**Fibrous Porous Carbon Electrocatalysts for Hydrazine Oxidation by
using Cellulose Filter Paper as Precursor and Self-Template**

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Abstract

Hydrazine is often regarded as one of the most appealing fuels for fuel cells due to its high energy content, and also because it gives off only environmentally benign byproducts when it is used in fuel cells (cf. many other fuels produce the greenhouse gas CO₂). However, current electrocatalysts for the hydrazine oxidation reaction (HOR) in direct hydrazine fuel cells involve the expensive, unsustainable noble metals such as Pt. Herein, using cellulose filter paper both as a precursor and a self-template, we show the synthesis of nanoporous carbon electrocatalysts that can efficiently electrocatalyze HOR. To make the electrocatalysts, first cellulose filter paper is modified with metal-amine complexes and then with silica shells. After carbonization of the resulting composite material at different temperatures, followed by removal of the silica shells, nanoporous carbon-based electrocatalysts are obtained. Notably, the intertwined structure of the cellulose matrix in the paper is taken advantage of to serve as self-template, allowing the formation of the desired fibrous, nanoporous carbon electrocatalysts. The materials show good electrocatalytic activity toward HOR, giving low overpotential and high current density. Thus, such nanoporous carbons can be good candidate materials to replace conventional metal-based catalysts commonly used in HOR and other related reactions.

1. Introduction

Fuel cells are promising energy converting systems with great potential to contribute to our rapidly growing need of alternative energy sources and to alleviate our continued dependence on fossil fuels [1,2]. Compared with many compounds that can serve as fuels in fuel cells, hydrazine has several advantages due to its superior theoretical standard equilibrium potential, high energy density, and clean oxidation – in a sense that it gives off only environmentally benign byproducts (*i.e.*, N₂ and H₂O) during its use in fuel cells [3–6]. However, the catalysts used for hydrazine oxidation reaction (HOR) in direct hydrazine fuel cells (DHFC) currently involve mainly the scarcely available, expensive noble metals such as Pt [6,7]. In order to replace such unsustainable electrocatalysts with more sustainable ones, and thereby make various fuel cells find large-scale applications, there are currently research activities focusing on three major fronts [8-16]. The first one involves alloying Pt or noble metal catalysts with other inexpensive, non-noble metals, whereby the overall amount of Pt in the catalysts is reduced without compromising the catalysts' activity [10-12]. The second approach is centered around finding suitable porous support materials for Pt or other noble metals to increase the metals' accessible surface area, and thereby catalytic activity per unit mass [13,15]. The third and final one involves the development of entirely new, noble metal-free or metal-free (nano)materials that can catalyze the reactions in question [6,8,9,16]. Among these materials, recently heteroatom-doped carbon materials have especially become a subject of huge interest, because despite possessing no metallic moieties they show unprecedented, high electrocatalytic activity for a number of reactions, with values that can rival those of Pt. These metal-free, catalytically active materials are typically composed of carbon black [17], carbon

nanotubes [18], graphene [19,20], mesoporous carbon [2,6], carbon nanoneedles [21] or their variants, and various heteroatom-dopants.

The origin of the electrocatalytic activity in these materials is now generally believed to be the presence of heteroatom dopants (such as N, O, B, P, S or Se) in the extensive conjugated sp^2 - sp^2 linkages or π -orbital electron delocalized graphitic domains of their carbon nanostructures [21-26]. These heteroatom dopants are shown, experimentally and theoretically, to be able to perturb the electronic structure of the carbon lattice, generating partially positively and negatively charged groups on the material without substantially compromising the material's conductive properties [14,22,23,25]. This means, for example, due to its similar size as a C atom, a N dopant atom can easily be doped into a carbon nanostructure by replacing a carbon atom. More importantly, due to its more electronegativity compared with a C atom, the doped N atom donates its electron to the delocalized π -system of the carbon matrix and creates partially positively and negatively charged moieties in the material [13,27]. The latter, in turn, enables the carbon material to interact strongly with reactants (*e.g.*, O_2) and promote the chemical transformation of the reactants (*e.g.*, by weakening the O=O bond of O_2 during the oxygen reduction reaction (ORR) [25]). This is, in fact, how heteroatom dopants are generally believed to make carbon materials electrocatalytically active. Supporting this further, on the contrary, pure carbon nanomaterials possessing no such heteroatom dopants display no, or only poor, electrocatalytic activity.

