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*}

^aInstituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain,

^bInstitut 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

Keywords

hydrothermal carbon; mesoporosity; electrocatalysis; oxygen reduction reaction; H₂O₂ 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, ZnCl₂ has been used as removable structure-directing agent. The final mean pore 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 H₂O₂ synthesis. N-doped catalyst with an intermediate nitrogen content (4 wt%) and around 80% of pore volume in the mesopore range provided significantly better performance than a catalyst of comparable composition but differing in the porous structure, *i.e.* 70 % of pore volume in the microporous range.

1. Introduction

* Corresponding author: Tel.: + 34 976733977; fax.: +34 976733318 E-mail address: jegarcia@icb.csic.es

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 H₂O₂ from organic solvents. However, this multistep method is hazardous, energy-intensive and difficult for in situ H₂O₂ production [1]. Considerable efforts have been dedicated to develop efficient and on-site H₂O₂ production methods, which cannot only considerably reduce the cost for H₂O₂ synthesis, transport, storage, and handling but also facilitate the subsequent application process.

Direct synthesis of H₂O₂ has been achieved from H₂ and O₂ under plasma [2] or on various catalysts [3-6]. These methods offer a continuous mode for H₂O₂ production and enable its decentralized generation. However, they suffer from potential explosion of H₂/O₂ gas mixture. Another alternative method is the electroreduction of O₂ through a two-electron pathway, which enables the in situ production of H₂O₂ 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 O₂ and the oxidation of H₂ in two separate cells, thus avoiding the contact between the two reagents and making the process intrinsically safer compared to the direct reaction of H₂ with O₂.

The electrochemical reduction of O₂ to H₂O occurs through the transfer of four electrons (1 or 2), whereas the partial reduction of O₂ to H₂O₂ involves the transfer of two electrons (3 or 4).

Catalysts that reduce O₂ with four electrons are sought for fuel cell application in order to avoid fuel cell degradation by H₂O₂. On the other hand, a highly selective two-electron reduction catalyst to hydrogen peroxide is also attractive as explained above for the production of H₂O₂. Different designs of H₂/O₂ fuel cells for the synthesis of H₂O₂ have been proposed, with the electrolyte being 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. Defects in the sp² 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,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 prepare mesoporous hydrothermal carbon. One of these approaches is nanocasting, which requires multiple steps and the use of hazardous reagents [29]. Fechler et al.[30] prepared aerogel-like mesoporous bodies in one pot by using hypersaline conditions during hydrothermal carbonisation.

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 a completely metal-free 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 pyrolyzed 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 all the Zn 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. Finally, the carbon materials were pyrolysed 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 pyrolysing 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 $\text{H}_2\text{O}:\text{EtOH}$ (1:4) solution containing 9.22 mg of $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ precursor. After drying at room temperature overnight the solid was calcined in N_2 at 573 K during 2 hours using a heating rate of 1K/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 $\text{H}_2\text{O}:\text{EtOH}$ (1:4) solution containing 9.22 mg of $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ precursor. After drying at room temperature overnight, the solid was calcined in N_2 atmosphere at 1173 K during 1 hour 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 according to the BJH method (Barrett-Joyner-Halenda) using the DataMaster V4.0 software and assuming slit pore geometry. BJH model developed in 1951 which is

based on the Kelvin equation and corrected for multilayer adsorption, is most widely used for calculations of the pore size distribution in the mesoporous and part of the macroporous range [31]. Microporous volume (V_{μ}) was estimated by Density Functional Theory (DFT method), which is applicable to materials with both micro and mesopores [32]. The model fitted quite well to the isotherm with a standard deviation of $\sim 0.05 \text{ cm}^3 \text{ g}^{-1} \text{ STP}$. CHNS analyses were carried out by combustion in a ThermoFlash 1112 elemental analyzer equipped with a TCD detector. Oxygen analysis was done by direct assay which involves pyrolysis of the sample at 1343 K in a nickel/carbon bed under a known He flow. The outlet flow, after passing through a separation column, ends in a TCD detector. The oxygen content of sample is quantified on the basis of CO analyzed.

SEM analysis was carried out with a microscope SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and with an analyzer EDX Röntec XFlash of Si(Li). The samples were sputtered with gold previously to measurements. The images were obtained from the secondary electron signal.

HR-TEM was carried out using a FEI TECNAI F30 electron microscope equipped with Gatan Energy Filter and cold field emission gun (FEG) operated at 300 kV with 1.5 Å lattice resolution. TEM specimens were prepared by ultrasonic dispersion in ethanol and a drop of the suspension was applied to a holey carbon support grid.

