



Nitrogen-doped activated carbon with micrometer-scale channels derived from luffa sponge fibers as electrocatalysts for oxygen reduction reaction with high stability in acidic media



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ARTICLE INFO

Article history:

Received 25 July 2014

Received in revised form 17 October 2014

Accepted 19 October 2014

Available online 23 October 2014

Keywords:

activated carbon
luffa sponge fibers
oxygen reduction reaction
electrocatalysts
acidic media

ABSTRACT

Nitrogen-doped multichanneled activated carbon (NMAC) has been prepared for application as electrocatalysts for oxygen reduction reaction (ORR) in fuel cells. The NMAC is prepared by carbonizing luffa sponge fibers in NH_3 and subsequent activation with KOH. The NMAC possesses densely packed and parallel channels with diameters of 3–13 μm and wall thickness of 0.4–1.8 μm . After activation micro- and mesopores are generated on the channel walls, forming a hierarchically porous structure. The NMAC exhibits excellent electrocatalytic performance for ORR both in alkaline and acidic media with high electrocatalytic activity and long-term operation stability. In particular, the NMAC has prominent stability in acidic media, keeping stable after about 7 hours and retaining 88.5% of the initial current density after 12 hours in 0.5 M H_2SO_4 solution. Because the active sites are located on the inner surface of the micrometer-scale channels the performance degradation caused by peeling, aggregation, and crack during operation can be avoided, resulting the high stability. Considering the abundance of luffa fibers on earth, the present NMAC materials are highly promising in various applications such as electrocatalysts, supercapacitors, and templates for supporting various functional materials.

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1. Introduction

Fuel cells are highly promising energy conversion devices due to their high efficiency, renewability, and low emission [1,2]. The oxygen reduction reaction (ORR) at the cathode is one of the most important factors influencing the performance of the fuel cells. Electrocatalysts are crucial for the occurrence of the ORR and determine its potential and current density. Traditionally, Pt nanoparticles supported on high surface area carbon materials are used as the ORR catalysts [3–5]. However, the high cost, limited supply, activity deterioration with time, and CO poisoning severely hinder their widespread application. Much effort has been devoted to the search for alternative catalysts to Pt and some Pt-free catalysts such as transition metal chalcogenides [6], Pd-based alloys [7,8], gold nanoclusters [9], and metal-polyaniline composites [10,11] have been found to have electrocatalytic activity for ORR. Recent research indicates that nitrogen-doped carbon materials (NCMs) such as nanotubes [12,13], nanofibers [14], graphene [15], and mesoporous carbon [16] possess excellent

electrocatalytic performance for ORR in alkaline media with high activity, long-term operation stability, and tolerance to crossover effect, even better than the commercial Pt/C catalysts. However, the NCMs behave not well in acidic media, which seriously hampers their widespread application in proton exchange membrane fuel cells [17,18].

Apart from the intrinsic property the electrocatalytic performance of the catalysts is also dependant on their microstructure and assembly form. Generally, increasing the surface area of the catalysts can increase the active sites exposing towards the electrolyte, and thus increasing the electrocatalytic activity for ORR, as exhibited by the mesoporous carbon [16]. However, even for these porous materials only the surface layer contributes to the catalytic reaction because the pores are present only on the surface or the pore size are too small and shallow to allow the deep penetration of the electrolyte. Furthermore, the reaction rate is not only affected by the effective surface density of the catalytic site but also by the renewing rate of the electrolyte solution near the active sites, which depends on the size of the transporting channels. It has been reported that the ORR catalytic activity can be improved by forming macroporous structure [19–21], which was ascribed to the facile mass transfer in the macropores and multidimensional mass transport paths [22]. It is

