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FULL PAPER

# Green synthesized nitrogen-doped carbon-based aerogels as environmental friendly catalysts for the oxygen reduction in microbial fuel cells

Gian Paolo Salvador,*[a] Matteo Gerosa,[a] Adriano Sacco,[a] Nadia Garino,[a] Micaela Castellino,[a] Giulia Massaglia,[a] Luisa Delmondo,[b] Valeria Agostino,[a,b] Valentina Margaria,[a] Angelica Chiodoni,[a] and Marzia Quaglio[a]

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**Abstract:**. In this work we present a green approach to the synthesis of nitrogen-doped carbon-based aerogels with good conductivity and catalytic properties. With the aim to design an easily sustainable process, the starting precursors were selected among abundant waste-related organic materials. The naturally-derived polysaccharide agar worked as the carbon source in a water solution, while an amino acid, glycine or lysine has been used as the nitrogen source. By this synthesis approach, nitrogen defects were created into a 3D porous aerogel: they successfully acted as active catalytic sites for the reaction of oxygen reduction to water as demonstrated by electrochemical measurements. The best performing materials have been tested as cathodes in microbial fuel cells for 50 days, in conditions close to those the device could face in a real environment. The glycine derived carbon aerogels with the higher content of pyridinic nitrogen, as confirmed by several morphological characterizations, showed the best performance.

## Introduction

Since the 1950s many changes have been observed in the earth environment. Natural and anthropogenic activities are responsible for climate changes and global warming. The human influence, in particular, is evident from the increasing in greenhouse gases (GHG) concentration in the atmosphere. GHG are in charge not only for the observed warming of the atmosphere and oceans, but also for the changes in the global water cycle, in the reduction of snow and ice and in global mean sea level rise. Limiting climate changes via substantial and sustained reductions of greenhouse gases is not postponed any longer.[1]

Carbon dioxide emissions from fossil fuel combustion and industrial processes contribute, nowadays, to about 78% of the total greenhouse gas emission. [2]

In order to give an active answer to the climate changes due to fossil fuel utilization, the search for novel energy-related technologies continues. Among all the explored possibilities, microbial fuel cells (MFCs) are, undoubtedly, an interesting solution because they can combine a green energy production with wastewater remediation and/or monitoring. [3,4]

The first generation MFCs were made of two chambers (anodic and cathodic, respectively) (see Figure S1a in the Supporting Information) separated by a proton-exchange membrane (PEM). In the cathodic chamber a liquid electrolyte containing an electron acceptor was necessary in order to be reduced by electrons and protons, generated at the anode and migrated to cathode through the external circuit and the PEM, respectively. The most common soluble mediator in MFCs is potassium hexacyanoferrate (III). [5]

Unfortunately, this chemical is not a suitable choice for a sustainable electricity generation in MFCs, because it is potentially toxic for humans and for the environment, requires regular replenishing or supplying by means of an external peristaltic pump setup, due to its low rate of regeneration, and it diffuses through the membrane, eventually decreasing the overall performance of the MFCs over long-term operation.

Switching to oxygen as the electron acceptor gives the opportunity to decrease the fabrication costs and the environmental impact, since no chemical electrolytes are needed. This leads to a simplification in the MFC architecture: one chamber for both anode and cathode and PEMs can be avoided. Moreover, having one chamber only, just one pumping setup can be used to supply or recycle the catholyte (see Figure S1b in the Supporting Information). [6,7,8]

In acidic solutions, the oxygen reduction reaction (ORR) at cathode can occur via two different processes: [9]

1) a four-electron pathway: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($E'^\circ$ = 0.816V)

2) a two-electron pathway: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ($E'^\circ$ = 0.295V)

Unfortunately, even if the two-electrons pathway is thermodynamically favoured, it produces hydrogen peroxide that is poisonous for microorganisms and electrodes, causing a decrease in MFCs performance. It is, therefore, necessary to promote the four-electrons reaction by means of the introduction of a catalyst in the cathode.

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[a] Dr. G.P. Salvador, Dr. M. Gerosa, Dr. A. Sacco, Dr. N. Garino, Dr. M. Castellino, Dr. G. Massaglia, Miss V. Agostino, Dr. V. Margaria, Dr. A. Chiodoni and Dr. M. Quaglio
Centre For Sustainable Future Technologies (CSFT@Polito)
Instituto Italiano di Tecnologia
Corso Trento 21, Torino, 10129, Italy
E-mail: gianpaolo.salvador@iit.it
[b] Miss L. Delmondo and Miss V. Agostino
Applied Science and Technology Department
Politecnico di Torino
Corso Duca degli Abruzzi 24, Torino, 10129, Italy

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Platinum is the best performing oxygen reduction catalyst, able to promote the four-electron pathway. [10]

However, since platinum is an expensive and little abundant metal, its practical application must be limited. Many efforts have been made to reduce cathode costs by decreasing Pt loading onto carbon-based materials or seeking for other non-Pt catalysts. [11]

The attention for substituting Pt was, firstly, devoted to use cobalt- or iron-based phtalocyanines, [12] manganese oxides, [13,14] lead oxide [15] and so on.

The synthesis of these materials, however, involves toxic or non-environmental friendly reagents and/or precursors, giving complaints both on their production and on their disposal or recycle after the device - operation life - end.

Another possibility to replace platinum is doping carbon-based materials (as those cited for the two-chamber MFCs in the Supporting Information) by heteroatoms such as nitrogen, sulphur or boron, giving rise to good ORR catalysts. [16,17,18,19]

Whatever is the choice for Pt substitution, in order to enhance the ORR catalysis and, consequently, the MFC overall performance, it is necessary to increase the surface area of the selected material and realize an optimized 3D-structure in order to have more catalytic centres without precluding oxygen to enter the structure.

Aerogels are a class of materials that can be the answer to these requests. In 1989 Pekala [20] synthesized the first organic aerogels by the reaction between resorcinol and formaldehyde using acid or base as catalysts.

These organic aerogels can be converted to high carbon content “carbon aerogels” via a pyrolysis step, which results in a higher electrical conductivity. [21]

As stated for common carbon-based materials, doping carbon aerogels with heteroatoms such as N, S or B can enhance their electrocatalytic activity.