Similarly, there have been reports, *albeit* relatively few, on heteroatom-doped carbon-based materials that can electrocatalyze HOR in the same way. Our group was actually the first to show that carbon-based nanomaterials can electrocatalyze HOR, with the report some three years ago that freestanding carbon nanoneedles made from cotton-derived cellulose can electrocatalyze HOR [21]. In a follow up work, we found

that heteroatom-doped mesoporous carbons derived from polymer (polypyrrole) could also serve as highly active electrocatalysts for HOR, with catalytic activity close to that of Pt [6]. In fact, the latter materials still remain the best in terms of electrocatalytic activity among non-Pt materials reported for HOR so far, to the best of our knowledge. Notably in both works, silica was used with or around the carbon precursor as a template or a shell, and thereby to endow the carbon materials high porosity and good electrocatalytic activity. Recently, Yang et al. [28] reported a carbon electrocatalyst for ORR using iron-doped filter paper as a precursor. In the work though, no silica or metal oxide shell was employed as a protecting shell and/or a template with the carbon precursor. As it becomes evident soon below, the products obtained after carbonization of such precursors that possess no silica/metal oxide in them have lower electrocatalytic performance for HOR (compared with the ones produced from the precursors containing silica).

To this end, herein we report the synthesis of a N-doped nanoporous carbon material for HOR electrocatalysis from cellulose filter paper, using the filter paper's cellulose material as a precursor and the material's porous matrix as a self-template (Figure 1). To attain this, silica shells were deposited around the cellulose structure in the filter paper, and this was followed by carbonization and then removal of the silica from the carbonized products. Having silica, and also metal-amine groups, with the precursor made the carbon materials to have larger surface area, higher degree of graphitization, greater density of desired heteroatom dopant moieties and higher electrocatalytic activity (compared with the corresponding materials synthesized without using silica shells and metal amine complexes).

2. Experimental Section

2.1. Reagents and Chemicals

Qualitative-grade cellulose filter paper (QFP, Fisherbrand™, P8 Grade) was purchased from Fisher Scientific. Anhydrous ethanol was obtained from Pharmco-AAPER. Ferric chloride (99.0%), 2-propanol, hydrazine monohydrate (98%), Nafion®, ammonium hydroxide (27%), phosphate buffer saline (10% PBS, pH 7.4) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich.

2.2. Synthesis of porous carbon-derived from filter paper (PCDFs)

First, one QFP (P8, *ca.* 7 cm in diameter) was cut into small pieces and washed with anhydrous ethanol. The small pieces of QFP were then kept in 10 mL of aqueous solution of ferric chloride (0.01 M) for 30 min and washed with ethanol afterwards. Subsequently, the Fe(III)-functionalized pieces of QFP were soaked in 10 mL of ammonia solution (27%) for 30 min, and then taken out and washed with ethanol. After this step, they were quickly placed in 5 mL of tetraethyl orthosilicate (TEOS) for 60 min and washed with ethanol. The resulting silica-coated Fe(III)-functionalized pieces of QFP (SiO₂/Fe(III)/QFP) were dried overnight at 80 °C, and subsequently placed on a quartz boat to be subjected to pyrolysis as follows.

The pyrolysis of SiO₂/Fe(III)/QFP was performed under inert (Ar) atmosphere in a temperature programmable tube furnace in four steps (as depicted in Figure S1). The materials were heated first at a rate of 10 °C min⁻¹ from room temperature to 100 °C, and then kept at 100 °C for 2 hours. Immediately after this, the materials were heated at a rate of 1 °C min⁻¹ from 100 to 200 °C, and then kept at 200 °C for 2 hours. In the third step, the materials were further heated to 300 °C at the same heating rate and kept at 300

°C for 2 hours. In the last heating step, the materials were heated at a rate of 10 °C min⁻¹ to a final pyrolysis temperature of 700, 800, 900 or 1000 °C, and kept at this temperature for 2 hours. Finally, the materials were let to cool down to room temperature.

To etch the silica shells off of the carbonized products, the materials were placed in a Teflon autoclave and treated with 25 mL of aqueous NaOH solution (2.0 M) under hydrothermal condition at 100 °C for 24 hours. The materials were then washed with deionized (DI) water by sonication and separated from the solution by centrifugation. They were washed again with DI water until the supernatant had a neutral pH. Finally, the materials were dried under ambient conditions. Using these procedures, four different heteroatom-doped carbon materials (depending on the final pyrolysis temperature used) were finally obtained, and they were named as PCDF-T (which is to mean “porous carbon-derived from filter-paper” and where “T” indicates the final pyrolysis temperature).

