Chemical Engineering Journal 242 (2014) 285–293

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Preparation and characterization of monodisperse, micrometer-sized, hierarchically porous carbon spheres as catalyst support

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## HIGHLIGHTS

- Micrometer-sized porous carbon spheres were prepared by hydrothermal and polymer carbonization method.
- The porous carbon spheres were excellent matrix for immobilizing nobel metal nanoparticles.
- The obtained Au/C catalysts possess higher catalytic activity toward the reduction of 4-nitrophenol.
- The activity factor κ of Au_5/C is 28.46 $s^{-1}$ $g^{-1}$.

## GRAPHICAL ABSTRACT

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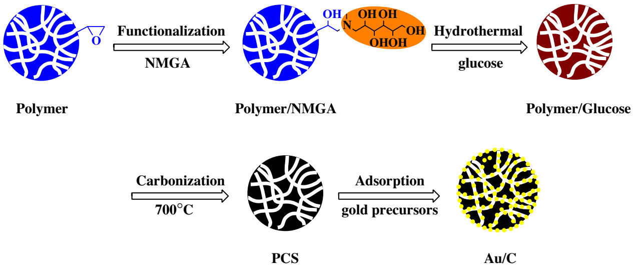

## ARTICLE INFO

*Article history:*
Received 28 September 2013
Received in revised form 15 December 2013
Accepted 28 December 2013
Available online 7 January 2014

*Keywords:*
Monodisperse
Micrometer-sized
Hierarchical
Porous carbon spheres
Catalyst

## ABSTRACT

Monodisperse, micrometer-sized, hierarchically porous carbon spheres (PCS) were successfully fabricated by employing a hard template under hydrothermal condition and followed by further carbonization. D-Glucose and porous polymer microspheres modified with N-methyl-D-glucamine (NMGA) were used as carbon source and template, respectively. The porous carbon spheres were characterized by scanning electron microscopy, X-ray powder diffraction, and $N_2$ adsorption–desorption measurements. The results reveal that the PCS with amorphous colloidal structure are highly monodispersed and have a hierarchically pore size distribution. PCS with these features are excellent matrix for loading noble-metal nanoparticles. The PCS adsorb gold precursors and sub-sequently generate in situ Au nanoparticles (AuNPs). The deposited AuNPs with the size of 15–30 nm are well dispersed in PCS' pores. The resulting gold–carbon (Au/C) composite microspheres show high performance toward the reduction of 4-nitrophenol (4-NP).

## 1. Introduction

Over the past decades, due to their high specific surface area, surface functionality, high chemical stability, good electrical and thermal conductivity, porous carbon materials have widespread applications such as sorbents [1–3], supercapacitors [4], lithium ion batteries [5,6], fuel cell electrodes [7,8], and catalyst supports [9–16]. From the viewpoint of materials chemistry, porous carbon materials with different morphology and microstructure such as fiber [17], film [18], nanotube [19] and microsphere [20] have been synthesized successfully. Especially, the synthesis of porous carbon microspheres has particularly received much attention for column packing, fillers or catalyst supports [21–23]. Key to realization of these applications is to synthesize the porous carbon microspheres

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http://dx.doi.org/10.1016/j.cej.2013.12.089

with uniform particle size, well dispersity and hierarchical pore structure by a simple and efficient method.

To date, many efforts have been made to fabricate these versatile porous carbon spheres with different particle size and pore structure [20,24–31]. Template carbonization methods have attracted much attention for the preparation of ordered porous carbon microspheres [8,32–36]. Template carbonization synthetic procedure for porous carbon microspheres is as follows: (1) preparation of the carbon precursor/inorganic template composite, (2) carbonization, and (3) removal of the inorganic materials by using silica template. In general, structurally rigid porous silica particles were adopted as the templates to prepare porous carbon microspheres. Nevertheless, there are many defects by using porous silica as template because the removing silica template after carbonization is a very fussy, highly-cost and time-consuming process. Recently, polymer latex has been successfully employed as the template for the synthesis of mesoporous carbon forms and hollow carbon nanospheres. Compare with synthesis of porous carbon materials by using silica template, the polymer template method has been regarded as a simple and effective route in controlling the morphology and microstructure of porous carbon materials because polymer latex/carbon precursor composite was carbonized simultaneously at high temperature without post treatment of the polymer template. However, studies on well-dispersed, porous carbon microsphere have not been reported by using such an approach.