Ex-situ XPS spectra were recorded with an ESCA+ (Omicron) system equipped with Al/Mg radiation source to excite the sample. Calibration of the instrument was done with Ag 3d_{5/2} line at 368.27 eV. All measurements were performed under UHV, better than 10^{-10} Torr. Internal referencing of spectrometer energies was made using the dominating C 1s peak of the support at 284.6 eV. The program used to do curve fitting of the spectra was CasaXPS after baseline Shirley subtraction.

Cyclic voltammetry (CV) and rotating disk electrode (RDE) studies were conducted in a glass cell in 0.1M KOH supporting electrolyte using Autolab PGSTAT30 potentiostat equipped with an analogue linear sweep generator at the sweep rate of 10 mV s^{-1} . Ag/AgCl electrode and Pt wire electrode were used as the reference electrode and the counter electrode, respectively. Unless otherwise stated, all potentials hereinafter are referred to the reversible hydrogen electrode (RHE)

For the catalyst ink preparation, 10.0 mg of the catalyst sample, 5 mL isopropanol, and 50 μL Nafion solution (5 wt%) were mixed and dispersed by sonication until a homogeneous ink was formed. For the rotating ring disk (RDE) measurements, the

working electrode (Pine instruments) was prepared by loading 52.5 μL of catalyst ink onto a pretreated glassy carbon (GC) electrode (5.5 mm diameter and 0.2376 cm geometric area) and then dried at room temperature. The catalyst loading was set at 445 $\mu\text{g}\cdot\text{cm}^{-2}$. The benchmark Pt/C catalyst was charged with a 20 wt% Pt/C (Sigma-aldrich) catalyst at a loading of 125 $\mu\text{g}\cdot\text{cm}^{-2}$.

All aqueous solutions were prepared using ultrapure water (18 M Ω cm, <3 ppb TOC) and supra-pure KOH (Sigma–Aldrich). In O₂-reduction experiments O₂ was constantly bubbled through the solution in order to maintain the saturation level.

The apparent number of electrons transferred per O₂ molecule was calculated using the first-order Koutecky–Levich equation:

$$\frac{1}{J_D} = \frac{1}{J_k} + \frac{1}{J_d}$$

where J_k is the kinetic current density and J_d is the diffusion-limited current density through the expression $J_d = B \omega^{1/2} = 0.62 n F \gamma^{-1/6} D_{O_2}^{2/3} C_{O_2} \omega^{1/2}$. Here n is the number of electrons; F is the Faraday constant; γ is the kinematic viscosity of the electrolyte; D_{O_2} is the oxygen diffusion coefficient ($1.95 \times 10^{-5} \text{cm}^2\cdot\text{s}^{-1}$) [19], C_{O_2} is the bulk oxygen concentration in the electrolyte ($1.15 \times 10^{-6} \text{mol}\cdot\text{cm}^{-3}$) [33]; and ω is the angular velocity of the electrode. The kinetic current density (J_k) and the Koutecky–Levich slope ($1/B$) can be obtained from a plot of $1/J$ vs. $\omega^{-1/2}$ for different rotating rates (400, 900, 1600, 2000, 2500 rpm)

DC electrical conductivity (σ) was measured by a four point probe method using a Keithley 4200 instrument provided with four source measurement units and a preamplifier. Cylindrical specimens ($d = 13$ mm, $t \sim 1$ mm) were prepared by pressing the powder samples at ~ 5 Tm. In order to improve pellet consistency, the powder samples were mixed with ~ 30 wt% of poly(vinylidene fluoride) (Aldrich 182702). Bulk resistivity (ρ) was calculated applying the expression:

$$\rho = 2\pi s F \frac{V}{I}$$

where s is the distance separation between the equidistant collinear probe needles (= 2.24 mm), F is a geometrical correction factor accounting for sample thickness and lateral sample dimensions, V is the potential between the central probes and I is the current intensity circulating between the outer probes.

Results and discussion

Figure 1 shows representative HR-TEM images of nitrogen and sulphur doped materials. After hydrothermal synthesis, the materials consist of an aggregation of primary particles of around 10 nm (Figure 1 a and c). These particles have a quasi-spherical morphology and a nano-onion structure with its layers formed by curved and short fragments. Onion-like morphologies has been also reported for larger carbon nanosphere materials prepared by hydrothermal carbonisation of glucose [34]. After pyrolysis at 1173 K (Figure 1 b and d), the primary particles are still visible especially at the edges of the agglomerates but sintering of the particles has occurred and the onion-like morphology is less apparent.

Figure 1. TEM images of doped materials as synthesized under hydrothermal conditions and after pyrolysis at 1173 K: (a) HTC-N, (b) HTC-N-1173, (c) HTC-S, (d) HTC-S-1173.