Additionally, for comparison, we have synthesized three control materials without using silica shells or Fe(III) ions, under otherwise similar synthetic conditions. In the first case, a material was made without deposition of silica shells around the QFP (by skipping the TEOS impregnation step). In the second case, a material was made without using ferric chloride. In both cases, after being subjected to pyrolysis the resulting materials were treated with NaOH under hydrothermal conditions. Finally, a third reference material was prepared following the procedure reported in Yang et al. [28]. In this case, a Fisherbrand™, P8, QFP was annealed at 240 °C for 2 hours in a muffle furnace at a heating rate of 2 °C min⁻¹. The resulting material was then impregnated with aqueous ferric nitrate solution (1% wt./wt.). Finally, the material was heated in a tube furnace under N₂ atmosphere at a heating rate of 2 °C min⁻¹, and in the

middle of which it was successively kept at 180, 240 and 900 °C for 2, 2 and 1 hour, respectively. The final product was ground into powder and washed with 0.5 M of H₂SO₄ solution at 85 °C for 6 hours to remove the iron species on it. The resulting three control materials were labeled as PCDF/NFe (where “NFe” represents “no Fe”), PCDF/NS (where “NS” represents “no silica shells”) and PCDF/Lit (where “Lit” represents “literature procedure” [28]), respectively. The temperature of 900 °C was purposely chosen as the final pyrolysis temperature for making all the control materials here, because based on previous studies for related materials in related reactions carbon nanomaterials treated at this temperature often show the highest electrocatalytic activity [2,6,21,26], which also happens to be the case for the PCDF materials reported in this work (*vide infra*).

2.3. Instrumentation and characterization

The surface properties of the materials were determined with nitrogen (N₂) adsorption/desorption measurements at 77 K using a Micromeritics TriStar-3000 (Micromeritics Instrument Corp., USA). The surface area of the materials was obtained by the Brunauer-Emmet-Teller (BET) method and the pore size distribution of the materials was acquired by the Barrett-Joyner-Halenda (BJH) method. The morphology of PCDFs was examined by scanning electron microscopy (SEM) using a Zeiss Sigma Field Emission scanning electron microscope. X-ray photoelectron spectra (XPS) of the materials were obtained with ESCALAB 250 X-ray photoelectron spectrometer equipped with an Al K α radiation as a source ($h\nu = 1486.6$ eV).

2.4. Electrocatalysis

The electrochemical and electrocatalytic properties of PCDF materials were studied using a PAR Versastat3 (Princeton Applied Research) instrument. The electrocatalytic hydrazine oxidation reaction (HOR) over the materials was measured with cyclic voltammetry in the potential range of -0.8 to 1.0 V at a scan rate of 0.01 V s⁻¹. The experiment was performed in 15 mL of aqueous hydrazine solution with concentrations ranging from 5 to 50 mM in PBS (10 %) at room temperature. The electrochemical cell for the measurement was put together in a three-electrode configuration, consisting of a saturated calomel electrode (SCE) as the reference electrode, a graphite rod (diameter: 1.5 mm) as the counter electrode, and a glassy carbon electrode containing the catalysts synthesized above as the working electrode. The working electrode was assembled by depositing on the top of the glassy carbon electrode 2 μL of each catalyst (the carbon materials) from their corresponding homogeneous suspensions as 0.1 g L⁻¹ in 2-propanol, followed by deposition of Nafion (5% in 2-propanol), and finally drying the film in air for 5 min.

2.5. Electrochemical Analysis

The electron transfer number (n) involved in HOR was determined from the plot of I/A versus $v^{1/2}$ (Figure S3b) using equation 1 (Eqn. 1) below [6]:

$$\frac{I}{A} = 3.01 \times 10^{-5} \cdot n \cdot [(1 - \alpha)n_{\alpha}]^{\frac{1}{2}} \cdot C \cdot D^{-\frac{1}{2}} \cdot v^{\frac{1}{2}} \quad (1)$$

where I is current, C is the concentration of hydrazine in the PBS solution (50 mM), D is the diffusion coefficient in solution, which can be obtained with the Cottrell equation (Eqn. 2 below), A is the area of the electrode ($A = 0.071 \text{ cm}^2$), n_{α} is the number of electrons involved in the rate-determining step, and α is the electron transfer coefficient,

which can be determined from the linear dependence of peak potential (E_p) with the logarithm of the potential scan rate (v) (Figure S3a), according to equation 3 (Eqn. 3) below.