We utilized a functionalized, porous hard templating route together with hydrothermal and further carbonization treatment to fabricate micrometer-sized PCS with high monodispersity and hierarchical pores (Scheme 1). Scanning electron microscopy images show that the PCS are micrometer-sized and have colloidal structures. According to $N_2$ adsorption–desorption isotherms and pore size distributions, the PCS are characteristic of hierarchical pores. X-ray powder diffraction pattern reveals that the PCS are amorphous structure. Hydrodynamic size measurement indicates that the PCS have a relative narrow particle size distribution. On the other hand, metal nanoparticles (MNPs) like Au nanoparticles have attracted considerable attention due to their unique physicochemical properties and their extensive applications in catalysis. However, due to their high surface energy, MNPs tend to be easily aggregated, resulting in obvious decrease in catalytic activities. In order to stabilize MNPs catalysts, polymers [37–39], resins [40,41], metal oxides [42,43], silica [44–46] and carbon materials [25,47,48] have been used as supports to anchor them. These synthetic methods usually result in single functional supports. The process of metal salt precursors to MNPs is generally achieved in the presence of reductants. Inspired by this study, The as-synthesized PCS were further employed as matrix to prepare Au/C composite microspheres by an in situ approach. After the carbonization of the Polymer/Glucose, the oxygen-containing groups in glucose molecules and Polymer/NMGA were partially transformed to reductive moieties in the PCS, which can adsorb gold precursors and directly reduce them into AuNPs. The catalytic activities of Au/C composite microspheres have been investigated as heterostructured catalysts and the results demonstrate that the Au/C composite microspheres possess higher performance toward the reduction of 4-nitrophenol than many other currently available AuNPs-supported materials.

## 2. Material and methods

### 2.1. Materials

Porous polymer microspheres (PGMA/EDMA) were provided by Nano-Micro Technology Company, China. N-methyl-D-glucamine (NMGA), anhydrous D-Glucose were purchased from Aldrich. Anhydrous alcohol and chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium borohydride ($NaBH_4$) and 4-NP were purchased from Alfa Aesar. Water was purified by distillation followed by deionization using ion exchange resin.

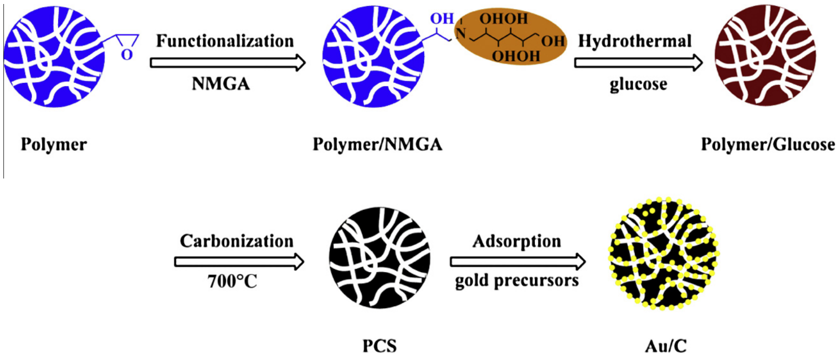
### 2.2. Modification of porous polymer microspheres with NMGA

To modify the template, 2.5 g PGMA/EDMA microspheres were dispersed in 100 mL anhydrous ethanol. A transparent solution by dissolving 5 g NMGA in 30 mL deionized water was then added. The resulting mixture was stirred in water bath at 60 °C for 20 h. The white product was filtrated and rinsed repeatedly with deionized water and anhydrous ethanol, and dried at 80 °C overnight. The obtained sample was denoted as Polymer/NMGA.

### 2.3. Synthesis of monodisperse porous carbon spheres

In a typical synthesis, 8 g anhydrous D-glucose was dissolved in 25 mL deionized water to form a clear solution. To this solution, 1.0 g modified polymer microspheres was added and mixed thoroughly by ultrasonic treatment in water bath. The homogeneous suspension was sealed into a 40 mL Teflon-lined stainless steel autoclave and hydrothermally treated at 180 °C for 24 h. The resulting dark brown product was filtrated and rinsed repeatedly with deionized water and anhydrous ethanol, and finally dried at 80 °C overnight. As a result, this recipe gave about 4.4 g of the hydrothermal carbonization (HTC) derived composite which were denoted as Polymer/Glucose.

The dried Polymer/Glucose composite microspheres were transferred to a quartz boat in a tubular furnace for further carbonization in 5% $H_2$/Ar (100 mL/min). The temperature program was as



**Scheme 1.** Synthesis of monodisperse, micrometer-sized, hierarchically porous gold–carbon (Au/C) composite microspheres.