Carbonization and Preparation of Nitrogen-Doped Porous Carbon Materials from Zn-MOF and Its Applications

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Abstract: Nitrogen-doped porous carbon (NPC) materials were successfully synthesized via a Zn-containing metal-organic framework (Zn-MOF). The resulting NPC materials are characterized using various physicochemical techniques which indicated that the NPC materials obtained at different carbonization temperatures exhibited different properties. Pristine MOF morphology and pore size are retained after carbonization at particular temperatures (600 °C-NPC 600 and 800 °C-NPC 800). NPC 800 material shows an excellent surface area 1192 m 2 /g, total pore volume 0.92 cm 3 /g and displays a higher CO 2 uptake 4.71 mmol/g at 273 k and 1 bar. Furthermore, NPC 600 material displays good electrochemical sensing towards H 2 O 2 . Under optimized conditions, our sensor exhibited a wide linearity range between 100 µM and 10 mM with a detection limit of 27.5 µM.

Keywords: metal-organic framework; nitrogen-doped porous carbon; carbonization; tuning pore size; CO 2 capture; H 2 O 2 electrochemical sensor

1. Introduction

Porous carbon materials have been regarded as significant porous materials because of their distinctive properties such as pore size, extraordinary surface area and good electrochemical activities [1–3]. They have extensive applications in many fields including catalysis, biosensors, fuel cells and supercapacitors [4–11]. In this sense, 3D porous carbon-based structures are promising to numerous applications, such as contamination removal, gas sorption/separation, and electrode materials [2,12,13]. In particular, CO 2 capture purpose nitrogen-doped porous carbon (NPC) materials were used, because of its stability, low cost and performance [14,15]. For CO 2 capture, the pore size of porous material plays a significant role, ultramicropores of ~4 Å to ~8 Å are predominantly suitable for CO 2 sorption [16,17]. The preparation of porous carbon materials has been synthesized in a known way such as template and activation method [18,19]. Generally, template progression devours a larger quantity of organic or inorganic template and the synthesizing processes are complicated. Activation methods such as KOH and NaOH can afford a high surface area but needed a huge amount of activation agents. To avoid such complication, recently metal-organic framework (MOF) materials have gained tremendous attentions to prepare the porous carbon materials through single step carbonization method. For instance, the recently reported porous carbon material derived from Zn-MOF, having ultramicropore size (~4 Å to ~8 Å) showed excellent CO 2 capture properties [20]. Since MOFs have gained tremendous attention due to their diverse structures with tunable pore shapes, sizes, volumes, and surface chemistry. Therefore, MOFs have prospective applications in gas storage/separation,
electronic devices, chemical sensors, catalysis, and biomedical applications [21–26]. The multifunctional MOFs are often chosen to synthesize porous carbon materials; MOF-templated straightforward synthesis provided the high-quality nanoporous carbon with a well-ordered pore size and significant surface area. The morphology of nanoporous carbon can be tuned by optimizing the carbonization method (such as temperature, time, and atmosphere) [1,27,28]. Recently, MOF-derived metal/metal oxide embedded porous carbon materials [29,30] are used in the electrodes for electrochemical sensors [31,32]. But, maintaining the pristine MOF morphology of the resulting porous materials from the carbonization process is a difficult task due to the shrinkage of framework/decomposing organic ligand during carbonization, therefore, a systematic study is necessary [33].

Additionally, hydrogen peroxide (H$_2$O$_2$) is a toxic oxidizing agent, being used in various fields such as biomedical science, environmental science, food, textile and chemical industries [34–36]. Therefore, H$_2$O$_2$ determination is of practical importance for both environmental and industrial purposes. It has been well established that Zn based material modified electrodes are used for H$_2$O$_2$ detection [37,38].

Therefore, herein, we reported the preparation of NPC materials from {Zn$_2$(BDC)$_2$(DABCO)} (Zn-MOF) [11] at various temperatures under a N$_2$ atmosphere (Scheme 1). The properties of the resulting NPC materials such as morphology, pore size, pore-volume, CO$_2$ uptake and H$_2$O$_2$ electrochemical sensing were investigated.

