



Short communication

Effects of catalyst aging on the growth morphology and oxygen reduction activity of nitrogen-doped carbon nanotubes



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ABSTRACT

This work reports some effects that aging time of the used catalyst (Fe/MgO) has on the produced N-doped carbon nanotubes. In particular, the catalyst age affects the synthesized nanomaterials with respect to morphology, surface composition and electrocatalytic behavior towards the electrochemical oxygen reduction.

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1. Introduction

Fuel cells for low temperature applications are the subject of intensive research because they could reduce consumption of primary fossil fuels and greenhouse gas emissions. Difficulties come from the sluggish kinetic behavior of cathodic oxygen reduction reaction (ORR). Platinum and Pt-alloys are currently the best catalysts for this reaction [1,2]. Nevertheless, due to the natural scarcity and cost of platinum, finding alternative non-precious materials is a necessary and very attractive challenge. In the last years, many efforts have been devoted to demonstrate that nitrogen-doped carbon nanostructures, like graphene and nanotubes (N-CNTs), have great potential as Pt substitutes in ORR [3–5]. Their specific electronic properties are extraordinarily improved by the presence of nitrogen species which disturb the uniform π -cloud of carbon nanotubes [6] and increase the localized density of states at the Fermi level [7]. In N-CNTs these modifications impart a n-type dopant activity and an enhancement of the electrocatalytic activity [8,9]. Furthermore, many papers show that the ORR activity of N-CNTs can be modified by varying preparation method, precursor nature and composition of the catalyst used in the nanotube synthesis [10–15].

In this work we present some surprising preliminary data about the effect of the aging time of the catalyst used in the nanotubes synthesis, particularly concerning the morphology and electrocatalytic properties of the obtained N-CNTs.

2. Material and methods

2.1. Catalyst preparation

All chemicals and solvents were purchased from Sigma Aldrich and used as received without further purification. Synthesis of N-CNTs was performed by a catalytic reaction of 1,1,3,3-tetramethylguanidine over a catalyst based on MgO modified with an iron salt solution (Fe/MgO). MgO was synthesized by thermal decomposition ($T = 400\text{ }^\circ\text{C}$, N_2 , flow rate = $100\text{ cm}^3\text{ min}^{-1}$, 4 h) of $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. Modification with iron was obtained by suspending MgO in a $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution ($w/w\% = 11$) and sonicating it for 1 h. After filtration and drying ($T = 115\text{ }^\circ\text{C}$, N_2 flow, 5 h), the powder was pyrolysed ($T = 300\text{ }^\circ\text{C}$, N_2 , flow rate = $100\text{ cm}^3\text{ min}^{-1}$, 7.5 h). The final product was placed in a closed vial without other precautions.

Synthesis of N-CNTs was carried out in a vertical quartz tube reactor (N_2 , flow rate = $95\text{ cm}^3\text{ min}^{-1}$). For each preparation 300 mg of Fe/MgO were used. After 25 min in N_2 flow at $T = 25\text{ }^\circ\text{C}$, the catalyst was heated slowly ($6\text{ }^\circ\text{C min}^{-1}$) up to $T = 800\text{ }^\circ\text{C}$. At this temperature an aliquot of 1,1,3,3-tetramethylguanidine was added drop

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wise (2.6 mL h^{-1} , 70 min). At the end, the reaction was interrupted by quenching the reactor to $T = 25 \text{ }^\circ\text{C}$. The day after the reactor was placed into a furnace and heated up to $T = 400 \text{ }^\circ\text{C}$ (N_2 , flow rate = $100 \text{ cm}^3 \text{ min}^{-1}$, $6 \text{ }^\circ\text{C min}^{-1}$). Then, the nitrogen flow was stopped, the reactor was opened and the sample left 2 h under static air to burn amorphous carbon. After quenching to $T = 25 \text{ }^\circ\text{C}$ the black powder was lixiviated under sonication in $0.5 \text{ M H}_2\text{SO}_4$ ($t = 90 \text{ min}$) to eliminate Fe/MgO. Finally, after filtration and washing, the sample was dried ($T = 100 \text{ }^\circ\text{C}$, N_2 flow, 16 h). To study Fe/MgO aging effects onto nanotube morphology and electrocatalytic properties, a single Fe/MgO batch was prepared. Aliquots were withdrawn at 1, 6, 10, 70 days from preparation and were employed to synthesize a relevant N-CNT sample, labeled CNT1, CNT2, CNT3 and CNT4 in the following.

