Carbon 101 (2016) 57–61

Contents lists available at ScienceDirect

Carbon

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

Graphitized hollow carbon spheres and yolk-structured carbon spheres fabricated by metal-catalyst-free chemical vapor deposition

Xufan Li [a], Miaofang Chi [c], Shannon M. Mahurin [d], Rui Liu [d], Yen-Jun Chuang [a], Sheng Dai [d], Zhengwei Pan [a, b, *]

[a] College of Engineering, University of Georgia, Athens, GA 30602, USA
[b] Department of Physics and Astronomy, University of Georgia, Athens, GA 30602, USA
[c] Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[d] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

A R T I C L E I N F O

Article history:
Received 4 November 2015
Received in revised form
30 December 2015
Accepted 13 January 2016
Available online 18 January 2016

A B S T R A C T

Hard-sphere-templating method has been widely used to synthesize hollow carbon spheres (HCSs), in which the spheres were firstly coated with a carbon precursor, followed by carbonization and core removal. The obtained HCSs are generally amorphous or weakly graphitized (with the help of graphitization catalysts). In this work, we report on the fabrication of graphitized HCSs and yolk–shell Au@HCS nanostructures using a modified templating method, in which smooth, uniform graphene layers were grown on SiO_2 spheres or Au@SiO_2 nanoparticles via metal-catalyst-free chemical vapor deposition (CVD) of methane. Our work not only provides a new method to fabricate high-quality, graphitized HCSs but also demonstrates a reliable approach to grow quality graphene on oxide surfaces using CVD without the presence of metal catalysts.

1. Introduction

In recent years, the synthesis of hollow carbon spheres (HCSs) has attracted considerable attention because of the promising potentials of HCSs in energy storage and conversion [1–8] and in catalytic and adsorption-based application [1,9,10], owning to their many unique features, such as spherical morphology, low density, high specific surface areas, large void space fraction, outstanding thermal and chemical stability, etc. Hard-templating-based methods were widely used to synthesize the HCSs [1]. Typically, the templates, mainly silica spheres [2–6,9–16] and polymer spheres [7,8,17,18] having monodisperse size and spherical shape, were firstly coated with a thin layer of a carbon precursor (e.g., glucose [5–7], resorcinol-formaldehyde resin [3,4,9–13], dopamine [14,15], and petroleum pitch [16]) to form a core–shell structure, followed by carbonization of the shell and etching removal of the core. The as-synthesized HCSs preserved the morphology and size of the templates, forming negative replicas of the templates. Besides the HCSs, the template approaches also enable to synthesize novel yolk–shell structures, in which one or several movable nanoparticles are encapsulated inside a HCS (e.g., Au@HCS), when core–shell nanoparticles (e.g., Au@SiO_2) are used as the templates [14]. Such yolk–shell carbon structure is beneficial for catalytic and electrochemical applications [5,6,10,14].

The carbon shells of the HCSs fabricated by the templating methods are generally amorphous, which have poor electrical conductivity and are not ideal for some applications such as lithium-ion batteries [1]. To obtain graphitized carbon shells, graphitization catalyst, such as Fe-containing species [8,18], was frequently added into the carbon precursor coating layer in the coating process, which promoted the graphitization of carbon precursor in the carbonization process. However, the obtained carbon shells were only weakly graphitized, exhibiting turbostratic or localized graphitic structures. Herein, we report on the fabrication of graphitized, monodisperse HCSs and yolk–shell Au@HCS nanostructures using a new, modified templating method, in which smooth, uniform graphene layers were grown on SiO_2 spheres or Au@SiO_2 nanoparticles via metal-catalyst-free chemical vapor deposition (CVD) of methane. Our work not only provides a new method to fabricate high-quality HCSs but also demonstrates a reliable approach to grow quality graphene on oxide surfaces using methane CVD without the presence of metal catalysts.

* Corresponding author. College of Engineering, University of Georgia, Athens, GA 30602, USA.
E-mail address: panz@uga.edu (Z. Pan).

