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Short Communication

Sulfonation of ordered mesoporous carbon supported Pd catalysts for formic acid electrooxidation

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ABSTRACT

A novel supporting material containing benzenesulfonic acid (BSA) groups and ordered mesoporous carbons (OMCs) was first prepared by in situ radical polymerization of 4-styrenesulfonate and isoamyl nitrite under ambient conditions. Then, Pd nanoparticles were deposited on as-produced OMCs (f-OMCs) by the $NaBH_4$ reduction method. The structure and nature of the resulting composites were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and nitrogen adsorption–desorption. The results show that BSA groups are created and the texture and surface chemistry are altered, whereas the ordered porous structure is maintained. The electrocatalytic properties of the Pd/f-OMCs catalysts for formic acid oxidation (HCOOH) have been investigated by cyclic voltammetry and chronoamperometry methods, and excellent electrocatalytic activity can be observed.

1. Introduction

Recently, OMCs, as new forms of carbon, were widely applied in many fields for their high surface areas, high electrical conductivity, good chemical stability, and significant mechanical strength [1,2]. Due to the high surface areas in the case of its outside walls and central hollow structure, OMCs can be used as catalyst supports for a variety of applications in fuel cells [3–5]. In all these studies nonfunctionalized OMCs were used for the preparation of the catalysts, but it must be considered that OMCs contain a small amount of surface oxygen groups, which can be disadvantageous to anchor noble metal particles onto the framework of OMCs for their application in the area of catalysis [6–9]. Thus, it is important to require a functionalized carbon surface with specific affinities and reactivities. The functionalization of OMCs with hydrophilic groups is expected to improve the dispersibility of the modified OMCs. Early efforts on the functionalization of OMCs by oxidation with nitric acid indicate that harsh oxidation conditions led to degradation of the meso-structural order [10,11]. In addition to acid treatment, many other efficient modification methods on the carbon surface, such as grafting through electrochemical or chemical reduction of aryl diazoniums and reductive alkylation or arylation, have been developed and can be applied for functionalization of OMCs [12–15]. Nevertheless, there is so far no report on functionalization of OMCs with BSA groups and on the use of such materials as metal nanoparticle catalyst supports in fuel cells. So the use of functionalized OMCs, with controllable textural properties and surface chemistry, with the purpose of improving the performance of these fuel cells, is an interesting field of research.

In this paper, functionalized BSA groups were first grafted onto the surface of OMCs by in situ radical polymerization of 4-styrenesulfonate and isoamyl nitrite under mild conditions (see Fig. 1). Through a combination of the advantages of Pd catalysts (e.g., high catalytic activity) and the unique features of f-OMCs (e.g., hydrophilic functional surface, high surface area), the resulting Pd/f-OMCs catalysts show excellent electrocatalytic activity and stability for HCOOH electrooxidation.

2. Materials and methods

OMCs, synthesized by incipient wetness impregnation of SBA-15 silica as described [3], were employed as the support. Specifically, 0.2 g of OMCs was dried overnight at 120 °C in a branched flask and then mixed with 1.2 g of 4-aminobenzenesulfonic acid. Later, 4 mL of isoamyl nitrite was added dropwise with a syringe under vigorous stirring. The stirring was continued for 1 h at room temperature, and the reaction temperature was gradually raised to 70 °C, and the reaction was continued at 70 °C for 1.5 h. The resulting product was repeatedly washed with dimethylformamide and hot chloroform several times, and then dried at 30 °C overnight in a vacuum oven. The obtained sample was denoted as f-OMCs.

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Sixty milligrams of f-OMCs was dispersed in 2 mL of 6 mg mL^{-1} $PdCl_2$ solution and stirred for 1 h. Then 40 mL 0.02 M $NaBH_4$ solution was added to the system and stirred at 30 °C for 12 h. The resulting composites were obtained and washed with deionized

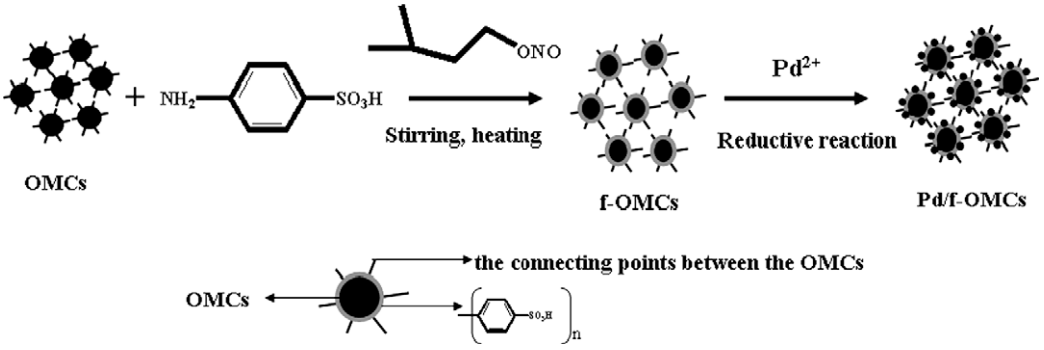

Fig. 1. Schematic procedure for the preparation of Pd nanoparticles on covalent functional OMCs.