As an example, Wolgemuth et al. [22] proposed a hydrothermal carbonization of glucose and 2-pyrrol-caboxaldehyde, mediated by borax. Elumeeva et al. [23] studied N-doped carbon-based aerogels prepared by means of the - salt templating - method that includes non-volatile ionic liquids as precursors. Many other works involving N-doping carbon materials, doped or not by other heteroatoms, used or not in MFCs, have been proposed[24,25,26,27].

At the best of our knowledge, the higher performance for these materials in MFCs are those published by Zhang et al[28]. In any case, the precursors and/or the synthesis strategies employed are not completely environmental friendly and/or not as cheap as the scale-up process requires in order to put MFCs on the market. Moreover, we tried to test our materials, in devices that were as much closer as possible to a real environmental application (for example, using a fresh inoculum).

In our work, we propose a simple sol-gel synthesis in which natural green precursors (agar and amino acids as carbon and nitrogen sources, respectively) were mixed in a water solution under mild conditions (less than 90 °C, at ambient pressure) to form a gel.

Agar has been selected as the carbon source, because it is a natural polysaccharide, extracted from a group of red algae, that become a gel at room temperature, without the need to add any inorganic chemicals as catalysts. [29]

Choosing two different types of amino acids, namely glycine (with one N atom in its structure) and lysine (with two N atoms in its molecule) (Figure S2 in the Supporting Information), it was possible to evaluate the influence of the N source on material catalytic performance and characteristics.

Different agar and amino acid relative concentrations were also investigated in order to establish the influence of the precursor content on the oxygen reduction performance.

The agar-based gel was transformed into an organic aerogel by means of the freeze drying technique, which consists in freezing the liquid inside the sample and then removing it by sublimation. Afterwards, the aerogels were carbonized via a pyrolysis step.

The ultimate goal of this study was to prepare electrodes that work as cathodes in MFCs. It was, therefore, necessary to test them in MFCs under operational conditions, close to those they could face in a real environment, for long periods (at least one or two months), because of either a biological system was involved or the necessity of retrieving information about performance stability.

It was, therefore, necessary a selection, among all the samples prepared with different agar and amino acids amounts, for reducing the overall test costs in terms of time and economic effort. The choice has been carried out taking into account the results obtained from rotating ring disk electrode (RRDE)-based electrochemical measurements, that are well-known in the literature as the best tool for studying the electrocatalytic material properties. [30,31,32]

The best performing N-doped C-based (NC) aerogels (one for those prepared from glycine and one from lysine) were used to fabricate cathodes and tested in MFCs for 50 days.

According to the electrical characterization carried out during the cell tests, the MFCs containing the glycine-derived NC aerogels had the best performance as catalysts for oxygen reduction reaction.

In order to investigate the reason of the different behaviour between glycine and lysine-derived NC aerogels, several characterizations, such as field emission scanning electron microscopy (FESEM), nitrogen adsorption-desorption isotherms, energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), have been exploited.

## Results and Discussion

The nitrogen-doped carbon-based aerogels, with different agar and amino acids concentrations as reported in Table 3, have been analyzed for their ORR-related electrocatalytic activity in order to select the best catalysts to prepare cathodes to be tested in MFCs. This screening was necessary because of the economic and technical effort, which is related to the setup of several tests in MFCs, simultaneously.

For simplifying the comprehension, sample names in the following paragraph will follow the notation provided in Table 3 in the Experimental section.

The catalytic activity of the fabricated aerogels was assessed through cyclic voltammetry measurements in $O_2$- and $N_2$-saturated electrolytic solutions. The results are reported in Fig. 1a, as an example, for two of the studied samples: similar curves

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were indeed obtained for the other aerogels. All the measured voltammograms present a noticeable capacitive behavior, as can be easily observed by the difference between cathodic and anodic currents. In addition, all the curves exhibit a typical reduction peak, located in the range -0.3 ÷ 0.4 V, which is the fingerprint of the oxygen reduction reaction: in fact, it is worth to notice that the peaks disappear when $O_2$ is removed from the solution. This demonstrates that these aerogels are able to catalyze the ORR. In order to quantify the electrochemical activity of the samples, ORR polarization curves were measured through a RRDE equipment in 4-electrodes configuration: the disk current, $I_D$, is associated to the direct 4-electrons reduction of oxygen to hydroxide (because the reaction is conducted under alkaline conditions), while the ring current, $I_R$, is related to the indirect 2-electrons reduction to hydrogen peroxide. [33]

The results of these measurements are reported in Figure 1b and 1c and show that for the samples under investigation the ring currents are 10 ÷ 20 times lower with respect to the corresponding disk currents. This imply a predominant 4-electrons reduction pathway, as witnessed by the calculus of electron transfer number n and peroxide percentage $HO_2^-$%, evaluated by employing equations (1) and (2):

$$n = 4\,x\,\frac{I_D}{I_D + {I_R}/{N}} \qquad (1)$$

$$HO_2^-\% = 200\,x\,\frac{{I_R}/{N}}{I_D + {I_R}/{N}} \qquad (2)$$

where N is the ring current collection efficiency. In Figure 1d these two quantities are reported as a function of the potential. With the exception of samples containing larger concentrations of agar and amino acid (i.e. NC3G and NC3L), all the aerogels are characterized by n values well above 3, with low or null dependency on the applied potential. This reflects in peroxide percentages lower than 40%. More specifically, an electron transfer number equal to 3.6 was obtained for the samples prepared with lowest amino acid concentration (namely NC1G and NC1L), which makes them the best candidate as ORR catalysts in MFC cathodes. This result is very important because gives the opportunity to prepare electrodes using a smaller amount of chemicals thus implying a decrease in the environmental impact and a reduction in the production costs. The worse performance associated to the higher amount of amino acids and agar can be ascribed to the reduced surface area values (few tens of $m^2/g$) which do not allow good catalytic performance.