http://dx.doi.org/10.1016/j.carbon.2016.01.043
0008-6223/

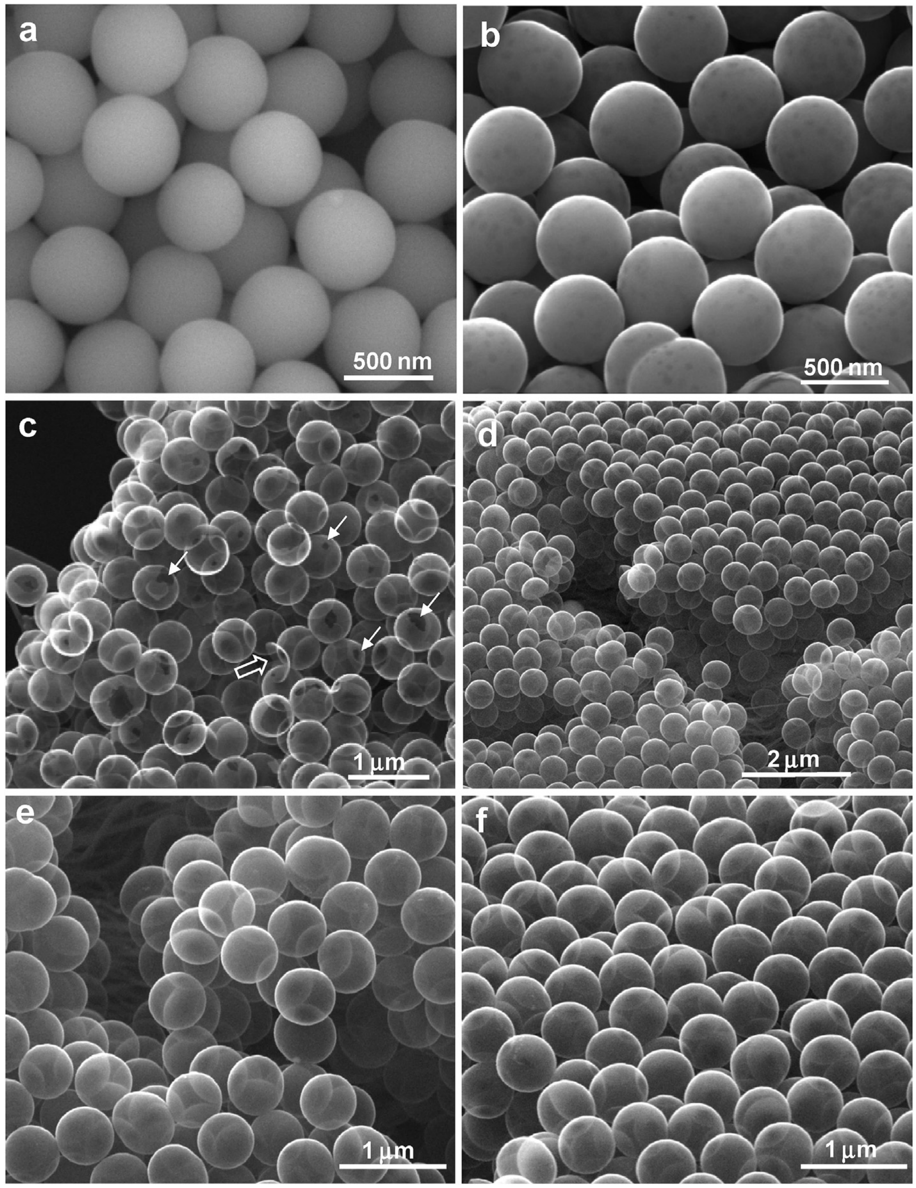

Fig. 1. SEM images of HCSs. (a) Micro-sized SiO_2 spheres. (b) Carbon-coated SiO_2 spheres (after CVD growth). (c) HCSs after 3 min growth. (d,e) HCSs after 5 min growth. (f) HCSs after 8 min growth. The white arrow heads in (c) indicate the holes on spheres. The hollow arrow head in (c) indicates a graphene hemisphere.

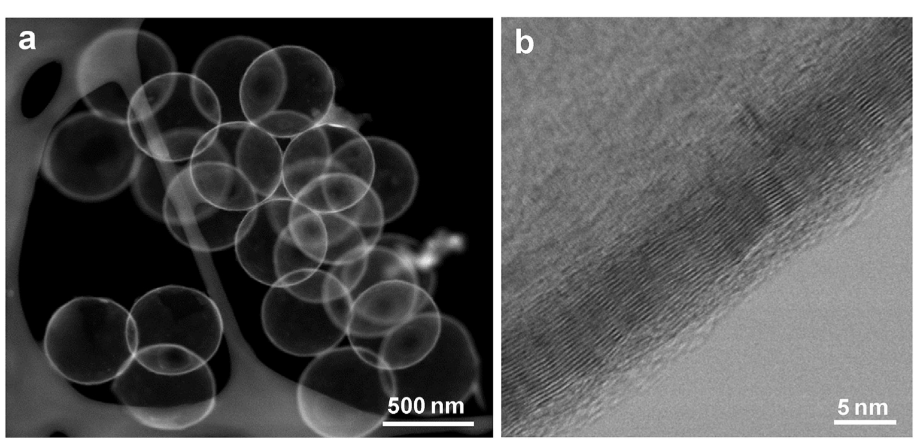

Fig. 2. TEM images of HCSs. (a) Z-contrast dark-field STEM image of a cluster of HCSs. (b) HRTEM image of the wall of a HCS.