



Regular Article

Stöber synthesis of tannic acid–formaldehyde resin polymer spheres and their derived carbon nanospheres and nanocomposites for oxygen reduction reaction

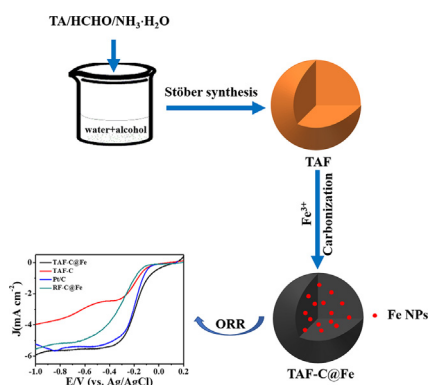


Minmin Liu ^{a,1}, Chao Cai ^{a,1}, Jian Li ^a, Jing Zhao ^a, Wei Teng ^b, Rui Liu ^{a,*}

^a Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education, School of Materials Science and Engineering, and Institute for Advanced Study, Tongji University, Shanghai 201804, China

^b State Key Laboratory for Pollution Control, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 March 2018

Revised 21 May 2018

Accepted 21 May 2018

Available online 23 May 2018

Keywords:

Stöber
Tannic acid
Carbon
Iron
ORR

ABSTRACT

We report a facile Stöber approach to prepare polyphenol-based resin polymer spheres using tannic acid and formaldehyde as reactants. The tannic acid–formaldehyde (TAF) spheres directly convert into carbon spheres with monodispersity and structural integrity. In addition, TAF–Fe complex spheres are carbonized into Fe nanoparticles (NPs) decorated carbon spheres (TAF–C@Fe), which are successfully applied as electrocatalysts for oxygen reduction reaction (ORR) in alkaline media. The electrocatalyst exhibits similar catalytic activity but better methanol tolerance performance to 20% commercial Pt/C in alkaline media. This feasible strategy presents a novel precursor for fabricating and tailoring the structure, composition, and size of polyphenol resin and derived carbon-based materials for energy conversion and storage.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

Polymer and carbon nanospheres with controllable size and architecture are enthusiastically appealing in many fields such as catalysis, bioengineering, sustainable energy and environment protection [1–5]. In the past several decades, numerous of efforts have

* Corresponding author.

E-mail address: rui.liu@tongji.edu.cn (R. Liu).

¹ Equally contribution

been made in the preparation, characterization and applications of polymer colloids and their derived carbon-based nanomaterials. Various polymeric precursors, such as glucose [6,7], dopamine [8–10], phenol-formaldehyde resin [11–13] and conducting polymers [14–16], have been successfully used to synthesize uniform nanospheres and then converted into carbon nanospheres through a pyrolysis process. On the other hand, a series of synthetic routes have been developed for the synthesis of robust, low-cost and environmentally benign polymer nanospheres. Stöber synthesis is a general approach for the preparation of colloidal silica spheres by hydrolysis of silicon alkoxide in alcohol/water solvent with a base catalyst (e.g. aqueous ammonia solution) [17–19]. The size of the obtained silica sphere can be tuned between 150 and 500 nm by changing the reaction parameters including ethanol concentration, ammonia concentration and reaction time. Since Liu et al. reported the extension of Stöber synthesis in the preparation of resorcinol-formaldehyde (RF) polymer spheres, many RF resin derived carbon nanoparticles and nanocomposites have been successfully prepared [11,20,21]. In this extended Stöber synthesis, RF resins form four-coordinate covalently bonded silica-like frameworks through polymerization between resorcinol and formaldehyde. Therefore, similar morphologies and nanostructures between silica and RF are obtained under Stöber conditions.

Carbon nanospheres have been recognized as the promising ORR catalysts for energy conversion devices. For example, Lu and the coworkers have synthesized polydopamine nanospheres under Stöber conditions and converted them into the monodisperse and size-controlled carbon nanosphere for ORR [22]. Moreover, the ORR capacity can be obviously enhanced when electroactive metal NPs are decorated onto the carbon nanospheres. For example, platinum NPs have been decorated on the surface of RF derived carbon nanospheres through ethylene glycol reduction, which have shown the excellent ability in ORR [11,23,24]. Jaroniec et al. have used cysteine-modified RF polymer nanosphere as a support to incorporate different metal NPs (e.g. Au, Ru, Mn or Fe) on the carbon sphere for in a variety of applications including catalytic reaction, fuel cell and Li-ion battery [25]. However, the above synthesis either involves the use of external reducing agent or extra step to post-modify the functional surface. Therefore, the development of a facile and feasible approach with a suitable precursor to prepare polymer nanospheres and the derived carbon nanospheres/nanocomposites still remains to be a great challenge.

