Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Mesoporous carbon doped with N,S heteroatoms prepared by one-pot auto-assembly of molecular precursor for electrocatalytic hydrogen peroxide synthesis

Laura Roldán[a], Lai Truong-Phuoc[b], Alejandro Ansón-Casaos[a], Cuong Pham-Huu[b], Enrique García-Bordejé[a,*]

[a] Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain
[b] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), ECPM, UMR 7515 du CNRS-Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France

ARTICLE INFO

Article history:
Received 19 October 2016
Received in revised form 1 December 2016
Accepted 15 December 2016
Available online xxx

Keywords:
Hydrothermal carbon
Mesoporosity
Electrocatalysis
Oxygen reduction reaction
H_2O_2 synthesis

ABSTRACT

A bottom-up approach based on hydrothermal carbonization of organic molecules has been used to prepare carbon materials doped with either nitrogen or sulfur or both. To generate mesopores, $ZnCl_2$ has been used as removable structure-directing agent. The final mean mesopore size depended on the type of dopant element. The doped materials exhibited remarkable activity as electrocatalyst in oxygen reduction reaction with nearly complete selectivity to H_2O_2 synthesis. Two pyrolysis temperatures (973 K and 1173 K) were used that yield materials with different electric conductivity, dopant content and porosity but comparable electrocatalytic performance. N-doped catalyst with an intermediate nitrogen content (4 wt%) and around 80% of pore volume in the mesopore range provided the best performance among the catalysts tested.

1. Introduction

Hydrogen peroxide is a potential energy carrier and an environmentally friendly oxidant for various chemical industries and environmental remediation. It is manufactured industrially by the anthraquinone process, an indirect batch method requiring sequential hydrogenation, oxidation of anthraquinone molecules, and extraction of H_2O_2 from organic solvents. However, this multistep method is hazardous, energy-intensive and difficult for in situ H_2O_2 production [1]. Considerable efforts have been dedicated to develop efficient and on-site H_2O_2 production methods, which cannot only considerably reduce the cost for H_2O_2 synthesis, transport, storage, and handling but also facilitate the subsequent application process.

Direct synthesis of H_2O_2 has been achieved from H_2 and O_2 under plasma [2] or on various catalysts [3–6]. These methods offer a continuous mode for H_2O_2 production and enable its decentralized generation. However, they suffer from potential explosion of H_2/O_2 gas mixture. Another alternative method is the electroreduction of O_2 through a two-electron pathway, which enables the in situ production of H_2O_2 at moderate temperature and under atmospheric pressure while avoiding the danger of explosion [7]. The electrochemical approach has the relevant advantage of performing the reduction of O_2 and the oxidation of H_2 in two separate cells, thus avoiding the contact between the two reagents and making the process intrinsically safer compared to the direct reaction of H_2 with O_2.

The electrochemical reduction of O_2 to H_2O occurs through the transfer of four electrons (1 or 2), whereas the partial reduction of O_2 to H_2O_2 involves the transfer of two electrons (3 or 4).

$$O_2 + 4H^+ + 4\,e^- \rightarrow 2H_2O\,(acidicenv.)E_0 = 1.23\,V \tag{1}$$

$$O_2 + 2H_2O + 4\,e^- \rightarrow 4\,OH^-\,(basicenv.)E_0 = 0.40\,V \tag{2}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2\,(acidicenv.)E_0 = 0.70\,V \tag{3}$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2{}^- + OH^-\,(basicenv.)E_0 = 0.06\,V\ldots \tag{4}$$

Catalysts that reduce O_2 with four electrons are sought for fuel cell application in order to avoid fuel cell degradation by H_2O_2. On the other hand, a highly selective two-electron reduction catalyst to hydrogen peroxide is also attractive as explained above for the production of H_2O_2. Different designs of H_2/O_2 fuel cells for the synthesis of H_2O_2 have been proposed, with the electrolyte being

---

* Corresponding author.
E-mail address: jegarcia@icb.csic.es (E. García-Bordejé).