**Scheme 1.** Synthesizing pathway of NPC materials from Zn-MOF.

2. Methods

2.1. Materials

Zn(NO$_3$)$_2$·6H$_2$O, (98%) and H$_2$BDC, (98%) were bought from Sigma-Aldrich (Burlington, MA, USA), DMF, (≥99.8%) was purchased from Merck (Darmstdt, Germany), (DABCO, 98%) was purchased from Alfa Aesar (Lancashire, UK). All other compounds used throughout this study were of an analytical grade. The electrochemical experiments were performed using a three-electrode system-CHI model 824B workstation with a screen printed carbon electrode (SPCE)/chemically modified SPCE as a working electrode, Ag/AgCl (in 3 M KCl) as a reference electrode, and Pt wire as an auxiliary electrode. SPCE was purchased from Zensor R&D (Taichung, Taiwan). A phosphate buffer solution (0.1 M, pH 7 PBS) was prepared by mixing 0.1 M, NaH$_2$PO$_4$, and Na$_2$HPO$_4$. To compare the various electrodes performance, 5 mM of FeCN solution used as a probe. Briefly, the FeCN solution was prepared using...
5 mM of K₃[Fe(CN)₆] and K₄[Fe(CN)₆], and 0.1 M KCl used as a supporting electrolyte. For H₂O₂
detection, 100 mM of H₂O₂ prepared from 9.8 M of H₂O₂ (30 wt%).

2.2. Preparation of Zn-MOF, [Zn₂(BDC)₂(DABCO)]

The Zn-MOF was prepared [39] by, a mixture of Zn(NO₃)₂·6H₂O (5.41 mmol, 1.609 g), H₂BDC (5 mmol, 0.83 g), DABCO (2.5 mmol, 0.28 g) in DMF (60 mL) was taken out into a Teflon-lined
autoclave and heated to 120 °C, 2 days later cooling down to room temperature. The Zn-MOF was
washed with DMF and dried at room temperature overnight. Further this material was used for the
carbonization process.

2.3. Preparation of NPC Materials

The NPC materials were prepared through a single-step carbonization method [31]. The 0.400 g
of Zn-MOF was transferred into a silica crucible boat and then placed in a furnace chamber. The NPC
materials obtained at target temperatures (500, 550, 600, 700, 800, or 900 °C) under an N₂ atmosphere
for a 5 h duration. The resulting materials obtained at 500, 550, 600, 700, 800, and 900 °C are assigned
as NPC₅₀₀, NPC₅₅₀, NPC₆₀₀, NPC₇₀₀, NPC₈₀₀ and NPC₉₀₀ respectively.

2.4. Electrode Preparation

Prior to electrode modification, the bare SPCE was precleaned electrochemically by potential
cycling between −1 and +1 V vs. Ag/AgCl for 6 cycles in 0.1 M pH 7 PBS. NPC₇ modified SPCE
(SPCE/NPC₇) was prepared by the following procedure: 10 µL of 2000 ppm (2 mg mL⁻¹) respective
NPC₇ dispersed in acetonitrile suspension was drop coated on precleaned SPCE, and allowed for
dry on the hot plate at 40 °C for 15 min. The NPC₇ prepared by carbonization under the increasing
temperature of 500, 550, 600, 700, 800 and 900 °C. The corresponding modified electrode designated as
SPCE/NPC₅₀₀, SPCE/NPC₅₅₀, SPCE/NPC₆₀₀, SPCE/NPC₇₀₀, SPCE/NPC₈₀₀, SPCE/NPC₉₀₀, respectively.

2.5. Characterization

The purity of MOF and NPC materials were investigated by powder x-ray diffraction (PXRD)
using a Bruker D8 advance instrument (Billerica, MA, USA) equipped with CuKα radiation (λ = 1.54178
Å). The morphology of MOF and NPC materials were observed by high-resolution scanning electron
microscopy (HR-SEM, JEOL JEM-7600F instrument, Akishima, Japan). The NPC materials morphology
was characterized by transmission electron microscopy (TEM, using a JEM-2010 instrument, Tokyo,
Japan) at a voltage of 200 KV. The synthesized NPC materials were also recorded with a Raman spectra
on a CCD detector (Stanford Computer Optics Inc., Berkeley, CA, USA) using a He-Ne laser with an
excitation wavelength of 632.8 nm. The Zn element presence was investigated by inductively coupled
plasma-mass spectrometry (ICP-MS, Japan Agilent 7500ce, Tokyo, Japan). The elemental analysis (C,
N, O) was executed by an elementar vario EL III CHN-OS elemental analyzer (Germany). N₂ gas
adsorption, CO₂ gas adsorption of all materials were measured using micrometrics (Norcross, GA,
USA) and the gas sorption analysis purpose, the materials were dried at 120 °C for 12 h under vacuum.

3. Results and Discussion

3.1. Structure, Morphology, and Composition of NPC Materials

Synthesized Zn-MOF structure and porous properties was checked by PXRD, SEM and N₂ gas
sorption measurements (Figure 1a–d). As expected, the synthesized MOF showed a well-defined
crystallinity and surface area of 1700 m²/g, and good agreement with the literature [40]. The pore
size of Zn-MOF was calculated by the NLDFT method, it reveals two micropores (0.75 and 1.4 nm)
(Figure 1d). The SEM images revealed the particle shapes of Zn-MOF was a mixture of the cube, brick,
and rod-like shapes (Figure 2c).
The MOF was further exploited to a one-step direct carbonization method to produce the NPC materials. The detailed preparation method is given in Section 2.3. The morphology, crystallinity and surface area of NPC materials were examined by PXRD, SEM, TEM, Raman analysis, \textit{N}_2 gas sorption isotherms, ICP-MS, and elemental analysis.