Table 1 displays the parameters of textural characterisation by N₂ physisorption of the different materials used as catalyst. The adsorption isotherms and pore size distribution are presented in Figure 2. The introduction of ZnCl₂ during the preparation of undoped HTC entails the development of a 26% of mesoporosity compared to the ZnCl₂-free preparation that yielded a carbon material devoid of mesoporosity [35]. The mesoporosity accounts for 26%, 78%, 65% and 72% of total pore volume and the average pore sizes are 3.5 nm, 8.2 nm, 34 and 32 nm for un-doped, N-doped, S-doped, dual N,S-doped HTC, respectively (Table 1 and Figure 2). Thus, the dopant molecule governs the resulting structure leading to different average mesopore sizes. The pores are widely distributed in the mesoporous range for doped samples, between 5-30 nm for N-doped and between 10-100 nm for S-doped and N,S-codoped samples (Figure 2). The sample HTC-N-Zn-973 was prepared similarly to HTC-N-973 but the Zn was not washed before pyrolysis. When the sample is pyrolyzed at 973 K, the remaining ZnCl₂ played the role of activating agent, yielding a very different carbon material which is endowed with the highest surface area and pore volume consisting mainly of micropores. The change of the pyrolysis temperature from 973 to 1173 K affects very marginally to the porosity. There is a slight decrease of Surface area when the pyrolysis temperature is increased to 1173 K for N-doped and N,S co-doped HTC materials. The chemical characterization (Table 2) shows the effective doping with N, S or both, which remain on carbon materials even after pyrolysis at high temperatures.

Table 1. Textural parameters obtained from N₂ (77 K)

sample	BET Area S _{N2}	Total pore volume (VT)	Micropore volume ^a (V _μ)	Mesopore volume (V _m)	Percentage mesopores (V _m /VT*100)	Average pore diameter (D _p)
	m ² g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	%	nm
HTC-973	520	0.27	0.20	0.07	26	3.5

HTC-N-973	450	0.48	0.14	0.34	68	8.2
HTC-N-1173	342	0.37	0.09	0.28	75	10
HTC-N-Zn-973	1510	0.77	0.54	0.23	28	<2
HTC-S-973	559	0.66	0.15	0.51	75	34
HTC-S-1173	546	0.90	0.15	0.75	83	35
HTC-N,S-973	477	0.37	0.14	0.23	62	33
HTC-N,S-1173	329	0.28	0.10	0.18	63	37

^a obtained by DFT model applied to N₂ adsorption isotherm

Figure 2. N₂ adsorption isotherms and pores size distribution estimated using the BJH method (inset) for HTC- (a), HTC-N- (b), HTC-N-Zn- (c), HTC-S- (d), HTC-N,S- (e) after pyrolysis at 973 K (solid line) and 1173 K (dashed line).

Table 2. Chemical characterisation by elemental analysis and XPS of electrocatalyst

Elemental analysis	Weight ratios		
	N/C	S/C	Zn/C
wt%			

					wt%		wt%		at%
	C	O	N	S	e.a.	XPS	e.a.	XPS	XPS
HTC-973	95.3	3.5	0.16	0.0	0.0	0.0	0.0	0.0	0.04
HTC-N-973	88.5	5.7	4.7	0.0	5.3	4.0	0.0	0.0	0.11
HTC-N-1173	84.4	10.2	4.0	0.0	4.8	4.0	0.0	0.0	0.07
HTC-N(2.6)-1173	89.2	7.1	2.7	0.0	3.0	2.4	0.0	0.0	0.06
HTC-N(10.5)-1173	85.7	7.3	5.9	0.0	6.9	6.7	0.0	0.0	0.05
HTC-N-Zn-973	77.0	17	4.2	0.0	5.5	3.9	0.0	0.0	0.15
HTC-S-973	88.7	3.3	0.10	6.7	0.0	0.0	7.6	15.0	2.3
HTC-S-1173	91.1	2.6	0.15	4.1	0.0	0.0	6.3	13.2	3.2
HTC-N,S-973	84.9	6.3	3.7	3.6	4.3	4.0	4.2	10.3	5.7
HTC-N,S-1173	84.3	8.0	3.05	4.1	3.6	4.0	4.9	10.3	6.0

The N 1s XPS peak of N-doped materials (Figure 3a) was fitted to four components denoted as pyridine N at 398.3 ± 0.1 eV, pyrrolic N at 400 ± 0.1 eV, quaternary N at 401 ± 0.1 eV and nitrogen oxide species at 404 ± 0.1 eV as described in the literature [36-38]. The nitrogen type undergoes a remarkable modification after pyrolysis at 973 K. The as-synthesized HTC-N contains exclusively pyrrolic nitrogen in agreement with the molecular structure of the used precursor. In the pyrolysed sample (HTC-N-973), the amount of pyridinic and quaternary nitrogen increases, which stems from the conversion of pyrrolic nitrogen present in hydrothermally-synthesised material since there is not additional source of nitrogen. Therefore, the basic carbon structure changed from 5-membered to 6-membered ring coordination when the HTC-N material is pyrolysed. This is in agreement with the conversion of furanic-based HTC material to a graphitic one when it is pyrolyzed at high temperature as reported by other authors [39].