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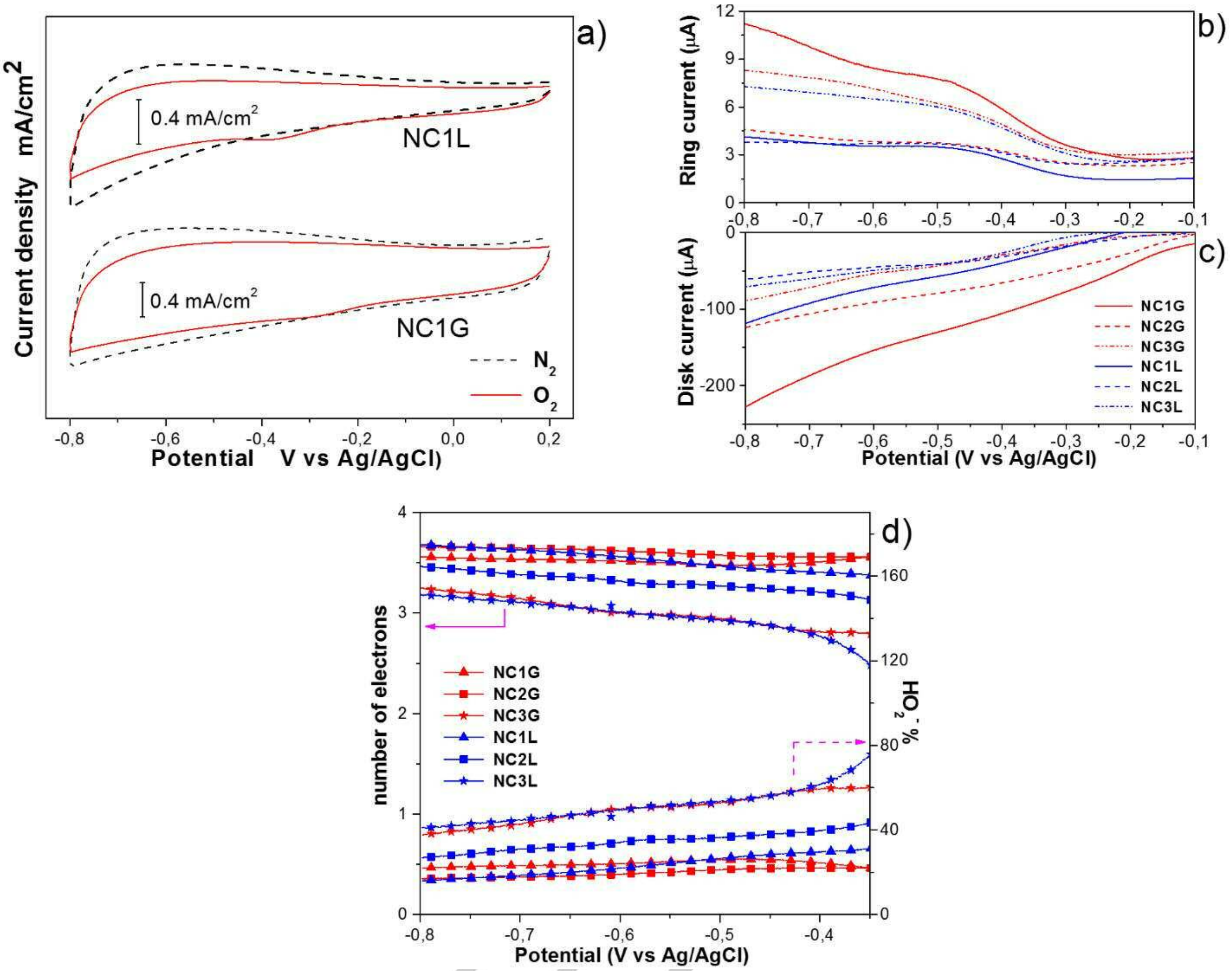

**Figure 1.** (a) Cyclic voltammograms of NC1L and NC1G samples in $O_2$- and $N_2$-saturated KOH solutions. (b) Ring and (c) Disk currents measured for aerogels at 2500 rpm rotation speed and different potentials. (d) Comparison of electron transfer number (left axis) and peroxide percentage (right axis) evaluated from the RRDE measurements of the different aerogel samples at 2500 rpm rotation speed and different potentials.

The best samples as stated by the electrochemical measurements were investigated by Raman spectroscopy in order to evaluate their graphitic features (see Supporting Information for details) and their electrical conductivity, because a high conductivity is essential for preparing good-performing electrodes.

The results, shown in Figure S3 (Supporting Information), give evidence of a good graphitization of the materials.

In accordance to Raman Spectroscopy outcome, the conductivity of NC aerogel was found to be 8 S/m, with negligible dependency on the amino acid content. Such a value guarantees an effective electron transfer toward the reaction sites.

After having confirmed their good conductivity and catalytic features, the samples were used to prepare cathodes, according to the procedure described in the experimental section, and then tested in a one-chamber MFC (see Figure S1b in the Supporting Information) for 50 days under a 1000 Ohm external load. Figure 2 shows the voltage (a), current density (b) and power density (c) trend versus time for cells containing different cathodes: NC1G, NC1L, carbon paper and Pt/carbon paper. Because of the complexity and irregularity of the aerogel geometry, the current density and the power density were calculated by dividing the corresponding current and power by the material weights (carbon paper: 292mg, carbon paper/Pt: 295mg, NC1L and NC1G: 6.61mg). The complexity of the aerogel geometry makes hard the porosity evaluation (which is necessary in order to calculate the real area of the cathode) by means of nitrogen adsorption and BET method because of the presence in our samples, at most, of macro- and micro-pores. An estimation of the sample porosities, evaluated as voids percentage in the material framework, has been tried by means of imageJ software (https://imagej.nih.gov/ij/) analysis of several FESEM images of the samples. The error associated to this method is as high as that related to BET measurements. On the other hand weighting the samples gave values that are more reliable with negligible errors. For this reason, the results obtained dividing by weight, the current and the power, are reported in Figure 2, while the results obtained dividing them

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by area are reported in Figure S4 in the Supporting Information, to let easier a comparison with the performance reported in literature..

