

Article

Hydrothermal Carbon/Carbon Nanotube Composites as Electrocatalysts for the Oxygen Reduction Reaction

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Abstract: The oxygen reduction reaction is an essential reaction in several energy conversion devices such as fuel cells and batteries. So far, the best performance is obtained by using platinum-based electrocatalysts which make the devices really expensive, and thus, new and more affordable materials should be designed. Biomass-derived carbons were prepared by hydrothermal carbonization in the presence of carbon nanotubes with different oxygen surface functionalities to evaluate their effect on the final properties. Additionally, nitrogen functional groups were also introduced by ball milling the carbon composite together with melamine. The oxygen groups on the surface of the carbon nanotubes favour their dispersion into the precursor mixture and the formation of a more homogenous carbon structure with higher mechanical strength. This type of structure partially avoids the crushing of the nanotubes and the carbon spheres during the ball milling, resulting in a carbon composite with enhanced electrical conductivity. Undoped and N-doped composites were used as electrocatalysts for the oxygen reduction reaction. The onset potential increases by 16% due to the incorporation of CNT and nitrogen, which increases the number of active sites and improves the chemical reactivity, while the limiting current density increases by 33% due to the higher electrical conductivity.

Textural and morphological properties of carbon nanotubes and oxidized carbon nanotubes.

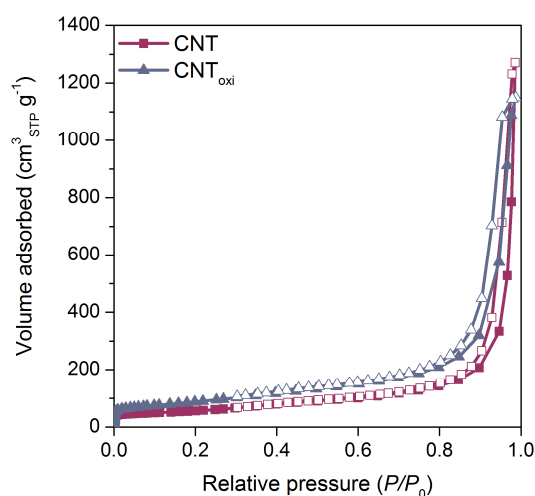
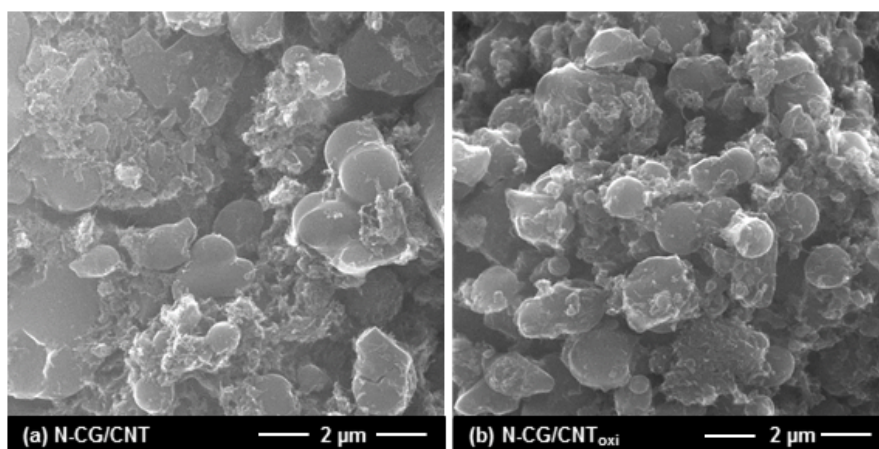


Figure S1. N₂ adsorption-desorption isotherms of carbon nanotubes and oxidized carbon nanotubes.

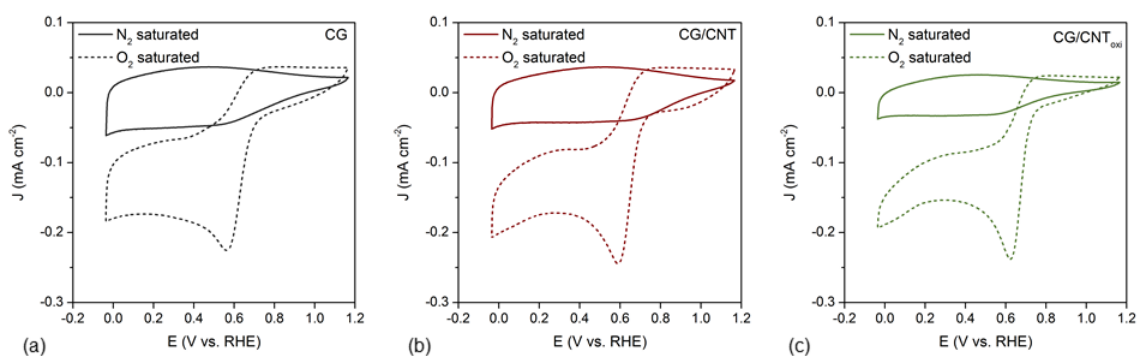
Table S1. Textural properties of carbon nanotubes and oxidized carbon nanotubes.