Herein, we report the use of Stöber method for the preparation of uniform tannic acid-formaldehyde (TAF) resin spheres and their conversion to carbon spheres and metal-carbon composites. Tannic acid (TA, molecular structure in Fig. S1) is a renewable and ubiquitous natural polyphenol extracted from plants. Each TA molecular contains inherent pyrogallol- and catechol-like sites that can in principle function for both hydrogen-bonding and coordination interactions. Hence, TA can be coordinated with different metal ions to form stable TA-metal complex [26]. In addition, TA as a precursor has been proved to transform into carbon material. For example, Wei et al. have fabricated high-performance Fe₃C/Fe-N-C catalysts by coating iron-tannin source onto cellulose fibers, followed by grinding with dicyandiamide, carbonization, and acid etching [27]. Dai et al. have reported the mechanochemical assembly of TA-metal with surfactants, and then converted into ordered mesoporous carbon [28]. In this work, we first systematically study the Stöber synthesis of TAF nanospheres and the effects of synthesis factors on the resulted particle size of TAF sphere. Followed by the successful conversion into carbon nanospheres, TAF-Fe complex is obtained by taking advantage of chelating effect of the remaining pyrogallol- and catechol groups in TAF. TAF-Fe complex is then converted into Fe NPs loaded carbon sphere an excellent electrocatalyst for ORR with good catalytic performance and superb intolerance to methanol crossover effects.

2. Experimental section

2.1. Materials

Iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98%), cobaltous nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%), ethanol (C₂H₅OH, 99.7%), ammonia solution (NH₃·H₂O, 25–28%), formaldehyde (CH₂O, 98%), potassium hydroxide (KOH), isopropyl alcohol ((CH₃)₂CHOH, 99.7%) and nafion solution (5%) were obtained from Sinopharm Chemical Reagent Co., Ltd. TA(C₇₆H₅₂O₄₆) was purchased from Aladdin Industrial Corporation. Ultrapure water with a resistivity of 18.0 MΩ·cm was used as aqueous solutions prepared by Direct-Q[®]3.

2.2. Synthesis of TAF and RF spheres

In a typical synthesis, NH₃·H₂O (0.1 mL, 25 wt%) was added into a solution (total volume: 28 mL) containing absolute ethanol and DI water with different EtOH/water volume ratio (28:0, 20:8, 14:14, 8:20, 0:28). Subsequently, tannic acid (0.1 g) was added and continually stirred until completely resolution. Then, 0.28 mL of formaldehyde solution was added to the system and kept for 24 h under stirring at 30 °C. Next, the reaction solution was transferred into a Teflon-lined autoclave and heated at 100 °C for 24 h under a static condition. After the temperature was cooled down, the product was collected by centrifugation and air-dried at 60 °C for 12 h. TA NPs were obtained using the similar procedure without adding formaldehyde. RF nanospheres were prepared according to the literature [11].

2.3. Synthesis of TAF-C@Fe, TAF-C@Co and RF-C@Fe

To synthesize TAF-C@Fe, the above-obtained TAF spheres (prepared from EtOH/water: 20/8) were immersed in FeCl₃ solution (0.05 M) and stirred for 6 h. Then, the samples were collected by centrifugation and dried at 60 °C. The precursors were heated up to 350 °C and kept for 30 min, then heated at 900 °C for 1 h under N₂ atmosphere with a heating rate of 5 °C min⁻¹. RF-C@Fe was obtained using the same method. TAF-C@Co was synthesized using the same method except for the replacement of metal ions.

2.4. Characterization

Transmission electron microscopy (TEM) and High resolution TEM images were performed on a JEM-2100FE electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDS) analysis of the materials were examined on a Quanta200 (FEI, Hillsboro, Oregon, USA). Fourier transform infrared (FTIR) spectra were recorded with KBr discs on a Bruker EQUINOX 55 spectrometer (Equinox 55 Bruker Banner Lane, Coventry, Germany). Nitrogen sorption isotherms were measured at 77 K with a Quadachrome adsorption instrument (Autosorb-iQ3; Quantachrome, America). Before the analysis, the catalysts were degassed at 200 °C for 6 h. The surface area was determined using the Brunauer–Emmett–Teller (BET) method based on adsorption data in the relative pressure (P/P₀) range of 0.05 to 0.3. Powder X-ray diffraction (XRD) measurement was carried on a D/MAX 2550 powder diffractometer (D/max 2550 V, Rigaku, Tokyo, Japan) using Cu–Kα radiation with a Ni filter (λ = 0.154059 nm) at 30 kV and 15 mA) with scanning rate of 3 deg/min with the sample deposited on a microscope glass. The powder sample was deposited on an iron alloy substrate for X-ray photoelectron spectroscopic (XPS) analysis, which was performed on an ESCALAB 250Xi operated at 120 W.

Download English Version:

<https://daneshyari.com/en/article/6989920>

Download Persian Version:

<https://daneshyari.com/article/6989920>

[Daneshyari.com](https://daneshyari.com)