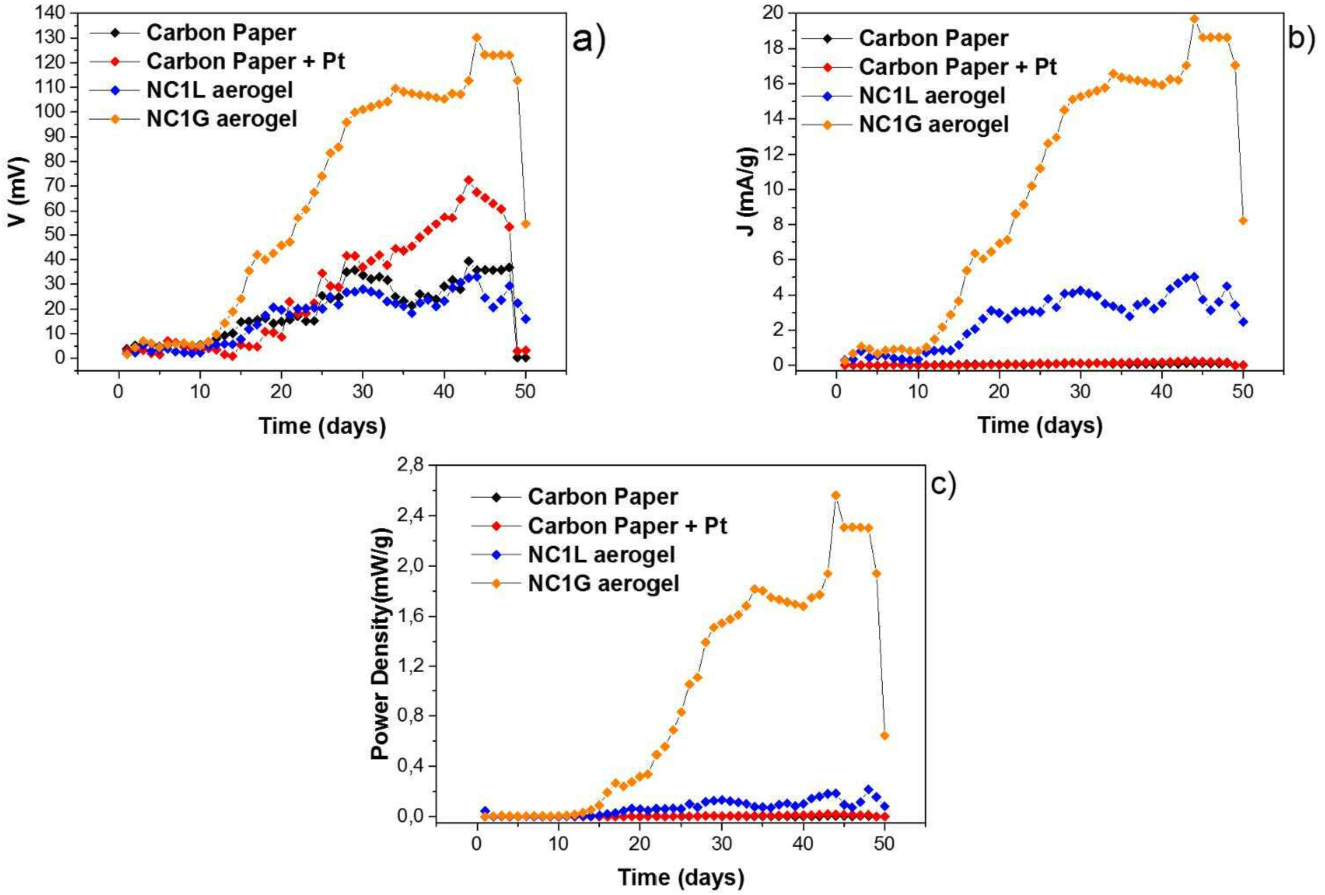

**Figure 2.** (a) Voltage, (b) current density and (c) power density trend during 50 days' test of MFCs with different cathodes: carbon paper (black diamond), Pt/carbon paper (red diamond), NC1L aerogel (blue diamond) and NC1G aerogel (orange diamond).

In Table 1 are summarized all the best values for the daily average electrical parameters investigated. All the MFCs showed a start-up time, necessary for biofilm formation at the anode, equal to about 10 days.

**Table 1.** Best values of the daily average electrical parameters

| SAMPLE | VOLTAGE (mV) | CURRENT DENSITY (mA/g) | POWER DENSITY (mW/g) |
|---|---|---|---|
| Carbon Paper | 39 | 0.13 | 0.0055 |
| Pt/Carbon Paper | 73 | 0.25 | 0.019 |
| NC1L | 33 | 5.02 | 0.22 |
| NC1G | 130 | 19.68 | 2.56 |

In terms of voltage (Figure 2a), MFCs with NC1G-based cathode, immediately, showed better performance than the other cells. MFCs, in which the cathode was made of Pt/carbon paper, needed a longer period to start increasing their performance, while the cells with the other two materials had the same behavior all over the experiment duration. If current density (Figure 2b) and power density (Figure 2c) trends were taken into account, both NC aerogels showed better performance than the commercial material with or without platinum. In any case, the materials prepared starting from glycine as N source gave better results than the lysine ones.

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In order to understand which are the reasons because NC1G samples worked better than the NC1L ones, a series of morphological and compositional characterizations have been performed.

Field emission scanning electron microscopy and energy dispersive X-ray spectroscopy have been used to analyse the morphology and the composition of the samples. In Figure 3 two representative images of the samples before and after pyrolysis are reported at the same magnification. The morphology of all the investigate samples is similar, no matter the amino acid content. The thermal treatment, in fact, induces the formation of large pores, from few microns up to few hundreds of microns, enhancing, in this way, the channel formation.