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	S_{ext} (m^2/g)
CNT	224	0.08	234
CNT _{oxi}	319	0.12	488

**Figure S2.** SEM micrographs of N-doped composites with carbon nanotubes and with oxidized carbon nanotubes.**Table S2.** Integrated areas of the peaks D and G obtained by Raman spectroscopy.

Sample	A_D	A_G	A_D/A_G
CG	1418	511	2.8
CG/CNT	1291	580	2.2
CG/CNT _{oxi}	1190	715	1.7
N-CG/CNT	1115	808	1.4
N-CG/CNT _{oxi}	1055	1039	1.0

Electrochemical measurements

**Figure S3.** Cyclic Voltammograms measured at a scan rate of 5 mV s^{-1} in an electrolyte saturated with N_2 and O_2 for carbonized glucose (a), composite CG/CNT (b) and composite CG/CNT_{oxi} (c).

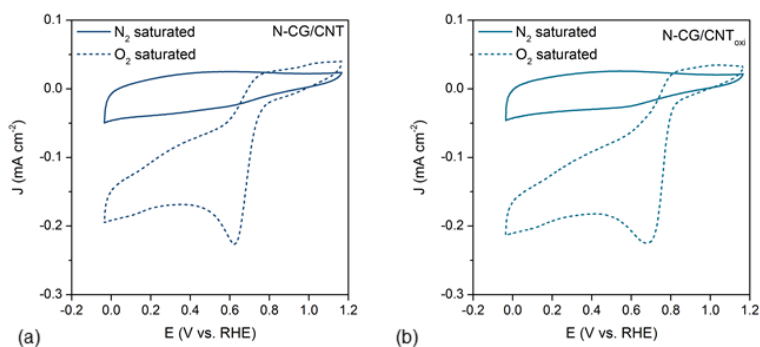


Figure S4. Cyclic Voltammograms measured at a scan rate of 5 mV s^{-1} in an electrolyte saturated with N_2 and O_2 for N-doped composites prepared with CNT (a) and CNT_{oxi} (b).

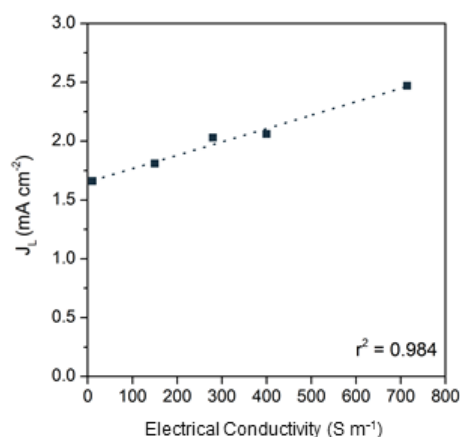


Figure S5. Relationship between the limiting current density and electrical conductivity.

Equations

The oxygen reduction reaction (ORR) in basic media can be explained by two different mechanisms. The first one is a dissociative mechanism of four-electrons known as direct mechanism (reaction 1), while the second is related to an associative mechanism of two-electrons known as indirect mechanism (reaction 2 and 3) in which the formation of by-products occurs.



In the measurements performed with the ring-disk electrode (RRDE), the reduction of oxygen occurs in the disk, while the formation of hydrogen peroxide is detected in the ring. Therefore, the currents detected in the disk and the ring can be expressed as equation 1 and 2, respectively.

$$I_D = I_{4e} + I_{2e} + I_{2e'} \quad (\text{S1})$$

$$I_R = N (I_{2e} - I_{2e'}) \quad (\text{S2})$$

Where I_D is the Faradaic current at the disk; I_{4e} is the Faradaic current related to the direct mechanism (reaction 1); I_{2e} and $I_{2e'}$ are the Faradaic currents related to the indirect pathway shown in reactions 2 and 3, respectively; I_R is the Faradaic current at the ring and N is the collection coefficient at the ring ($N = 0.249$).