The Cottrell equation that allows the determination of D is given by:

$$\frac{I}{A} = \left[n \cdot F \cdot C \cdot D^{\frac{1}{2}} \cdot \pi^{-\frac{1}{2}} \right] t^{-\frac{1}{2}} \quad (2)$$

where D is diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), A is the electrode area ($A = 0.071 \text{ cm}^2$), F is the Faraday constant (96486 C mol^{-1}) and C is the concentration of hydrazine (50.0 mM). After determining the value of n , the other parameters can be determined by using the plot of I/A versus $t^{-1/2}$, which can be obtained by chronoamperometry (Figure S3c and S3d) and by applying Eqn. 3:

$$E_p = k + \left[\frac{0.03}{\alpha \cdot n_\alpha} \right] \log v \quad (3)$$

where k is a constant and $n_\alpha = 1$.

3. Results and Discussion

3.1. Synthesis and characterization of PCDF materials

For the synthesis of the PCDF materials, QFP was used both as a precursor and a self-template. We chose conventional filter paper for this purpose because: 1) it is composed of cellulose, which we had found to be a good precursor to make electrocatalytically active graphitic carbon materials, due to its highly organized crystalline structure [1], and 2) we wanted to take advantage of the cross-linked fibrous cellulose structure in the filter paper as a self-template to produce a fibrous carbon nanomaterial with high surface area (after first coating it with silica shells). Coating the

surfaces of the cellulose fibers in the filter paper by silica shells could be achieved easily, thanks to the surface hydroxyl groups present on cellulose [21]. In fact, the surface hydroxyl groups are the major functional groups by which cellulose undergoes different chemical modification reactions, such as esterification, etherification, substitution, ion exchange and oxidation [29], and of course, here in this work, the silane-coupling and sol-gel reactions [30,31]. With these types of surface modification reactions, heteroatom-rich compounds can also be included into the cellulose filter paper, and ultimately be incorporated as heteroatom dopants in the final carbon materials. So, overall, by using the inter-wined cellulose structure as a template, the cellulose material and the metal-amine complexes as precursors, and the silica as protecting shell, the electrocatalytically active nanoporous carbons were synthesized.

In the synthetic procedure, the QFP was first impregnated with Fe(III) ions by soaking it in an aqueous solution of ferric chloride. In this solution and in the conditions the QFP is made and post-treated, the cellulose fibers in QFP would typically carry negatively charged surfaces and are, thus, capable of binding metal ions on their surfaces *via* electrostatic interaction as well as coordination/hydrogen bonding type interactions between the several O atoms present as OH groups (Cell-OH) on their surfaces and the metal ions [32]. Such processes of layer-by-layer assembly of metal ions and positively charged groups (*e.g.*, positively charged polymers) around cellulose, by taking advantage of the negatively charged surfaces of cellulose, has actually been utilized before to produce monolayers and multilayers of various groups around cellulose [21,33-36]. The same process is responsible for the adhesion of the Fe(III) ions around the cellulose fibers here, as well as the silicate species in the subsequent step. Specifically, the Fe(III) ions deposit around the cellulose fibers through the interactions between the Cell-OH groups and Fe(III) by standard complexation (where

the OH groups would replace one of the H₂O ligands around [Fe(H₂O)₆]³⁺). When then soaked in ammonia solution subsequently, the Fe(III)-immobilized QFP (presumably, Cell-(OH)/[Fe(H₂O)₆]³⁺) lets Fe(III)-amine complexes form around the cellulose fibers (most likely as Cell-(OH)/[Fe(H₂O)_{6-x}(NH₃)_x]³⁺ species) (Figure 1).

Finally, when mixed with tetraethyl orthosilicate (TEOS), the resulting Cell-OH-bound Fe(III)-amine groups can interact with silicate species *via* electrostatic interaction (between Fe(H₂O)_x(NH₃)_{6-x}]⁺³ and the O atoms of cellulose-OH) and form the material denoted as Fe(III)-amine/QFP. This is possible due to the interaction between the Fe(III)-amine/QFP and the silicate species produced by the hydrolysis and condensation of TEOS in the basic solution (or the sol-gel process). This interaction is favorable, again thanks to the large numbers of hydroxyl groups around cellulose nanofibers (Cell-OH). These hydroxyl groups in cellulose are known to be the main functional groups by which cellulose typically forms chemical bonding, undergoes chemical modification and/or interacts with other species and is able to form adhesion to them [34]. Thus, during the sol-gel process, electrostatic and hydrogen bonding between the Cell-OH groups and the silicate species formed from the hydrolysis and condensation of tetraethoxysilane (TEOS) are expected to occur [35]. So, this interaction between Cell-OH-bound Fe(III)-amine groups and silicate species *via* electrostatic interaction (between Fe(H₂O)_x(NH₃)_{6-x}]⁺³ and the O atoms of cellulose-OH) as well as *via* hydrogen bonding interactions between them [36] formed the silica coating around the cellulose fibers in QFP. After washing with ethanol and letting it to dry under ambient conditions, the silica-coated Fe(III)-amine/QFP material was formed.