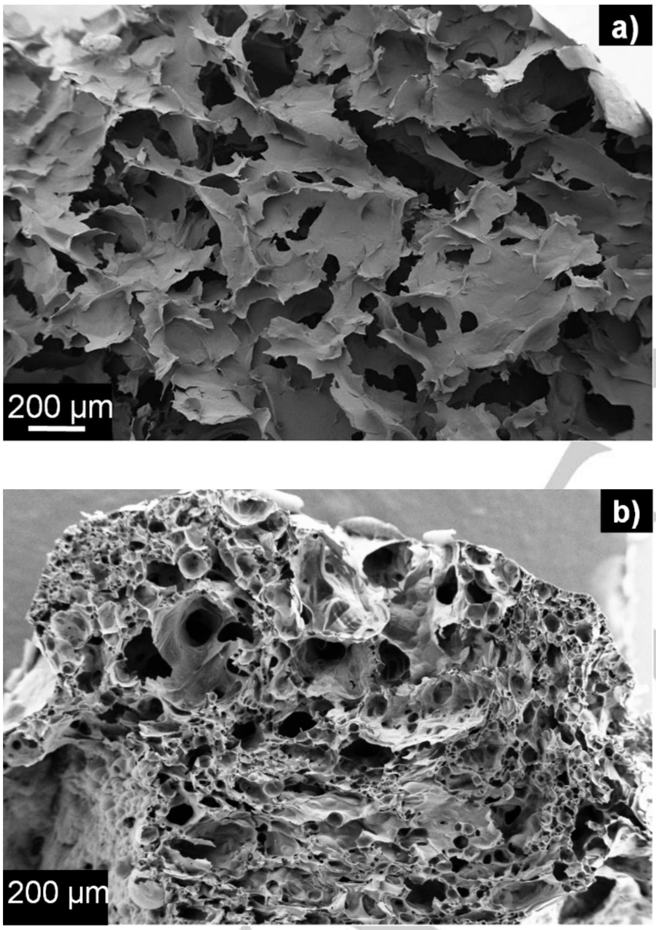

**Figure 3.** FESEM images of a) N-doped organic aerogel and b) N-doped carbon aerogel

The high surface area observed is an important characteristic that a cathode should possess to enhance the ORR performance in MFCs used for wastewater treatments, since oxygen is dissolved in water and needs relatively large pores for the water flow through the cathode.

The formation of multi-scale pores guarantees also an enhancement of the material surface area, providing, in this way, a larger number of catalytic sites. The NC aerogel surface average values are about 320 $m^2/g$ according to the nitrogen adsorption-desorption isotherms evaluation and they have been estimated by Brunner-Emmett-Teller (BET) plots. This value is comparable with those obtained in literature for aerogel prepared from natural precursors. [34] Slightly lower values were observed in the case of NC1L samples (about 270 $m^2/g$) than in NC1G ones and this could be one of the reason for their lower cell performance as already stated by Wohlgemuth et al. [22]

Another possible responsible for the different behavior of NC aerogels during the MFC test is the nitrogen amount and the type of defects that are formed inside the different materials by amino acid addition. For this reason, the nitrogen presence has been investigated before and after the pyrolysis step both in terms of concentration of N and the nature of nitrogen bonds in NC aerogels.

Two different techniques have been exploited: energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS).

From both EDS (Figure S5) and XPS (Figure S6a) the presence of nitrogen as consequence of amino acid addition to the agar solution is confirmed. The nitrogen is still present after the pyrolysis step as stated by EDS (Figure S5) and XPS (Figure S6b). By a comparison between the data collected after the thermal treatment (Figure 4b for EDS and Figure 4d for XPS, respectively) show a decrease in the N content. This is more evident for lysine-derived samples (-50% from EDS and -54% from XPS results) than for the glycine ones (-36% from EDS and -29% from XPS results), making the N content almost equal in all samples, regardless of the amino acid. By comparing the EDS and XPS data, it was also possible to establish that nitrogen is distributed uniformly through all the samples, but the greater part of it is located on the surface, namely more available for oxygen reduction.

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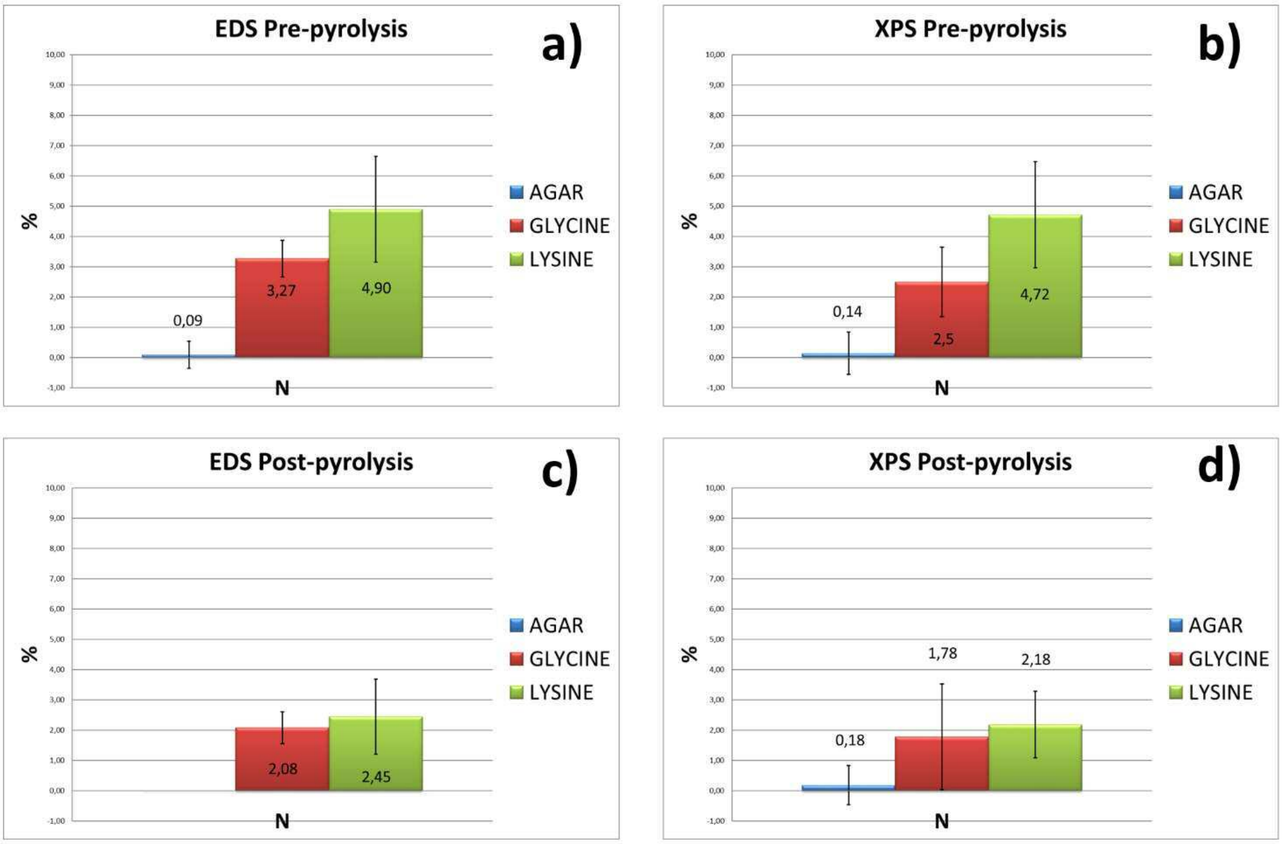

**Figure 4.** Average N content calculated from EDS data before (a) and after (b) pyrolysis and from XPS before (c) and after (d) pyrolysis, as well.