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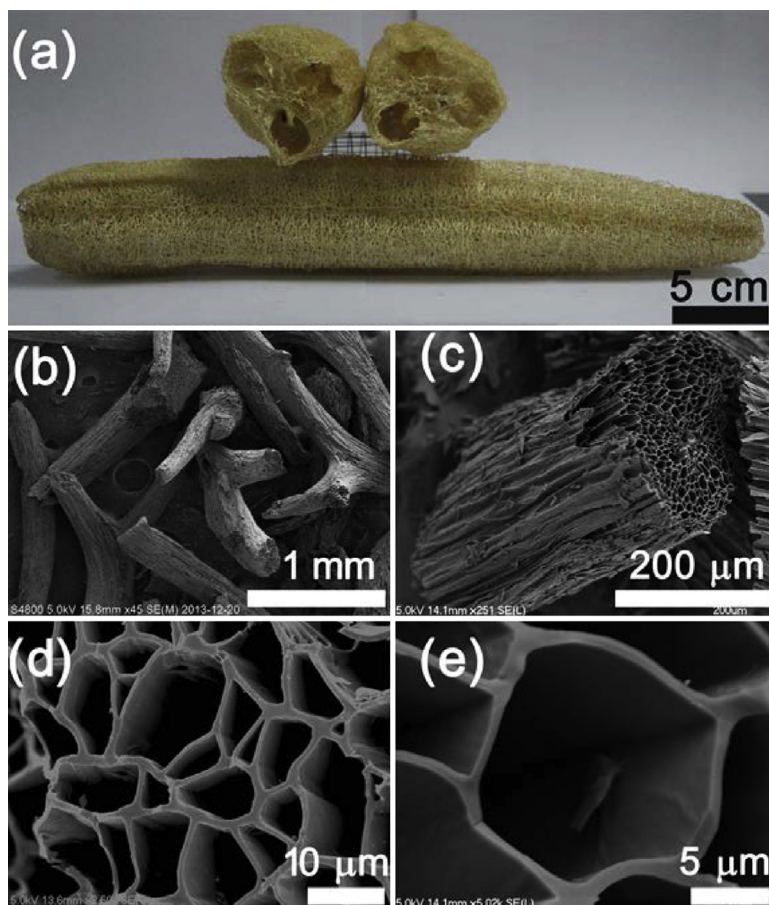


Fig. 1. (a) Optical image of the luffa sponge, (b–e) SEM images of the AC900NH₃.

considered that the macropores with appropriate size allowing the electrolyte solution to flow inward and outward efficiently benefit the catalytic reaction. Therefore, the electrocatalysts with hierarchical porous structure from subnanometer- to micrometer-scale enabling full utilization of the catalysts are ideal for obtaining good catalytic performance. Natural plant materials possess a rich variety of microstructures [23], which can be conveniently used as the precursors to prepare the carbon materials with different structures [24,25]. Among the different plant materials luffa sponge fibers have unique structure, i.e., the fibers are hollow with parallel micrometer-scale multichannels. This material is very attractive as the precursor to prepare the hierarchically porous carbon combining nano- to micrometer-scale features.

In this paper, nitrogen-doped multichanneled activated carbon (NMAC) was prepared by carbonization and activation from the luffa sponge fibers and their application as electrocatalysts for ORR was investigated. The NMAC possesses parallel-arranged channels with the size at micrometer scale. After activation micro- and mesopores were generated on the wall surface of the channels, forming a hierarchically porous structure. The NMAC exhibits excellent electrocatalytic performance for ORR both in alkaline and acidic media. Especially, the NMAC shows prominent stability in acidic media. Noting that the luffa sponge fibers are abundant on earth, the present NMAC materials are of high promise in various applications such as electrocatalysts, supercapacitors, and templates for growing various functional materials.

2. Experimental

The luffa sponge was collected from South China Plant Home in Guangzhou. Before heat treatment the luffa sponge was carefully washed with water and then dried at 60 °C. Carbonization of the luffa sponge fibers was conducted in a conventional tube furnace. In a typical process, 10 g of luffa sponge was heated at different temperatures (750, 900, and 1050 °C) for 2 h with the heating rate of 5 °C min⁻¹ in NH₃ atmosphere with a flow rate of 60 mL min⁻¹. Subsequently, the obtained carbon materials were mixed with KOH at a mass ratio of 1 to 2 and heated at 750 °C for 90 min with a heating rate of 8 °C min⁻¹ in N₂ atmosphere. After activation, the samples were washed with 1 M HCl and distilled water in sequence to remove the residual alkaline, followed by drying at 60 °C, obtaining the NMAC. The above obtained samples were denominated as AC750NH₃, AC900NH₃, and AC1050NH₃, respectively. The sample carbonized at 900 °C in NH₃ without activation is called C900NH₃. For comparison, the samples were also prepared by carbonization in N₂ at 900 °C without and with subsequent activation in N₂ at 750 °C, which we call C900N₂ and AC900N₂, respectively.

Scanning electron microscope (SEM, HITACHI S-4700), Raman spectroscopy (Renishaw RM-1000), X-ray diffraction (XRD, Rigaku D/Max 2500/PC), and transmission electron microscope (TEM, JEM-2100HR) were used to characterize the structure and morphology of samples. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to determine the composition. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer (USA). Before measurements, the samples

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