaches, such as self-assembly template processes [16], pyrolysis [17] reduction [18] and hydrothermal methods [19] have been carried out to prepare HCS with different yields and sizes. In terms of the controllability of size and shape in macro- or nano-scale, the template-based synthesis would be the most defined approach, because the spherical morphology of HCS can be easily tailored by adjusting the morphological feature and the diameter of the template cores. Commonly, two types of templates can be used for synthesizing the HCS, including hard templates (inorganic powder-based molds) [20] and soft templates (polymer sphere) [21]. In the case of hard template method, HCS can be fabricated by coating carbon sources onto the surface of inorganic powder followed by carbonization under inert conditions and subsequent removal of the templates using chemical etching. Compare with hard template method, the soft template route makes the synthesis process more rapid by obviating the need for the removal of template since the template decomposes during the carbonization. Polystyrene (PS) [21], polyvinylacetate (PVA) [22] and polymethyl methacrylate (PMMA) [23] are often used as templates and polyacrylonitrile (PAN) [23],

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phenolic formaldehyde (PF) resin [24] and sucrose [16] are well known precursor for preparing hollow carbon spheres due to their high yield of carbon conversion.

Herein, we introduce a controllable route to prepare hollow carbon hemisphere (HCHS) based on the HCS synthesis process for the purpose of designing support materials with new morphology for the electrocatalysts. In this work, PF and PS spheres are used as carbon source and templates, respectively. HCHS can be tailored from hollow sphere (HCS) to bowl-like structure (hemisphere) by adjusting the ratio of PF to PS. The HCHS is mainly in amorphous structure, and have a higher BET surface area of 507 m^2/g. Furthermore, HCHS is applied as the support material for synthesizing Pt nanoparticle catalysts (Pt/HCHS). The electrochemical characterization results show the Pt/HCHS exhibits larger electrochemical surface area (ECSA) and higher electrocatalytic activity for the methanol electro-oxidation in alkaline solution compared with Pt supported on commercial Vulcan XC-72 carbon black (Pt/CB) under the same Pt loading.

2. Experimental

2.1. Materials

Anhydrous ethanol, concentrated sulfuric acid (98 wt.%), potassium persulfate (KPS), resol precusor phenolic formaldehyde (PF) resin (56.43 wt.%) and styrene (St) were of analytical- grade and were purchased from the Beijing Chemical Agent Company. Styrene (St) was purified by the method of vacuum distillation and must be used within two weeks with storage temperature below 0 °C.

2.2. Preparation and modification of the template spheres

PS spheres were produced by emulsifier-free emulsion polymerization. A suitable amount of potassium persulfate was completely dissolved in deionized water and put into a 250 mL, four necked, round-bottom flask, which was put in a thermostated water bath, and then nitrogen was bubbled to the above mixture under vigorously stirring (200 rpm) for 30 min. When the temperature reached 65 °C, a suitable amount of styrene was added into potassium persulfate solution for polymerization, and the reaction was carried out at 70 °C for 12 h. The obtained PS spheres were immersed in concentrated sulfuric acid at 40 °C for 2 h to obtain sulfonated polystyrene template spheres. The dried template sphere (0.05 g) was immersed in 40 mL of ethanol at ambient temperature. A designed amount of PF resin solution (20 mL) was added and the solution was stirred at the temperature of 40 °C for 5 h. The obtained PF/PS composite spheres were further crosslinked at 60 °C for 24 h.

2.3. Preparation of HCHS

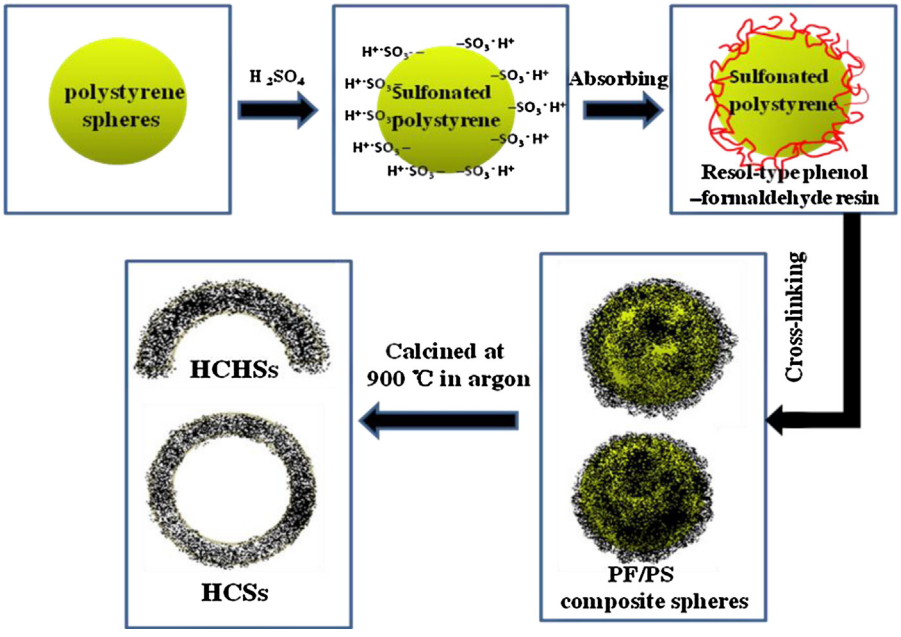
The HCHS with porous shells was prepared by the one-step carbonization of the PF/PS composite spheres at 900 °C in argon, avoiding the removal process of the template cores. The preparation process was as follows: the PF/PS composite spheres were first added into a tube furnace, and the temperature was raised to 900 °C with a heating rate of 5 °C/min. The samples were kept at 900 °C under an argon flow for 1 h, and were collected after it was cooled to room temperature.

2.4. Preparation of Pt nanoparticles supported on hollow carbon hemisphere (HCHS)

The HCHS (30 mg) was dispersed in 100 mL glycol with 4.61 mL of hexacholoroplatinic acid solution (0.01 mol/L), and the pH value was adjusted to 10. The solution was heated to 130 °C and stirring for 3 h. The products were washed and dried in vacuum. For comparison, Pt/CB was prepared under the same condition.

2.5. Characterization

Field emission scanning electron microscopy (FE-SEM, FE-JSM-6701F, JEOL) and transmission electron microscopy (TEM, JSM-2100 JEOL) were used to characterize morphology of the spheres, and FT-IR spectra were recorded on BRUKER EQUINOX 55 using KBr pellet samples. The Raman spectra was obtained with LabRAM HR800 (HORIBA Jobin Yvon) confocal Raman spectrometer and wide-angle X-ray powder diffractometer (Rigaku D/max-2500) was used to characterize the crystallinity of the materials.



Scheme 1. Preparation schematics of hollow carbon hemisphere (HCHS).