The dried silica-coated Fe(III)-amine/QFP was then subjected to pyrolysis, as illustrated in Figure S1, to different final temperatures, namely 700, 800, 900 or 1000 °C. The silica coating from the resulting carbonized material was finally removed by

stirring the carbonized materials in aqueous NaOH solution under hydrothermal condition (see Experimental section for more details). After removal of the silica coating from the carbonized composite material, fibrous carbon materials or electrocatalysts, labeled as cellulose paper-derived carbon fibrils (PCDF-700, PCDF-800, PCDF-900 and PCDF-1000), where the numbers represent the final carbonization temperature used to produce the particular material, were obtained.

The morphology of the resulting materials and their precursors was characterized by scanning electron microscopy (SEM) (Figure 2). Figure 2a shows the SEM image of the QFP before any treatment, and the image displays a fibrous as well as a porous structure. A similar structure is also observed in the SEM image of the material after subsequent heat treatment steps, especially for the one that was coated with silica shell before the heat treatment steps. Conversely, the morphology of the material appears slightly different when the steps of silica coating and/or metal-amine complexes is/are skipped. To be specific, when silica shell is not used, the resulting material (PCDF-NS) appears to have broken, micro-fibrous structure (Figure 2b). On the other hand, when the silica shell is used (whether metal-amine complexes are present or not), the carbon material shows more uniform fibrous structure after carbonization, and even after silica etching (Figure 2c and 2d). Moreover, the PCDF obtained by carbonization at 900 °C and removal of silica shells (PCDF-900) (Figure 2d) shows not only fibrous carbon nanostructures but also the highest surface area, among the materials we synthesized in this work (see Table 1 and details below). So, it can be said that the morphology of the materials vary according the specific synthetic conditions applied to make them, especially the final pyrolysis temperature and the presence or absence of silica coating around the precursors. While the pyrolysis temperature dictates the extent by which the precursor material ends up as the desired

carbon or graphitic material [21] and to what extent the materials shrinks, the silica shells protect the cellulose fibers from aggregating and uncontrollably growing into bulk materials during the pyrolysis steps.

Next, the materials were characterized by nitrogen (N_2) adsorption/desorption measurements. The N_2 adsorption/desorption isotherm of the PCDF-900 (Figure S2) shows a Type IV isotherm with an H2 type hysteresis loop, which is characteristic of mesoporous materials [37,38]. The BJH pore size distribution plot shows that the material has monodisperse pores with an average pore diameter of 4.4 nm. Furthermore, while the material synthesized at 700 °C (PDCF-700) has the smallest surface area ($220 \text{ m}^2 \text{ g}^{-1}$), the ones made at higher temperatures all have higher surface areas ($>450 \text{ m}^2/\text{g}$), whose values are close to one another (see Table 1). The reason for the lower surface area and lower porosity of PDCF-700 compared with the other materials is most likely because most of the hydrocarbon species from the precursor remain intact, or not released, during the carbonization of the precursor at 700 °C, whereas the opposite is true for the materials treated at pyrolysis temperatures higher than 700 °C. When it comes to pore sizes, PDCF-700 has bigger pores compared with the latter materials (Table 1); this is most likely because PDCF-700 undergoes less shrinkage due to the relatively lower pyrolysis temperature used to make it.