The 2p XPS peak of S-doped materials (Figure 3b) shows a doublet peak at 163.7 and 165 eV which is attributed to the C-S-C bonding derived from thiophenic group in as-synthesized HTC material [40]. There is another peak which intensifies after pyrolysis at 161.7 eV which is ascribable to ZnS sphalerite [40]. The Zn content determined by XPS is negligible for most of the samples, indicating that the washing step after hydrothermal synthesis is very efficient for the removal of ZnCl_2 salt, except for S-containing-samples in which the washing of Zn is not so effective and 1-2 at% of Zn is detected by XPS (Table 2). The peak at 161.7 eV confirms that Zn remains bound to S,

hindering the washing out of Zn with water, and eventually leading to the formation of ZnS upon pyrolysis.

Figure 3. N 1s (a) and S 2p (b) XPS peaks of HTC-N- and HTC-S-, respectively, before and after pyrolysis at 973 and 1173.

The prepared carbon materials were tested as electrocatalysts in ORR experiments. Figure 4 and Figure 5 shows the linear swept voltammogram (LSV) curves of materials pyrolysed at 973 and 1173 K, respectively. The onset potential, limiting current and

average number of transferred electrons are compiled in Table 3. The number of transferred electrons was calculated by the Koutecky-Levich plots (Figure S1 of Supplementary material) after performing the ORR at different rotating rates (400-2500 rpm). The number of electrons transferred is calculated as an average in the range 0.15-0.5 V vs. RHE (Figure S2 of Supplementary material).

Figure 4. LSV curves of carbon materials pyrolysed at 973K in O₂ saturated 0.10 M KOH solution with a rotating rate of 1600 rpm.

Figure 5. LSV curves of carbon materials pyrolysed at 1173K in O₂ saturated 0.10 M KOH solution with a rotating rate of 1600 rpm.

Table 3. Onset potential, limiting current density and transferred number of electrons obtained from LSV curves at 1600 rpm

electrocatalyst	Onset potential ^a	Limiting current density	number of electrons transferred ^b	Conductivity S m ⁻¹
	V	mA cm ⁻²		
HTC-973	0.75	2.75	1.7	0.095
HTC-N-973	0.83	3.37	1.9	0.12
HTC-N-1173	0.83	3.37	1.9	46
HTC-N(2.6)-1173	0.78	3.10	1.9	35
HTC-N(10.5)-1173	0.83	3.30	2.0	59
HTC-N-Zn-973	0.80	1.41	1.3	0.045
HTC-S-973	0.77	2.75	2.1	0.16
HTC-S-1173	0.80	3.27	1.8	54
HTC-N,S-973	0.80	2.95	2.0	0.053

HTC-N,S-1173	0.78	3.01	2.0	42
HTC-N-1173-Fe	0.81	4.73	2.7	27
HTC-N-Fe-1173	0.91	3.64	2.2	27

^a The onset potential is determined as the potential required for a current density of $-20 \mu\text{cm}^{-2}$ (vs. RHE)

^b It is calculated as the average of the electrons transferred in the potential range 0.15-0.5 V vs. RHE.

The un-doped catalyst (HTC-973) exhibits some activity that can be ascribed to oxygen functional groups and defects. Defects [41-43] and oxygen functional groups [44;45] of CNT have been reported to be active sites for O₂ activation in ORR and other selective oxidation reactions. Nevertheless, the onset potential, limiting current density and transferred number of electrons increased remarkably after doping with heteroatoms indicating that the dopant elements endows higher activity for the oxygen reduction reaction which is in good agreement with the literature reports. The highest onset potential and limiting current corresponds to the carbon materials doped with nitrogen. No beneficial effect is observed by the co-addition of S to N in HTC-N,S- catalysts. The sample that was not washed before pyrolysis (HTC-N-Zn-973) provided the lowest values of limiting current density and number of electrons. Although N content in this sample is comparable to HTC-N-973, the surface area of this sample is three-fold higher but consisting mainly of micropores which significantly hinder the diffusion of the reactant towards the active sites. This highly microporous sample exhibited also the lowest conductivity. The comparison of the performance between these two catalysts underscores the positive role played by mesoporosity in the electrochemical behaviour. The beneficial effect of a hierarchical porous structure over purely microporous material has been previously reported [46;47]. The impact in the limiting current and the onset potential of increasing the pyrolysis temperature from 973 to 1173 K is negligible for N-doped material and slightly positive for S-doped materials. The electronic conductivity is more than two orders of magnitude higher for the sample pyrolysed at higher temperature (Table 3), suggesting that the ORR performance is unaffected by an increase in conductivity when the conductivity is above a certain limiting value.