2.2. Physical characterizations

X-ray Photoelectron Spectroscopy (XPS) measurements were performed with a M-Probe Instrument (SSI) equipped with a monochromatic Al $K\alpha$ source (1486.6 eV). For all samples, the C1s peak was taken as the internal reference at 284.6 eV. Precision of reported binding energies (BEs) is approximately $\pm 0.2 \text{ eV}$. Uncertainty in spectral decomposition is estimated at $\pm 1\%$.

Energy-Dispersive X-ray Spectroscopy (EDX) compositional profiles were carried out on a Scanning Electron Microscope system (LEO 1430) equipped with a EDX detector (INCA, Oxford).

Transmission Electronic Microscopy (TEM) images were obtained by a Zeiss EFTEM LEO 912AB (120 kV) microscope. To obtain average characteristics many different sample areas were analyzed.

Raman spectra were collected by a Jasco RMP 100 microprobe equipped with a $50\times$ objective and connected by fiber optics to a frequency-doubled Nd:YAG laser ($\lambda_{\text{exc}} = 532 \text{ nm}$) and to a Lot Oriol MS25 spectrometer with a CCD detector. The laser power at the sample was in all cases of few milliwatts. An exposure time of 2 s was used and all spectra were obtained as sum of 100 accumulations. The estimated resolution was about 8 cm^{-1} .

Magnetic moment measurements were performed by means of a superconducting quantum interference device (SQUID) magnetometer, in the temperature range $2 < T < 300 \text{ K}$ at applied DC magnetic field $H = 1000 \text{ Oe}$, operating in the standard extraction technique mode. The magnetic susceptibility was obtained by the formula: $\chi \approx M/H$, valid for low fields, with M and H as the magnetization of the material and magnetic field strength, respectively.

Electrochemical characterization was performed in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ by the Thin Film Rotating Disk Electrode method using Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV). CNT catalyst aliquots (4 mg) were dispersed in water (1.02 mL), sonicated 5 min, then added with Nafion[®] (80 μL) and sonicated for 10 min; 14 μL of this mixture were pipetted onto the graphite tip (geometric surface area: $A = 0.07 \text{ cm}^2$) of a rotating disk electrode (EDI 101, Radiometer) and dried in a bottom-up position above a tungsten lamp (100 W). Electrocatalyst loading was 0.7 mg cm^{-2} .

A two-compartment cell with a graphite counterelectrode (Amel 201/S-016) and a AgCl/Ag external reference electrode (Amel) in $3 \text{ mol dm}^{-3} \text{ NaCl}$ was used. The potentiostat was AMEL mod. 7050. Before CV recording, the electrode was conditioned by cycling 45 min in N_2 saturated 0.1 M HClO_4 solution in the potential range $E = -0.275 \div +0.800 \text{ V}$, followed by 100 min cycling in O_2 saturated solution ($v = 5 \text{ mV s}^{-1}$, $\omega = 1600 \text{ rpm}$). CVs in O_2 were recorded in the same conditions at different rotation rates. To verify electrode stability and internal reproducibility several CVs at $\omega = 1600 \text{ rpm}$ were recorded in each run. After measurements in O_2 , CVs were again recorded in N_2 to obtain background faradaic currents for O_2 reduction data correction. LSV parameters: $\omega = 0 \text{ rpm}$, scan rates = 5, 10, 20, 50, 100 and 200 mV s^{-1} .