The total number of electrons (n) detected by each oxygen molecule can be determined by:

$$n = \frac{N_e}{N_{O_2}} \quad (S3)$$

Where N_e and N_{O_2} are the total number of electrons transferred and the total number of oxygen molecules participating in the ORR, respectively. These two parameters can be expressed as:

$$N_e = \frac{N_A \Delta t}{F} (I_{4e} + I_{2e} + I_{2e'}) \quad (S4)$$

$$N_{O_2} = \frac{N_A \Delta t}{F} \left(\frac{I_{4e}}{4} + \frac{I_{2e}}{2} \right) \quad (S5)$$

Where N_A is the constant of Avogrado and F is Faraday's constant.

Therefore, equation 3 can be expressed as:

$$\begin{aligned} n &= \frac{N_e}{N_{O_2}} = \frac{\frac{N_A \Delta t}{F} (I_{4e} + I_{2e} + I_{2e'})}{\frac{N_A \Delta t}{F} \left(\frac{I_{4e}}{4} + \frac{I_{2e}}{2} \right)} \\ n &= \frac{(I_{4e} + I_{2e} + I_{2e'})}{\left(\frac{I_{4e}}{4} + \frac{I_{2e}}{2} \right)} \end{aligned} \quad (S6)$$

The combination of equation 1, 2 and 6, results in:

$$n = \frac{4I_D}{I_D + \left(\frac{I_R}{N} \right)} \quad (S7)$$

Similarly, the production of hydrogen peroxide can be expressed as the fraction between the number of hydrogen peroxide molecules formed and the total number of oxygen molecules participating in the ORR:

$$H_2O_2 = \frac{N_{H_2O_2}}{N_{O_2}} \quad (S8)$$

Where $N_{H_2O_2}$ is the total number of hydrogen peroxide molecules that can be expressed as:

$$N_{H_2O_2} = \frac{N_A \Delta t}{F} \left(\frac{I_{2e}}{2} - \frac{I_{2e'}}{2} \right) \quad (S9)$$

The combination of equation equation 8, 9 and 5, results in:

$$\begin{aligned} H_2O_2 &= \frac{N_{H_2O_2}}{N_{O_2}} = \frac{\frac{N_A \Delta t}{F} \left(\frac{I_{2e}}{2} - \frac{I_{2e'}}{2} \right)}{\frac{N_A \Delta t}{F} \left(\frac{I_{4e}}{4} + \frac{I_{2e}}{2} \right)} \\ H_2O_2 &= \frac{2(I_{2e} - I_{2e'})}{I_{4e} + 2I_{2e}} \end{aligned} \quad (S10)$$

Finally, the combination of equation 1, 2 and 10, results in:

$$H_2O_2 = \frac{2 \left(\frac{I_R}{N} \right)}{I_D + \left(\frac{I_R}{N} \right)} \quad (S11)$$

The experimental potential was set according to the reference electrode employed: Ag/AgCl (KCl 3 mol L⁻¹). Then, the final potential was converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{RHE} = 0.059 \text{ pH} + E_{Ag/AgCl}^0 + E_{Ag/AgCl} \quad (S12)$$

Where pH refers to the pH of the electrolyte, $E_{Ag/AgCl}$ is the measured potential vs Ag/AgCl (KCl 3 mol L⁻¹) and $E_{Ag/AgCl}^0 = 0.21$ V (measured at 20 °C).

The kinetic current density (J_k) is calculated from the Koutecký-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_k} = \frac{1}{Bw^{1/2}} + \frac{1}{J_k} \quad (\text{S13})$$

Where J is the measured current density, J_k is the kinetic current density, J_L is the diffusion-limited current density, w is the electrode rotation rate (rpm), and B is:

$$B = 0.2nFC_0(D_0)^{\frac{2}{3}}\nu^{-\frac{1}{6}} \quad (\text{S14})$$

where n is the number of electrons transferred, F is the Faraday constant (96485 C/mol), C_0 is the bulk concentration of O_2 ($1.15 \times 10^{-3} \text{ mol cm}^{-3}$), D_0 is the diffusion coefficient of O_2 ($1.95 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and ν is the kinematic viscosity of the electrolyte ($0.009 \text{ cm}^2 \text{ s}^{-1}$).