http://dx.doi.org/10.1016/j.cattod.2016.12.020
0920-5861/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: L. Roldán, et al., Mesoporous carbon doped with N,S heteroatoms prepared by one-pot auto-assembly of molecular precursor for electrocatalytic hydrogen peroxide synthesis, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.12.020

an acidic solution, a basic solution or a solid polymeric membrane [8,9]. The latter option allows obtaining neutral and electrolyte-free solutions of H_2O_2 and recovering the energy released during reaction. An essential factor for the development of fuel cells for the cogeneration of chemicals and electricity is the identification of suitable electrocatalysts. The choice of the electrocatalyst is crucial for obtaining high selectivity toward the two-electron reduction of O_2 to H_2O_2 and to avoid further electrochemical reduction of H_2O_2 to H_2O by another two-electron reduction or the chemical disproportionation reaction of H_2O_2 [5]. Many potential electrocatalysts have been exploited for H_2O_2 production, including noble metals, metal alloys, and carbon materials. Oxygen reduction on metal alloys, such as Pd–Au and Pt–Hg, proceeds primarily through the two-electron pathways with selectivity of 71–92% (0.1–0.3 V *vs.* RHE, pH 1) [8–10]. However, the scarcity and high cost of noble metals hinders their wide application. Carbon materials are a promising alternative for H_2O_2 electrosynthesis due to their high abundance, low cost, and electroreduction activity. It has been found that carbon nanotubes, carbon fibers, graphite, and N-doped porous carbon are active for H_2O_2 production with production rates of 1.7–121 mmol h^{-1} g^{-1} and current efficiencies of 26.5–65.2% (pH 1–7), and their performance is related to material structure and doping [11–14]. Among various carbon materials, graphitic carbon materials are attractive for electrocatalysis due to their tunable surface area and good electrical conductivity [15]. Such structure endows this material with plentiful exposed catalytic sites and shortened diffusion paths [16], which are beneficial for H_2O_2 production from O_2 reduction. Deffects in the sp^2 carbon lattice can act as active sites for reactant adsorption or reaction during the electrocatalytic process [17] and thereby may improve the kinetics of oxygen reduction. Nitrogen doped carbon materials have been extensively studied in O_2 reduction reaction for fuel cell cathodes. N-doped CNTs have showed remarkable activity and high selectivity to 4-electron reduction [18,19]. Although the catalyst is claimed to be metal-free, the use of metal during N-CNT synthesis rises some concerns about the role of hardly detectable metal impurities [20]. Porous N-doped carbon have also been prepared using nanocasting routes using N-containing polymers which provided a 4-electron reduction [21,22]. Recently, nitrogen-doped mesoporous carbon synthesized from food-processing raw materials has been reported by Ba et al. [23], which displayed high ORR performance and relatively high stability as a function of cycling tests. Concerning H_2O_2 electrosynthesis, a high selectivity to H_2O_2 (two-electron reduction pathway) has been reported for metal-free N-doped carbons prepared from MOF [24] or using also a nanocasting strategy starting either from ionic liquids [11] or other N,C- containing molecules [12]. Hydrothermal carbonisation of N- and S-containing organic molecules has been employed to synthesize metal-free N-doped [25–27] and N,S-codoped [28] carbon materials. These materials were reported to exhibit a mixed 2-electrons/4-electrons reduction mechanism. Several approaches have been used to endow mesoporosity to hydrothermally prepared carbon. One of these approaches is nanocasting, which requires multiple steps and the use of hazardous reagents [29]. A one-pot method is using hypersaline conditions during hydrothermal carbonisation to prepare aerogel-like mesoporous bodies [30].

Herein, we have adopted hydrothermal carbonisation of biobased organic molecules as a method to prepare N-doped, S-doped and N,S co-doped carbon materials. This bottom-up approach enables the preparation of carbon material with controlled dopant content. To endow the carbon material with mesoporosity, the hydrothermal carbonisation has been carried out under hypersaline conditions using $ZnCl_2$, which is subsequently washed out from the resulting solid. The carbon materials have been pyrolized at two temperatures (973 K and 1173 K) to increase electrical conductivity and they have been characterised extensively in order to get more insight about their chemical and physical characteristics. Finally, they have been tested in electrocatalytic O_2 reduction reaction under alkaline conditions.