By fitting the high-resolution XPS spectra of nitrogen (see Figure 5) it was possible to recognize the different N species and estimate their percentage in the NC aerogels (see Table 2).

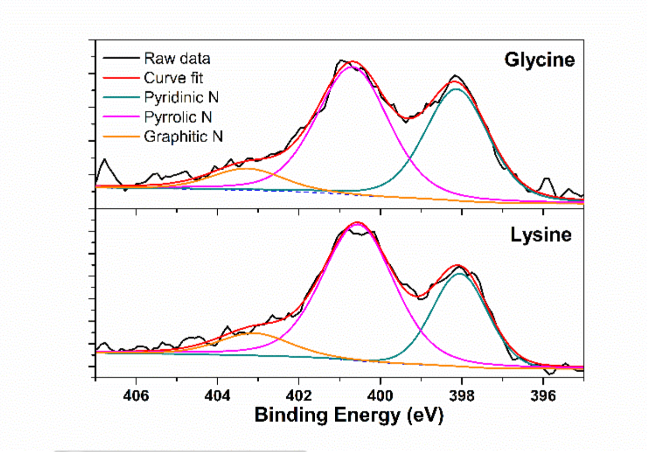

**Figure 5.** High-resolution XPS N spectra of a) glycine- and b) lysine-derived carbon aerogels.

**Table 2.** N functionalities percentage, estimated by fitting XPS high-resolution (HR) spectra of nitrogen.

| SAMPLE | PYRIDINIC | PYRROLIC | GRAPHYTIC |
|---|---|---|---|
| NC1G | 43.3% | 48.5% | 8.2% |
| NC1L | 32.0% | 55.5% | 12.5% |

Both in NC1G and NC1L samples nitrogen is present, for the most part, in the pyridinic form (peak at 398.6eV [10]) and in the pyrrolic one (400.5 eV [10]). While the pyrrolic N content is similar for both NC aerogels, the pyridinic one is higher in NC1G samples. The overall higher N content suitable for ORR species in NC1G samples than in NC1L ones, could result in a better catalytic performance for the glycine-derived aerogels than the lysine-derived ones, giving another possible explanation for the better

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NC1G performance as material for cathodes in MFCs than the NC1L ones.

Despite the controversy about the role of the different N forms in the ORR catalysis, many papers, nowadays, show that pyridinic N tends to be the most active species to promote ORR[35,36,37,38,39]. Zhang et al.[37] performed DFT (Density Functional Theory) calculations that showed how pyridinic N induces the highest spin density and the largest positive atomic charge density on the adjacent carbon atoms compared to the pyrrolic N and graphitic N, enhancing, in this way, the catalytic performance. The contribution of pyrrolic N and graphitic N to ORR catalysis, however, cannot be neglected, even if it is lower if compared to the pyridinic N one.

## Conclusions

Nitrogen-doped carbon based aerogels have been synthesized starting from natural precursors (agar and amino acids) using water as the non-toxic solvent by means of a green process (a typical sol-gel reaction under mild conditions) and without the need of any catalysts, followed by a freeze drying and a pyrolysis step at lower temperatures than those, normally, used to make graphite. The materials used to prepare the cathodes to be tested in MFCs were selected by means of electrochemical measurements, that stated how the samples containing the lower amount of nitrogen were better or equally performing than those containing higher nitrogen amounts. After the MFCs test, the cathodes prepared using aerogels where the N source was derived from glycine showed to be the better performing. This phenomenon can be ascribed to the higher content of the pyridinic form of nitrogen in these materials than that of lysine ones, despite of the total amount of N, that was, more or less, the same in the two different types of samples as confirmed by XPS and EDS.

## Experimental Section

**Materials**. All the reagents were purchased from Sigma-Aldrich, where not otherwise indicated.

**N-doped C-based aerogel preparation**. NC aerogels were prepared by a sol-gel method. Agar and amino acids with relative concentrations (see Table 3) were dissolved in distilled water (20 ml) under stirring and heating (85 °C) for 1 hour.

**Table 3.** Synthesis parameter summary

| SAMPLE[a] | AGAR AMOUNT (wt%) | AMINO ACID CONCENTRATION (mol/l) |
|---|---|---|
| NC1G and NC1L | 4 | 0.07 |
| NC2G and NC2L | 3 | 0.7 |
| NC3G and NC3L | 4 | 0.7 |

[a] N is nitrogen-doped, C is carbon-based, G is glycine and L is lysine in the samples name respectively

Once the reagents were solubilized, the solution was poured into plastic moulds and let rest until the gel formation. The gels were, then, left ageing overnight at ambient temperature and pressure in order to strengthen their structure.

After ageing, the gels were dried by means of a freeze dryer (Lio5PDGT-Cinquepascal) at -50 °C and 1mbar for two days. Next, the dried gels were heated at 900 °C in a vertical furnace (Carbolite VST 12/30/3216/) for 3 hours (heating rate: 2.5 °C/min) under an argon flow for transforming the organic aerogel into a NC aerogel.

**Cathode preparation**. NC aerogels were fixed to a commercial carbon-based support (GDS21000, FuelCell Earth LLC, USA) by means of a conductive carbon cement (LeitC, Agar Scientific) to guarantee the electrical contact between the two materials. For comparison's sake, a carbon paper as it is and the same carbon support treated with a Pt/C layer have been used to prepare a cathode for reference MFCs.