3. Results and discussion

Fig. 1A–D shows the TEM images of all samples prepared using Fe/MgO at different aging times. It is observed that surface morphology changes with increasing catalyst aging. The CNT1 sample (Fig. 1A) is characterized by the presence of bundles and multiwalled flexible nanostructures where a series of single, apparently independent, units form a nanochain with a diameter of $\sim 30 \text{ nm}$ and a wall thickness of $\sim 5 \text{ nm}$. Bundles are also present in CNT2 (Fig. 1B) with a nanostructure morphology that varies from nanochains to bamboo-like; diameters are greater (50 nm) than in CNT1. In CNT3 (Fig. 1C) a well-developed nanotube morphology appears with a continuous external wall and an internal structure clearly composed by nanocups. The average diameter is $\sim 50 \text{ nm}$ and the wall is thicker (10 nm) than in CNT2 (5 nm) and CNT1. Finally, in CNT4 (Fig. 1D) the well-defined CNT3 morphology is mostly lost even though some ordering still appears. Therefore, the nanostructure morphology becomes better organized with increasing catalyst aging time, until a threshold age is reached at which the catalyst is no longer suitable to sustain formation of well-structured nanotubes.

Fig. 1E shows the Raman sample spectra. Two bands are observed at $\sim 1350 \text{ cm}^{-1}$ (D band) and 1595 cm^{-1} (G band), the first one being attributed to disordered amorphous carbon and edge defects, the second one to the tangential vibrations of the graphitic carbon atoms [16]. The ratio of the two band intensities (I_D/I_G) is an estimate of the disorder level within N-CNTs [17]: the higher the value, the higher the extent of disorder and defects. For our samples I_D/I_G values are 1.28 (CNT1), 1.27 (CNT2), 1.22 (CNT3) and 1.31 (CNT4). This is an indication that N-CNTs are reasonably graphitized but also contain some disordered carbon and defects [18]. The smallest I_D/I_G value of CNT3 shows that the average size of domains attributable to in-plane crystalline wall structure [9] reaches a maximum with respect to other sample results. This is consistent with the above TEM observations.

Results of XPS atomic percent composition are reported in Fig. 2A. As seen, C is the main component (95–97%), followed by O (2–4%), which is in general accordance with XPS literature data of most carbons. In a further aspect, C and O amounts oppositely vary by 2–3 at.% in going from CNT1 to CNT4. Such variations are above the experimental uncertainty and apparently unrelated to the otherwise constant experimental conditions adopted (the constant end sample heating in air at $T = 400 \text{ }^\circ\text{C}$ is felt most relevant to show that the observed O/C variations are intrinsic sample features). Therefore, these elemental variations are surprisingly only attributable to increasing catalyst aging effects. Similar composition variations are observed for N1s that is only detected on CNT3 and CNT4 with a slight percentage increase in the latter instance. Finally, Fe signal, attributable to iron oxide, is only found in CNT4, possibly deriving from the catalyst Fe/MgO [19,20]. Since for low metal concentrations in CNTs XPS can give a false-negative information [21], further results of metal impurities were obtained by DC magnetic susceptibility (DC-MS) measurements [21] and EDX. Results are reported in Fig. 2A. In DC-MS results low amounts of paramagnetic centers are present in all samples and increase from CNT2 (6.2 ppm) to CNT4 (8.2 ppm) (the CNT1 sample amount was not enough for measurements). These results are confirmed by the EDX analyses, showing that magnetic metal impurities can be attributable to iron species. Hence, even though in low quantities, iron is present in all N-CNTs, these being again related to the catalyst age. In a further aspect, the presence of variable iron amount could be related to different sample nitrogen amounts. In fact, nitrogen groups are thermally unstable at $T = 800 \text{ }^\circ\text{C}$, but can be stabilized by iron by formation of a sort of N–Fe complex [22] so that it may be inferred that the higher is iron, the higher becomes the stability and quantity of carbon bound nitrogen. Fig. 2Ba–Bj shows C1s, O1s, and N1s XPS high resolution spectra for the samples. As outlined by peak deconvolution (Fig. 2Ba–Bd), many carbon species may contribute to the C1s region (sp^2/sp^3 carbon, single C–O/C–N bonds, carbonyls/quinones, carboxyl/ester groups [23–26]). These data are not considered further because no evidence was detected

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