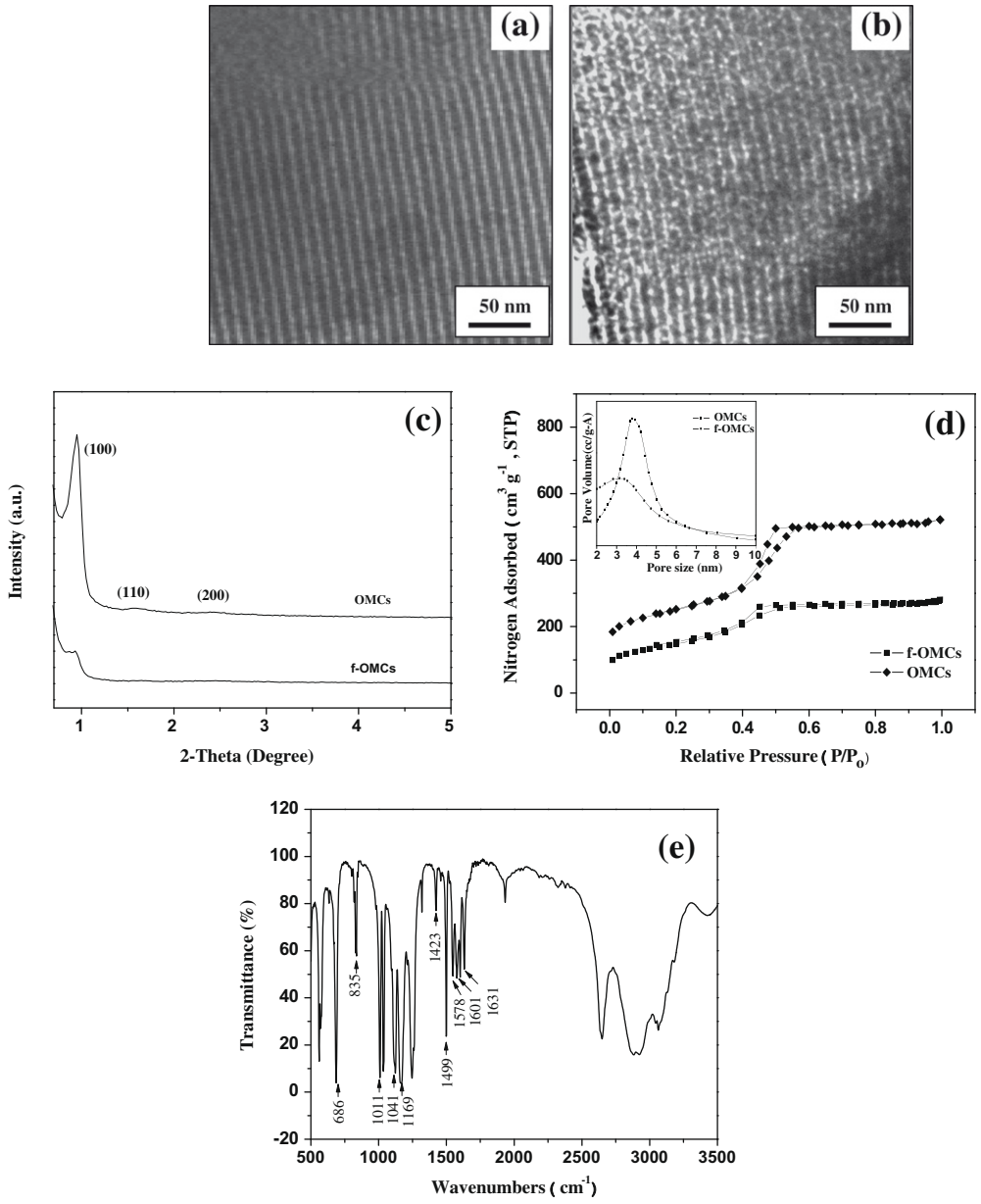

Fig. 2. (a and b) TEM image of OMCs and f-OMCs. (c) Small-angle XRD patterns of OMCs and f-OMCs. (d) Nitrogen adsorption–desorption isotherms of OMCs and f-OMCs. Inset: the pore size distributions for OMCs and f-OMCs. (e) FTIR spectra of f-OMCs.