The number of electrons transferred is very close to 2 for most of the doped materials. The exception is the un-doped material (HTC-973) and HTC-N-Zn-973 with 1.7 and 1.2 electrons transferred, respectively. The high selectivity to the two-electron reducing

pathway makes the N-doped catalyst very promising for electrocatalytic H_2O_2 synthesis. A well-defined plateau corresponding to the diffusion-controlled region is observed for the doped materials between 0.3 and 0.5V vs. RHE in the LSV plots. The presence of this plateau means that the two-electron reduction steps is clearly separated over these carbon materials [48]. The electrochemical H_2O_2 production was confirmed employing a photometrical peroxide test (Merk) [11]. The mesoporosity of these samples may favour the H_2O_2 desorption and diffusion, avoiding further re-adsorption and reduction. Other mesoporous doped carbons have also showed high selectivity to H_2O_2 [11].

N-doped carbons with three different nitrogen concentrations were synthesized by changing the amount of pyrrole-2-carboxaldehyde. When not stated, the standard pyrrole-2-carboxaldehyde amount in the initial mixture was 5.3 mmol and the sample was named as HTC-N. Samples with lower (2.6 mmol) and higher (10.5 mmol) amounts of pyrrole-2-carboxaldehyde were prepared and denoted as HTC-N(2.6) and HTC-N(10.5). After pyrolyzing at 1173 K, the N/C (wt%) in the resulting carbon materials ratio determined by XPS and elemental analysis are displayed in Table 2. The LSV curves of carbon materials with several nitrogen contents are shown in Figure 6. The onset potential is more positive and the current density increases when the nitrogen content increases from HTC-N(2.6)-1173 to HTC-N-1173. Further increase of the nitrogen content for HTC-N(10.5)-1173 has no beneficial effect. A poor catalytic performance has been reported for catalysts with too high N-content and it has been attributed to the disruption of the π -system that reduces the electron conductivity of the material [49]. In our case, the poorer catalytic performance of the catalyst with higher nitrogen content cannot be attributed to a decrease of conductivity (Table 3), therefore further research is needed to elucidate the exact reasons.

Figure 6. LSV curves of electrocatalysts with different nitrogen content in O₂ saturated 0.10 M KOH solution with a rotating rate of 1600 rpm .

Figure 7. LSV curves of electrocatalysts doped with nitrogen and containing Fe in O₂ saturated 0.10 M KOH solution with a rotating rate of 1600 rpm .

Two samples containing Fe were prepared on nitrogen doped carbon material as described in experimental section. Compared to HTC-N-1173, the materials containing Fe show very distinct behaviour in O₂ electroreduction (Figure 7). For HTC-N-Fe-1173 the effect of Fe addition is not very apparent providing slightly more positive onset potential but the limiting current and number of transferred electrons are similar. Nevertheless, HTC-N-1173-Fe exhibited a comparable onset potential but the limiting current and the number of transferred electrons is the highest among all the tested samples. The 2.7 electrons transferred for HTC-N-1173-Fe indicates that the addition of minor amounts of Fe dispersed on the N-doped materials triggers the 4-electron reduction process resulting in a mixed 2-electron and 4-electron reduction mechanisms. The high selectivity of our doped carbon materials toward the reduction of molecular oxygen to H₂O₂ suggests that during the reduction process the O-O bond of the adsorbed O₂ is not weakened to the point of causing its cleavage. Instead, an overall two-electron/two-proton reduction process takes place (Eq 4.: O₂→HO₂⁻→H₂O₂). The defects associated to doping sites are favourable for O₂ activation and reduction to HO₂⁻. The adsorption of O₂ on the surface of our doped carbon materials is weaker compared to that on metals such as Fe or Pt, which are known to promote the dissociation of the O-O bond, thus leading to higher selectivity toward the complete reduction of oxygen to water. Moreover, desorption of H₂O₂ after the two-electron reduction is favoured over the further reduction to water. The mesoporosity may help to the diffusion of H₂O₂ to the bulk liquid avoiding readsorption. All this contributes to the high performance of our doped carbon materials for the synthesis of H₂O₂ from O₂ electroreduction.