2. Experimental

For the preparations, anhydrous Glucose (Panreac), Pyrrole-2-carboxaldehyde (Sigma-Aldrich), 2-Thiophenecarboxaldehyde (Sigma-Aldrich) reagents were used.

For the synthesis of N-doped carbon materials, 3 g of anhydrous Glucose, 4.5 g of $ZnCl_2$, 0.50 g (5.3 mmol) of Pyrrole-2-carboxaldehyde and 1.5 mL of H_2O were thoroughly mixed. The mixture was transferred into a glass vessel that was introduced in a Teflon-lined autoclave and kept at 463 K under autogenous pressure for 19 h. Two additional samples varying the amount of pyrrole-2-carboxaldehyde, 2.6 mmol and 10.5 mmol, were prepared.

For the synthesis of S-doped carbon materials, 3 g of anhydrous Glucose, 4.5 g of $ZnCl_2$, 0.59 g (5.3 mmol) of 2-Thiophenecarboxaldehyde and 1.5 mL of H_2O were thoroughly mixed and treated in the autoclave in the same conditions mentioned above.

For the synthesis of dual N,S-doped carbon materials, 3 g of anhydrous Glucose, 4.5 g of $ZnCl_2$, 0.50 g of Pyrrole-2-carboxaldehyde, 0.59 g of 2-Thiophenecarboxaldehyde and 1.5 mL of H_2O were thoroughly mixed and treated in the autoclave as mentioned above.

To remove the $ZnCl_2$ present, the solid resulting after hydrothermal synthesis was immersed in 500 mL of distilled water and kept overnight under stirring. Subsequently, it was filtered, washed with abundant distilled water and dried at 383 K in an oven. The $ZnCl_2$ can be recovered after evaporation of the rinsing water and subsequently recycled. Therefore, the use of $ZnCl_2$ does not represent an environmental concern. Finally, the carbon materials were pyrolised at 973 K or 1173 K. The samples were denoted as HTC- followed by the doping heteroatoms (N, S or N,S) and followed by the pyrolysis temperature. One N-doped carbon sample named as HTC-N-Zn-973 was prepared by pyrolising at 973 K just after hydrothermal synthesis, *i.e.* the washing of Zn was not performed after hydrothermal synthesis but after pyrolysis.

Two samples containing Fe were prepared on nitrogen-doped carbon materials, for one sample the Fe was deposited after pyrolysis at 1173 K (HTC-N-1173-Fe) and for the other it was deposited before pyrolysis (HTC-N-Fe-1173). In both cases, the amount of Fe precursor was calculated to have a 0.5% Fe in the final carbon material. For the preparation of HTC-N-1173-Fe, 300 mg of HTC-N-1173 (85% C) were impregnated with 2 mL of a H_2O:EtOH (1:4) solution containing 9.22 mg of $Fe(NO_3)_2 \cdot 9H_2O$ precursor. After drying at room temperature overnight the solid was calcined in N_2 at 573 K during 2 h using a heating rate of 1 K/min. For the preparation of HTC-N-Fe-1173, 526 mg of HTC-N (after pyrolysis at 900 °C this material underwent a 57% weight loss) were also impregnated with 2 mL of a H_2O:EtOH (1:4) solution containing 9.22 mg of $Fe(NO_3)_2 \cdot 9H_2O$ precursor. After drying at room temperature overnight, the solid was calcined in N_2 atmosphere at 1173 K during 1 h using a heating rate of 1 K/min.

Surface areas were determined by N_2 adsorption at 77 K using a Micromeritics ASAP 2020 apparatus, after outgassing the samples for 4 h at 423 K. From the physisorption measurements with N_2, the specific surface area has been calculated by the BET (Brunauer, Emmet, and Teller) theory in the relative pressure range 0.01–0.10 following standard ASTM-4365, which is applicable to microporous materials. Total pore volume (VT) was calculated from the amount of N_2 adsorbed at a relative pressure of 0.99. Pore-size distribution was obtained from the adsorption branch of the N_2 isotherm

Please cite this article in press as: L. Roldán, et al., Mesoporous carbon doped with N,S heteroatoms prepared by one-pot auto-assembly of molecular precursor for electrocatalytic hydrogen peroxide synthesis, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.12.020