This layer is based on a mixture of 0.5 mg/cm$^2$ of Pt/C paste, 5 wt% of Nafion, 2-propanol and water. The mixture was applied on the inner side of the support and left to dry at room temperature for 1 day. [40]

On the other side of the support, which is exposed to air, a polytetrafluoroethylene (PTFE) layer has been deposited to favor the oxygen diffusion inside the MFC, minimizing water leakages.

A stainless steel wire has been inserted into the NC aerogel/carbon-based material for promoting the electrical contact.

**Cell setup**. A square-shaped single chamber MFC (Figure S1b in the Supporting Information) has been fabricated by an additive 3D printing technology (OBJECT30, Stratasys), with one side of the cathode directly exposed to air.

The area of both electrodes was 9 cm$^2$ while the inner volume occupied by the anodic electrolyte was 15 ml.

The anode, for all cells, was constituted by a carbon paper layer in which a stainless steel wire is used to transport electrons from the biofilm to the external load.

**MFC operation setup**. Experiments were conducted in duplicate at room temperature conditions (21±3 °C). A fresh sediment from Dora Baltea river in Valle d'Aosta (Italy) was used as inoculum, characterized by the presence of a mixed culture of bacteria.

MFCs were inoculated with freshwater sediment enriched cultures (10 % v/v). Being the cell a 1-chamber device, both the anode and the cathode share the same electrolyte based on 1 g/l sodium acetate (as carbon source, able to provide 8 electrons during its oxidation) and 0.31 g/l of ammonium chloride (as nitrogen source), dissolved into a phosphate buffer solution ($NaH_2PO_4$ 2.45 g/l; $Na_2HPO_4$ 4.28 g/l; KCl 0.10 g/l) with 10 ml/l of Wolfe's Vitamin solution (ATCC) and 10 ml/l Wolfe's trace mineral solution (ATCC).

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The working mode was a fed-batch one, characterized by a total electrolyte replacement every 2 days. The electrolyte was pumped using multiple channel syringe pumps (NE1600, New Era Instrument, USA). An external load $R_{ext}$ equal to 1 kΩ was applied in order to ensure the formation of biofilm and, at the same time, power production. The voltage ($V$) of MFCs was acquired every 10 minutes by a digital multimeter (Agilent, 34972A). The resultant current ($I$) was calculated by the Ohm's law ($I = V/R_{ext}$).

The total MFC experiment lasted 50 days.

**Characterizations**. The electrochemical measurements were carried out through a CH Instrument 760D electrochemical workstation and an ALS RRDE-3A rotating ring disk electrode apparatus. As working electrode, a BioLogic glassy carbon disk/Pt ring was used for all the measurements, while Pt was used as counter electrode and Ag/AgCl as reference electrode. $O_2$- and $N_2$-saturated 0.1 M KOH aqueous solutions were used as electrolytes.

The working electrode was properly polished with ethanol before the catalyst deposition carried out through the following procedure. The aerogel was reduced in powder and 4 mg of the resulted catalyst were dispersed in a solution containing 25 µl of water, 175 µl of 5% Nafion solution and 100 µl of 2-propanol. The mixture was ultrasonicated for several minutes to form a black dispersion. 10 µl of this formulation were cast-coated onto the disk surface to form a uniform film. The as-obtained deposition was dried at room temperature overnight. The final catalyst loading was 1 mg/cm$^2$.

Cyclic Voltammetry measurements were carried out in the potential range 0.2 ÷ -0.8 V vs Ag/AgCl with a 10 mV/s scan rate. [41,42]

ORR polarization curves were acquired in 4-electrode configuration by cathodically scanning the disk electrode from 0.2 V ÷ -0.8 V with fixed 5 mV/s scan rate and 2500 rpm rotation speed; the ring electrode was kept at fixed 0.2 V potential.

Surface areas were evaluated by measuring nitrogen adsorption-desorption isotherms at -196 °C using liquid nitrogen on a Quadrasorb Si from Quantachrome. Prior to the adsorption measurements, the samples were evacuated at 150°C under vacuum, overnight. The surface area was determined in the relative pressure range from 0.1 ÷ 0.3 of the Brunner-Emmett-Teller (BET) plot.

The graphitic features and electrical conductivity were evaluated by means of Raman spectroscopy and electrical measurements, respectively. Raman spectroscopy was performed by a Renishaw InVia Reflex Spectrometer ($\lambda_{ex}$ = 514.5nm). The electrical measurements were carried out in four-probes configuration using a Keithley 2635A source measure unit.

Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX) have been performed with a ZEISS Auriga equipped with an OXFORD X-ray detector to investigate the morphology and chemical composition. For each sample, the EDS analysis has been carried out by measuring 10 different points under the same collection conditions, in order to have an averaged quantification of the different elements over the entire sample. Aerogels before pyrolysis have been coated with few nanometers of platinum by means of a sputter Quorum Technologies 150T ES, to enhance their conductivity.

X-ray photoelectron spectroscopy (XPS) studies were carried out by a PHI 5000 Versaprobe scanning X-ray photoelectron spectrometer (monochromatic Al K-alpha X-ray source with 1486.6 eV energy, 15 KV voltage and 1 mA anode current), in order to investigate surface chemical composition. All core-level peak energies were referred to C1s peak at 284.5 eV and the background contribution in HR scans was subtracted by means of a Shirley function. Spectra were analysed using Multipak 9.6 dedicated software. As for EDS, with the same purpose, 10 measurements have been carried out for each sample.