Conclusions

N-doped, S-doped and N,S-codoped mesoporous carbons have been prepared by a sustainable hydrothermal carbonization method from bio-based precursors. The dopant content in the final material can be adjusted by choosing the amount of dopant-containing molecule in the precursor mixture. The porous structure, which is in the range of mesoporosity by virtue of ZnCl₂ addition, is also governed by the dopant element which determines the mean pore size. Both the dopant element and the mean pore size are preserved upon pyrolysis up to 1173 K. These metal-free materials were tested in electrochemical oxygen reduction reaction revealing that the doped materials outperformed the un-doped counterpart in terms of onset potential and limiting current density. Among the doped carbon materials, the best performance was provided by N-

doped carbon. This catalyst showed a total selectivity to the synthesis of H₂O₂. This fact is very relevant if it is compared to similar carbon catalysts, which use to show a mixed 2-electron and 4-electron reduction mechanism. It was found that the addition of only minor amounts of Fe after pyrolysis triggers the occurrence of the 4-electron reduction mechanism. Among the samples with different nitrogen contents, that with an intermediate N content (4 wt%) furnished the best electrocatalytic performance. A material of the same amount of N but different textural properties, *i.e.* three-fold higher surface area and significantly lower mesopore volume, provided worse catalytic performance pointing to the pivotal role played by a hierarchical porous structure.

Acknowledgements.

The financial support of European Commission (FREECATS project, FP7 Grant agreement n° 280658), from Spanish Ministry MINECO and the European Regional Development Fund (project ENE2013-48816-C5-5-R), and Regional Government of Aragon (DGA-ESF-T66 Grupo Consolidado) are gratefully acknowledged.

References

- [1] Campos-Martin JM, Blanco-Brieva G, Fierro JLG. Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process. *Angew Chem Int Ed* 2006;45(42):6962-84.
- [2] Yi Y, Zhou J, Guo H, Zhao J, Su J, Wang L, et al. Safe Direct Synthesis of High Purity H₂O₂ through a H₂/O₂ Plasma Reaction. *Angew Chem Int Ed* 2013;52(32):8446-9.
- [3] Edwards JK, Solsona B, Edwin N, Carley AF, Herzing AA, Kiely CJ, et al. Switching Off Hydrogen Peroxide Hydrogenation in the Direct Synthesis Process. *Science* 2009;323(5917):1037-41.
- [4] Edwards JK, Pritchard J, Lu L, Piccinini M, Shaw G, Carley AF, et al. The Direct Synthesis of Hydrogen Peroxide Using Platinum-Promoted Gold–Palladium Catalysts. *Angew Chem Int Ed* 2014;53(9):2381-4.
- [5] Landon P, Collier PJ, Papworth AJ, Kiely CJ, Hutchings GJ. Direct formation of hydrogen peroxide from H₂/O₂ using a gold catalyst. *Chem Comm* 2002;(18):2058-9.

- [6] Shibata S, Suenobu T, Fukuzumi S. Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen by Using a Water-Soluble Iridium Complex and Flavin Mononucleotide. *Angew Chem Int Ed* 2013;52(47):12327-31.
- [7] Siahrostami S, Verdaguer-Casadevall A, Karamad M, Deiana D, Malacrida P, Wickman B, et al. Enabling direct H₂O₂ production through rational electrocatalyst design. *Nat Mater* 2013;12(12):1137-43.
- [8] Yamanaka I, Onizawa T, Takenaka S, Otsuka K. Direct and Continuous Production of Hydrogen Peroxide with 93% Selectivity Using a Fuel-Cell System. *Angew Chem Int Ed* 2003;42(31):3653-5.
- [9] Yamanaka I, Tazawa S, Murayama T, Iwasaki T, Takenaka S. Catalytic Synthesis of Neutral Hydrogen Peroxide at a CoN₂C_x Cathode of a Polymer Electrolyte Membrane Fuel Cell (PEMFC). *ChemSusChem* 2010;3(1):59-62.
- [10] Jirkovský JS, Panas I, Ahlberg E, Halasa M, Romani S, Schiffrin DJ. Single Atom Hot-Spots at Au–Pd Nanoalloys for Electrocatalytic H₂O₂ Production. *J Amer Chem Soc* 2011;133(48):19432-41.
- [11] Fellinger TP, Strasser P, Antonietti M. Mesoporous Nitrogen-Doped Carbon for the Electrocatalytic Synthesis of Hydrogen Peroxide. *J Amer Chem Soc* 2012;134(9):4072-5.
- [12] Sheng X, Daems N, Geboes B, Kurttepel M, Bals S, Breugelmans T, et al. N-doped ordered mesoporous carbons prepared by a two-step nanocasting strategy as highly active and selective electrocatalysts for the reduction of O₂ to H₂O₂. *Appl Catal B: Environ* 2015;176–177:212-24.
- [13] Yamanaka I, Murayama T. Neutral H₂O₂ Synthesis by Electrolysis of Water and O₂. *Angew Chem Int Ed* 2008;47(10):1900-2.
- [14] Byers JC, Güell AG, Unwin PR. Nanoscale Electrocatalysis: Visualizing Oxygen Reduction at Pristine, Kinked, and Oxidized Sites on Individual Carbon Nanotubes. *J Amer Chem Soc* 2014;136(32):11252-5.
- [15] Shearer CJ, Cherevan A, Eder D. Application and Future Challenges of Functional Nanocarbon Hybrids. *Adv Mater* 2014;26(15):2295-318.
- [16] Wang DW, Su D. Heterogeneous nanocarbon materials for oxygen reduction reaction. *Ener Environ Sci* 2014;7(2):576-91.
- [17] Zhong G, Wang H, Yu H, Peng F. The effect of edge carbon of carbon nanotubes on the electrocatalytic performance of oxygen reduction reaction. *Electrochem Comm* 2014;40:5-8.
- [18] Gong K, Du F, Xia Z, Durstock M, Dai L. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* 2009;323(5915):760-4.
- [19] Tuci G, Zafferoni C, Rossin A, Milella A, Luconi L, Innocenti M, et al. Chemically Functionalized Carbon Nanotubes with Pyridine Groups as Easily