Surface chemical analysis of PCDF-900 was performed by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum shows the presence of C, N and O in the material (Figure 3a). The deconvoluted XPS spectrum for the C1s peak of PCDF-900 (Figure 3b) shows a strong C1s peak, which can be deconvoluted to three peaks corresponding to C=C-C (284.7 eV), C-O/C-N (286.1 eV), and C=O (287.5 eV) [1]. When also deconvoluted, the N1s peak shows a major peak at around 400.2 eV (Figure 3c) that can be attributed to pyrrolic/pyridone N moieties and another one at 401.1 eV

that can be attributed to graphitic-N species [6]. Additionally, the deconvoluted XPS peak for O1s (Figure 3d) reveals the presence of C=O (530.9 eV) and C-O (532.9 eV) species [18]. The peaks corresponding to C=O and C-O carbons are indicative of the presence of O-based functional groups in the materials. Signals corresponding to Fe2p and Si2p are also seen (Figure S9), but the peaks are very small, indicating that the amount of Fe in the PCDF materials is very small. The amount is also much lower than the original amount used along with the QFP for making the materials. So, the latter result suggests that most of the metallic species used for the synthesis of the material must have been removed upon treatment of the carbonized material with NaOH solution under hydrothermal condition.

3.2. Electrocatalytic Activities

The electrocatalytic activity toward HOR of the PCDF materials obtained at different pyrolysis temperatures and the three control materials was then investigated. Figure 4a shows the cyclic voltammograms (CV) of hydrazine oxidation over the materials in the presence of different concentrations of the hydrazine, ranging from 0 M to 50 mM, in PBS solution at pH = 7.4 in a potential range of -0.8 to 1.0 V at a scan rate of 10 mV s⁻¹. The peak current density is found to be directly proportional to the amount of hydrazine (or the degree of hydrazine oxidation) [21]. The results also show that PCDF-900's onset potential and peak potential are at -0.3 V and 0.1 V (versus SCE), respectively. These values are comparable to those of some of the best HOR electrocatalysts reported so far [6]. Figure 4b shows the CV obtained by setting the initial concentration of hydrazine as 50 mM in PBS solution at different scan rates, ranging between 10 and 100 mV s⁻¹, and the result is used to study the kinetics of the HOR over the PCDF materials. The peak current for the HOR is found to be directly

proportional to the square root of scan rate (Figure S3b), suggesting that the HOR over the PCDF materials is diffusion controlled [21]. Figure 4c shows the current density values of HOR at three different potentials over the PCDF materials prepared at different pyrolysis temperatures, and Figure 4d shows the peak potential and the current density at the peak potential for HOR over the PCDF materials prepared at the different pyrolysis temperatures. Based on these results, the most positive onset potential (highest overpotential) and the least peak current density are given by PCDF-1000, followed by PCDF-700, then PCDF-800, and finally PCDF-900 (Figures 4c, 4d and S4-S6). The results also indicate that PCDF-900's peak potential is close to 0 V and is the lowest negative onset potential (or least overpotential) of all the materials we have synthesized. The current density for HOR over PCDF-900 is also found to be the highest, with a value of 2.53 mA cm^{-2} at 0.06 V (*cf.* the corresponding values over PCDF-700, PCDF-800 and PCDF-1000 are 2.13, 2.05 and 1.76 mA cm^{-2} , respectively, at the same potential of 0.06 V).

Moreover, the electrocatalytic properties toward HOR of PCDF-900 is compared with other recently reported carbon materials made from different precursors in Table S1. Although precise comparison of the results in the table is not possible, due to the different experimental conditions employed in the different studies, the catalytic performance of PCDF-900 appears to be comparable to some of the best HOR electrocatalytic materials reported recently and better than several others.

When the total electron transfer number (n) in HOR over PCDF-900 is calculated using the Cottrell equation (see Experimental section), it is found to be around 4 [21], implying that the material essentially promotes a complete oxidation of hydrazine, in addition to giving good electrocatalytic activity. The value of electron transfer number is not exactly 4 (that is, the theoretically expected value for complete

HOR), because not all (100%) of the N₂H₄ can be converted to N₂, since some N₂H₂ intermediate species formed in the HOR reaction, as shown in Equations 1-3 below, can remain adsorbed on the surfaces of the carbon material or the electrocatalyst.

Moreover, the determination of electron transfer number is performed using peak-fitted equations (mainly, the Cottrell equation) on the experimental data obtained by chronoamperometry and cyclic voltammetry, and this also makes the number to deviate slightly from 4.

The stability of the catalyst was evaluated by chronoamperometry. As can be seen in the results in Figure S3 (Supporting Information), no significant change in the residual current density was observed after running the HOR over PCDF-90 for 1000 seconds, indicating that the carbon material we have synthesized and tested as electrocatalyst in our work is relatively stable during the HOR.