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[1] IPCC, 2013: Summary for Policymakers. In: Climate change 2013: the physical science basis. Contribution of working group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. [T.F. Stoker, D. Qin, G-K Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)] Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
[2] IPCC, 2014: Summary for Policymakers. In: Climate change 2014: *mitigation of climate change. Contribution of working group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* [O. Edenhofer, R. Pichs-Madruge, Y. Sokona, E. Farahani, S. Kadner, K. Seiboth, A. Adler, I. Baum, S. Brunner, P. Eickemeyer, B. Kreimann, j. Savolainen, S. Schlomer, C. Von Stechow, T. Zwickel and J.C. Minx (eds.)] Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
[3] A.E. Franks, K.P. Nevin, *Energies* **2010**, 3, 899-919
[4] M. Zhou, H. Wang, D.J. Hasset, T. Gu, *J. Chem. Technol. Biotechnol.* **2013**, 88, 508-518
[5] B.E. Logan, *Microbial Fuel Cells*, Wiley, **2008**
[6] T.H. Pham, J.K. jang, I.S. Chang, B.H. Kim, *J. Microbiol. Biotechnol*, **2004**, 14, 324-329
[7] Q. Yang, X. Wang, Y. Feng, H. Lee, J. Liu, X. Shi, Y. Qu, BN. Ren, *Fuel*, **2012**, 102, 478-482
[8] J.Liu, J. Liu, W. He, Y. Qu, N. Ren, Y. Feng, *J. Power Sources*, **2014**, 265, 391-396
[9] H. Rismani-Yazdi, S.M. Carver, A.D. Christy, O.H. Tuovinen, *J. Power Sources*, **2008**, 180, 683-694
[10] Y. Nie, L. Li, Z. Wei, *Chem. Soc. Rev.*, **2015**, 44, 2168-2201
[11] M. Zhou, M. Chi, J. Luo, H. He, T. Jin, *J. Power Sources*, **2011**, 196, 4427-4435
[12] E.H. Yu, S. Cheng, K. Scott, B.E. Logan, *J. Power Sources*, **2007**, 171, 275-281
[13] L. Zhang, C. Liu, L. Zhuang, W. Li, S. Zhou, J. Zhang, *Biosens. Bioelectron.*, **2009**, 24, 2825-2529
[14] I. Roche, K. Katuri, K. Scott, *J. Appl. Electrochem.*, **2010**, 40, 13-21
[15] J.M. Morris, S. Jin, J.Q. Wang, C.Z. Zhu, M.A. Urynowicz, *Electrochem. Commun.*, **2007**, 9, 1730-1734
[16] K.P. Gong, F. Du, Z.H. Xia, M. Durstock, L.M. Dai, *Science*, **2009**, 323, 760-764
[17] C.H. Choi, S.H. park, S.I. Woo, *Green Chem.*, **2011**, 13, 406-412
[18] L. Yang, S. Jiang, Y. Zhao, L. Zhu, S. Chen, X. Wang, Q. Wu, J. Ma, Z. Hu, *Angew. Chem. Int. Ed.*, **2011**, 50, 7132-7135

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[19] N. Garino, A. Sacco, M. Castellino, J.A. Munoz-Tabares, A. Chiodoni, V. Agostino, V. Margaria, M. Gerosa, G. Massaglia, M. Quaglio, *ACS Appl. Mater. Interfaces*, **2016**, 8, 4633-4643
[20] R.W. Pekala, *J. Mater. Sci.*, **1989**, 24, 3221-3227
[21] H. Sun, Z. Xu, C. Gao, *Adv. Mater.*, **2013**, 25, 2554-2560
[22] S-A. Wohlgemuth, R.J. White, M-G, Willinger, M-M. Titirici, M. Antonietti, *Green Chem.*, **2012**, 14, 1515-1523
[23] K. Elumeeva, N. Fechler, T.P. Fellinger, M. Antonietti, *Mater. Horiz.*, **2014**, 1, 588-594
[24] S. Fu, C. Zhu, J. Song, M.H. Engelhard, B. Xiao, D. Du, Y. Lin, *Chem. Eur. J.*, **2017**, 23, 10460-10464
[25] C. Cao, L. Wei, M. Su, G. Wang, J. Shen, *Biores. Technol.*, **2016**, 214, 348-354
[26] Y. Lu, N. Zhu, F. Yin, T. Yang, P. Wu, Z. Dang, M. Liu, X. Wei, *Biosens. Bioelectron.*, **2017**, 98, 350-356
[27] L-T. Song, Z-Y. Wu, F. Zhou, H-W. Liang, Z-Y. Yu, S-H. Yu, *Small*, **2016**, 46, 6398-6406
[28] X. Zhang, W. He, R. Zhang, Q. Wang, P. Liang, X. Huang, B.E. Logan, T.P. Fellinger, *ChemSusChem*, **2016**, 9, 2788-2795
[29] L. Delmondo, G.P. Salvador, J.A. Munoz-Tabares, A. Sacco, N. Garino, M. Castellino, M. Gerosa, G. Massaglia, A. Chiodoni, M. Quaglio, *Appl. Surf. Sci.*, **2016**, 388, 631-639
[30] J. Zhang, *PEM fuel cell electron catalysis and catalyst layers,* Springer, **2008**
[31] J. Rongzhong, D. Shaojun, *J. Phys. Chem.*, **1990**, 94, 7471-7476
[32] S-J. Lee, S.I. Pyun, S-K. Lee, S-J. Kang, *Isr. J. Chem.*, **2008**, 48, 215-228
[33] A.J. Bard, L.R. Faulkner, *Electrochemical methods: fundamentals and applications*, Wiley, **2001**
[34] M. Robitzer, D. Di Renzo, F. Quignard, *Microp. Mesop. Mater.,* **2011**, 40, 9-16
[35] X. Cui, S. Yang, X. Yan, J. Leng, S. Shuang, P.M. Ajayan, Z. Zhang, *Adv. Funct. Mater.*, **2016**, 26, 5708-5717
[36] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, *Science*, **2016**, 351, 361-365
[37] L. Zhang, Z. Xia, *J. Phys. Chem. C*, **2011**, 115, 11170-11176
[38] T. Xing, Y. Zheng, L.H. Li, B.C.C. Cowie, D. Gunzelmann, S.Z. Qiao, S.M. Huang, *ACS Nano*, **2014**, 8, 6856-6862
[39] J. Wu, L. Ma, R.M. Yadav, Y. Yang, X. Zhang, R. Vajtai, J. Lou, P.M. Ajayan, *ACS Appl. Mater. Interfaces*, **2015**, 7, 14763-14769
[40] S. Cheng, H. Liu, B.E. Logan, *Electrochem. Commun.*, **2006**, 8, 489-494
[41] Y. Liao, Y. Gao, S. Zhu, J. Zheng, Z. Chen, C. Yin, X. Lou, D. Zhang, *ACS Appli Mater. Interfaces*, **2015**, 7, 19619-19625
[42] D.J. Davis, A-R, Raji, T.N. Lambert, J.A. Vigil, L. Li, K. Nan, J.M. Tour, *Electroanalysis*, **2014**, 26, 164-

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