- Tunable N-Decorated Nanomaterials for the Oxygen Reduction Reaction in Alkaline Medium. *Chem Mater* 2014;26(11):3460-70.
- [20] Masa J, Xia W, Muhler M, Schuhmann W. On the Role of Metals in Nitrogen-Doped Carbon Electrocatalysts for Oxygen Reduction. *Angew Chem Int Ed* 2015;54(35):10102-20.
- [21] Liu R, Wu D, Feng X, Müllen K. Nitrogen-Doped Ordered Mesoporous Graphitic Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Angew Chem Int Ed* 2010;49(14):2565-9.
- [22] Sevilla M, Yu L, Feller TP, Fuertes AB, Titirici MM. Polypyrrole-derived mesoporous nitrogen-doped carbons with intrinsic catalytic activity in the oxygen reduction reaction. *RSC Adv* 2013;3(25):9904-10.
- [23] Ba H, Liu Y, Truong-Phuoc L, Duong-Viet C, Mu X, Doh WH, et al. A highly N-doped carbon phase "dressing" of macroscopic supports for catalytic applications. *Chem Comm* 2015;51(76):14393-6.
- [24] Liu Y, Quan X, Fan X, Wang H, Chen S. High-Yield Electrosynthesis of Hydrogen Peroxide from Oxygen Reduction by Hierarchically Porous Carbon. *Angew Chem Int Ed* 2015;54(23):6837-41.
- [25] Brun N, Wohlgemuth SA, Osiceanu P, Titirici MM. Original Design of Nitrogen-doped Carbon Aerogels from Sustainable Precursors: Application as Metal-free Oxygen Reduction Catalysts. *Green Chem* 2013;15(9):2514-24.
- [26] Wohlgemuth SA, Feller TP, Jaker P, Antonietti M. Tunable Nitrogen-doped Carbon Aerogels as Sustainable Electrocatalysts in the Oxygen Reduction Reaction. *J Mater Chem A* 2013;1(12):4002-9.
- [27] Alatalo SM, Qiu K, Preuss K, Marinovic A, Sevilla M, Sillanpää M, et al. Soy protein directed hydrothermal synthesis of porous carbon aerogels for electrocatalytic oxygen reduction. *Carbon* 2016;96:622-30.
- [28] Wohlgemuth SA, White RJ, Willinger MG, Titirici MM, Antonietti M. A one-pot Hydrothermal Synthesis of Sulfur and Nitrogen doped Carbon Aerogels with Enhanced Electrocatalytic Activity in the Oxygen Reduction Reaction. *Green Chem* 2012;14(5):1515-23.
- [29] Yu L, Brun N, Sakaushi K, Eckert J, Titirici MM. Hydrothermal nanocasting: Synthesis of Hierarchically Porous Carbon Monoliths and their Application in Lithium–sulfur Batteries. *Carbon* 2013;61(0):245-53.
- [30] Fechler N, Wohlgemuth SA, Jaker P, Antonietti M. Salt and Sugar: Direct Synthesis of high Surface Area Carbon Materials at low Temperatures via Hydrothermal Carbonization of Glucose under Hypersaline Conditions. *J Mater Chem A* 2013;1(33):9418-21.
- [31] Barrett EP, Joyner LG, Halenda PP. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J Amer Chem Soc* 1951;73(1):373-80.