In order to further assess the interplay between of the metal-amine as well as the silica coatings around the QFP precursor versus the carbon materials' electrocatalytic performance toward HOR, experiments using the three control materials (PCDF/NFe, PCDF/NS and PCDF/Lit) as electrocatalysts were performed. The samples included the carbon material synthesized from QFP without iron (PCDF/NFe) and the carbon material synthesized without silica protection (PCDF/NS). Additionally, the electrocatalytic activity of the carbon material we named PCDF/Lit and we have

synthesized by following the literature procedure as reported in Yang et al. [28], or by
pyrolyzing QCF without silica protection at 900 °C, was also measured (Figure S8).

Before this though, the surface area and pore size of these control materials
were measured and compiled in Table 1. Their surface areas are generally lower than
the PCDF materials, especially those made at temperatures of 800 °C and above. Their
XPS spectra were also acquired, which showed that the materials are composed
exclusively of carbon and oxygen (Figures 5a-5c), but undetectable amounts of N and
Fe species (Figure S10-12) unlike PCDF-900, which showed XPS signals
corresponding to N species (Figure 3) as well as Fe species. The peaks for Fe species
can be deconvoluted to Fe 2p_{3/2} (712.1 eV) and Fe 2p_{1/2} (725.3 eV) (Figure S9) that can
be attributed to metallic, oxidized or carbidic iron species [16].

Figure 5d shows the comparison of the HOR electrocatalytic activity or current
density at various potentials of the different control materials with respect to that of
PCDF-900, and Figure S8 shows the comparison of the values of peak potential and
current density of PCDF-900 with respect to those of the control materials. The results
indicate that PCDF/NFe gives the lowest catalytic activity, with a peak potential at
0.445 V; followed by PCDF/Lit, with potential at 0.217 V; and finally by PCDF/NS,
with a peak potential at 0.258 V. However, the catalytic activity of all these three
materials is still smaller than that of the PCDF-900. This difference in the catalytic
activity between the three materials, or the low electrocatalytic activity of the control
materials compared with that of PCDF-900, can be accounted by the fact that: 1) the
surface area of the three control materials is significantly lower than that of PCDF-900
(Table 1) and 2) the amounts of N dopant and metal (Fe) impurity, which are often
responsible for carbon materials' electrocatalytic activity [21,24], are smaller in the
control materials than in PCDF-900 (Figures S9-S12).

Moreover, since both PCDF/NS (the material made from QFP with ferric chloride but no silica shell coating) and PCDF/NFe (the material made from QFP without ferric chloride but with silica coating) showed less electrocatalytic activity than PCDF-900, it can be inferred that both iron and silica may have directly or indirectly made PCDF-900's to have better electrocatalytic activity. The roles of the silica shells can be associated with their ability to serve as nanoreactors, trapping the volatile carbon species and increasing the local pressure inside as well as their ability to serve as template, helping the formation of large surface area carbon material [21]. The roles of iron species, on the other hand, can be associated with their ability to assist with the graphitization of the amorphous carbon, and thereby making the material better as electrocatalyst [21,39]. Fe(III) ions may have especially played such a role better, because when we tried Co(III) ions in our experiments in lieu of Fe(III), the results as a whole were not as good. Nevertheless, further studies may still be required to fully elucidate the exact mechanism by which the Fe(III) and silica shells dictate PCDFs' ability to catalyze HOR.

To get some more insights on what may be responsible for the electrocatalytic activity of the materials we have synthesized, the ratios of N/C and O/C were determined (Figure 6). As can be seen in the results, the N/C ratio tends to follow the same trend as the catalytic activity of the materials whereas the O/C atomic ratio does not. This is not surprising since most of the O atoms in heteroatom-doped carbon materials reside as substituent groups (*e.g.*, -COOH, C-OH, etc.) rather than as part of the carbon framework. On the other hand, N dopant atoms in such materials exist within the framework on the material by replacing the sp² carbon atoms in the material. Hence, the later is not able to modulate the electronic and conductive properties of the materials, which typically influence carbon nanomaterials' catalytic activities.

4. Conclusion

In summary, we have demonstrated that a simple qualitative filter paper (QFP) can be used as a precursor and a self-template to produce efficient noble-metal-free, nanoporous carbon-based electrocatalysts for hydrazine oxidation reaction (HOR). Notably, the filter paper's cellulose material and intertwined structure have been taken advantage of to serve as a precursor and a self-template, respectively, to form highly porous carbon materials that have structures suitable for electrocatalysis. The resulting carbon materials have been found to electrocatalyze HOR with a low overpotential and high current density. Temperature dependent studies has revealed that in particular the material obtained with a pyrolysis temperature of 900 °C gives the best electrocatalytic activity toward HOR compared with the ones obtained at 700, 800 and 1000 °C. Moreover, impregnation of Fe(III) ions and silica shell protection around the QFPs have made the material to have higher surface area, better structure, and higher electrocatalytic performance in the reaction. Compared with other materials reported previously, the carbon materials reported herein have shown either better or comparable catalytic activity, making them great candidates to serve as viable alternative catalytic materials to metal-based electrocatalysts commonly used in direct liquid fuel cells.

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Figure and Table Legends

Figure 1. Synthesis of cellulose filter paper-derived carbon electrocatalyst for hydrazine oxidation reaction. The synthesis involved coating of the cellulose filter paper with Fe-amine complexes, followed by silica shells, and then pyrolyzing the composite material and etching the silica off of the carbonized product.

Figure 2: Scanning electron microscopy (SEM) images of a) qualitative cellulose filter paper (QFP), b) PCDF/NS, c) PCDF/NFe and d) PCDF-900.

Figure 3. Chemical surface analysis of PCDF-900 material (electrocatalyst): a) XPS survey spectra, and peaks corresponding to b) C 1s, c) N 1s and d) O 1s peak.

Figure 4. Electrochemical and electrocatalytic properties of PDCFs: a) cyclic voltammograms for hydrazine oxidation with different concentration of hydrazine at a scan rate of 10 mV s^{-1} at pH 7.4 in 0.1 M PBS in presence of PCDF-900, b) cyclic voltammograms at different scan rates for 50 mM hydrazine at pH 7.4 in 0.1 M PBS solution in presence of PCDF-900, c) current density of HOR for 50 mM hydrazine in 0.1 M PBS at three different potentials in presence of the different PDCF materials prepared at different pyrolysis temperatures, and d) peak potential and current density at the peak potential during electrocatalysis of HOR of 50 mM hydrazine solution in 0.1 mM PBS in the presence of the different PDCF materials prepared at different pyrolysis temperatures.

Figure 5. Chemical surface analysis and electrocatalytic activity of the control materials: a) XPS spectrum of the control material PCDF/Lit, b) XPS spectra of the control material PCDF/NS, c) XPS spectrum of the control material PCDF/NFe, and d) comparison of the current density for 50 mM hydrazine in 0.1 M PBS at three different potentials over the control materials and PCDF-900.

Figure 6. N/C atomic ratio (a) and O/C atomic ratio (b) calculated from XPS results. The parameters for the line deconvolutions of the XPS have been done according to references found in the National Institute of Standards and Technology's (NIST's) database. Furthermore, the full width at half maximum (FWHM) of the deconvoluted peaks of each element in the samples was restricted to a distinct value higher than 0.85 eV (*i.e.*, the linewidth of the Al K α X-ray source), as observed in Table S1.

1 **Table 1.** Textural properties of the catalysts.

Carbon Material	Surface area (m ² g ⁻¹)	Pore size (Å)
PDCF-700	225	54.9
PDCF-800	451	41.4
PDCF-900	493	42.9
PDCF-1000	476	36.9
PDCF/NFe	283	39.4
PDCF/NS	248	35.3
PDCF/Lit	239	30.2

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Figure 1. Preparation of PCDF electrocatalyst by doping Fe-amine complexes and silica impregnation, followed by pyrolysis step and silica core shell etching.

Figure 2: Scanning electron microscopy (SEM) images of a) qualitative filter paper (QFP), b) PCFD/NS, c) PCFD/NFe and d) PCFD-900.

Figure 3

a)

b)

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Figure 4. Electrochemical and electrocatalytic properties of PDCFs: a) cyclic voltammograms for hydrazine oxidation with different concentration of hydrazine at a scan rate of 10 mV s⁻¹ at pH 7.4 in 0.1 M PBS in presence of PDCF-900, b) cyclic voltammograms at different scan rates for 50 mM hydrazine at pH 7.4 in 0.1 M PBS solution in presence of PDCF-900, c) current density of HOR for 50 mM hydrazine in 0.1 M PBS at three different potentials in presence of the different PDCF materials prepared at different pyrolysis temperatures, and d) peak potential and current density at the peak potential of HOR of 50 mM hydrazine solution in 0.1 mM PBS in the presence of the different PDCF materials prepared at different pyrolysis temperatures.

Figure 5

Figure 6. N/C atomic ratio (a) and O/C atomic ratio (b) calculated from XPS results.