- [32] Evans R, Tarazona P. Theory of Condensation in Narrow Capillaries. *Phys rev lett* 1984;52(7):557-60.
- [33] Choi HC, Park J, Kim B. Distribution and Structure of N Atoms in Multiwalled Carbon Nanotubes Using Variable-Energy X-Ray Photoelectron Spectroscopy. *J Phys Chem B* 2005;109(10):4333-40.
- [34] Centi G, Barbera K, Perathoner S, Gupta NK, Ember EE, Lercher JA. Onion-Like Graphene Carbon Nanospheres as Stable Catalysts for Carbon Monoxide and Methane Chlorination. *ChemCatChem* 2015;7(18):3036-46.
- [35] Roldán L, Marco Y, García-Bordejé E. Bio-sourced mesoporous carbon doped with heteroatoms (N,S) synthesised using one-step hydrothermal process for water remediation. *Mic Mes Mater* 2016;222:55-62.
- [36] Florea I, Ersen O, Arenal R, Ihiwakrim D, Messaoudi C, Chizari K, et al. 3D Analysis of the Morphology and Spatial Distribution of Nitrogen in Nitrogen-Doped Carbon Nanotubes by Energy-Filtered Transmission Electron Microscopy Tomography. *J Amer Chem Soc* 2012;134(23):9672-80.
- [37] Nagaiah TC, Bordoloi A, Sánchez MD, Muhler M, Schuhmann W. Mesoporous Nitrogen-Rich Carbon Materials as Catalysts for the Oxygen Reduction Reaction in Alkaline Solution. *ChemSusChem* 2012;5(4):637-41.
- [38] Pels JR, Kapteijn F, Moulijn JA, Zhu Q, Thomas KM. Evolution of Nitrogen Functionalities in Carbonaceous Materials During Pyrolysis. *Carbon* 1995;33(11):1641-53.
- [39] Yu L, Falco C, Weber J, White RJ, Howe JY, Titirici MM. Carbohydrate-Derived Hydrothermal Carbons: A Thorough Characterization Study. *Langmuir* 2012;28(33):12373-83.
- [40] Smart RS, Skinner WM, Gerson AR. XPS of Sulphide Mineral Surfaces: Metal-deficient, Polysulphides, Defects and Elemental Sulphur. *Surf Interf Anal* 1999;28(1):101-5.
- [41] Cheng Y, Zhang J, Jiang SP. Are metal-free pristine carbon nanotubes electrocatalytically active? *Chem Comm* 2015;51(72):13764-7.
- [42] Jiang S, Li Z, Wang H, Wang Y, Meng L, Song S. Tuning nondoped carbon nanotubes to an efficient metal-free electrocatalyst for oxygen reduction reaction by localizing the orbital of the nanotubes with topological defects. *Nanoscale* 2014;6(23):14262-9.
- [43] Waki K, Wong RA, Oktaviano HS, Fujio T, Nagai T, Kimoto K, et al. Non-nitrogen doped and non-metal oxygen reduction electrocatalysts based on carbon nanotubes: mechanism and origin of ORR activity. *Ener Environ Sci* 2014;7(6):1950-8.
- [44] Duong-Viet C, Liu Y, Ba H, Truong-Phuoc L, Baaziz W, Nguyen-Dinh L, et al. Carbon nanotubes containing oxygenated decorating defects as metal-free catalyst for selective oxidation of H₂S. *Appl Catal B: Environ*, in press 16 A.D..

- [45] Li B, Su D. The Nucleophilicity of the Oxygen Functional Groups on Carbon Materials: A DFT Analysis. *Chem A Eur J* 2014;20(16):7890-4.
- [46] Brun N, Wohlgemuth SA, Osiceanu P, Titirici MM. Original design of nitrogen-doped carbon aerogels from sustainable precursors: application as metal-free oxygen reduction catalysts. *Green Chem* 2013;15(9):2514-24.
- [47] Wang X, Lee JS, Zhu Q, Liu J, Wang Y, Dai S. Ammonia-Treated Ordered Mesoporous Carbons as Catalytic Materials for Oxygen Reduction Reaction. *Chem Mater* 2010;22(7):2178-80.
- [48] Herrmann I, Kramm UI, Fiechter S, Bogdanoff P. Influence of Sulfur on the Pyrolysis of CoTMPP as Electrocatalyst for the Oxygen Reduction Reaction. *J Electrochem Soc* 2009;156(10):B1283-B1292.
- [49] Daems N, Sheng X, Vankelecom IFJ, Pescarmona PP. Metal-free doped carbon materials as electrocatalysts for the oxygen reduction reaction. *J Mater Chem A* 2014;2(12):4085-110.