The PXRD patterns of the NPC\textsubscript{500–700} samples showed the diffraction peaks for the formation of ZnO nanoparticle (Figure 2a). The \(2\theta\) peaks at 31.7 (100), 34.4 (002), 36.2 (101), 47.4 (102), 56.6 (110), 62.9 (103), 65.5 (200), 68.0 (112) and 69.1 (201) that are lattice planes of ZnO \cite{41}. The NPC\textsubscript{500}, NPC\textsubscript{550}, NPC\textsubscript{700} morphologies show the shrinking phenomenon of Zn-MOF during carbonization at this particular temperature (Figures S1 and S2). While the morphology retained from pristine MOF, brick, and rod shape at 600 \(^\circ\)C (Figure 2d,e and Figure S3). The PXRD pattern of the NPC\textsubscript{800} sample showed two broad peaks of graphitic carbon at 23 (002) and 44\(^\circ\) (101) (Figure 2b) \cite{7}. The absence of ZnO at higher carbonization temperature revealed when the temperature is close to its boiling point of ZnO (907 \(^\circ\)C) is reduced to Zn and evaporate.

Furthermore, the SEM revealed the morphology partially retained the pristine MOF with distorted graphitic carbon structures (Figure 2f,g and Figure S4), TEM images noticeably show the presence of an abundant interconnected and oriented multilayer graphene domains can be observed (Figure 3a,b). Further, by increasing the temperature to 900 \(^\circ\)C, the PXRD pattern indicated a mixture of graphite oxide (GO) and graphitic carbon. A broad peak at 20 \(\cong\)12 (0 0 1) the reflection of graphite oxide, 23\(^\circ\) and 44\(^\circ\) crystallographic planes of graphitic carbon, which possess the amorphous carbon structure. SEM (Figure 2h and Figure S5) and TEM (Figure 3c,d) images (900 \(^\circ\)C) shown are revealed the pristine MOFs have fully or partially cracked the shapes and the shrinkage of the whole framework.
Figure 2. (a,b) PXRD patterns NPC samples. SEM images of, (c) synthesized Zn-MOF at the 1 µm scale (before carbonization), (d–h) Zn-MOF after carbonization at different temperature. (d) NPC600 at the 1 µm scale, (e) NPC600 at the 100 nm scale, (f) NPC800 at the 10 µm scale, (g) NPC800 at the 1 µm scale and (h) NPC900 at the 1 µm scale.

Further, synthesized NPC materials were characterized by Raman spectroscopy for the degree of graphitization. The spectrum analyzed range between 1200 cm\(^{-1}\) to 1700 cm\(^{-1}\) bands were fitted with the spectra, 1180 cm\(^{-1}\) (\(A_1\) band), 1340 cm\(^{-1}\) (\(D\) band), and 1600 cm\(^{-1}\) (\(G\) band) [42]. Figure S6 shows significantly broadened \(D\) and \(G\) bands. Gaussian fitting was used to separate the \(A_1\), \(D\), \(G\) band and fitted after baseline subtraction. The \(I_D/I_G\) ratio increased while increasing the temperature, indicating the formation of disorder with a low degree of graphitization of NPC materials was obtained. The \(I_D/I_G\) ratio between \(D\) and \(G\) bands revealed the degree of graphitization in carbon-related materials. Temperature 500–700 °C carbonized materials obtained a higher degree of graphitization, due to the ZnO present in the carbon material. Because there is still a definite chemical interaction between ZnO and N atoms, the redshifts of the \(D\) bands by approximately 15 cm\(^{-1}\) to \(\approx1326\) were observed [43]. Further, as we increased the temperature (800 and 900 °C), ZnO-N adducts were not detected and were also evidenced by PXRD. As the ratio is higher, it could be a low degree of graphitization, particularly those materials carbonized at \(\geq800\) °C (see Table 1). The G band shifted to higher frequencies by approximately 6 cm\(^{-1}\) due to the nitrogen present in the NPC materials [44]. Chemical compositions of NPC were studied by ICP-MS and elemental analysis (Figure S7). The zinc contents were investigated by ICP-MS, increasing carbonization temperature results the decreasing zinc percentage are 51.7% (600 °C), 43.72% (700 °C), 4.95% (800 °C), 0.26% (900 °C) and an appreciable amount of nitrogen (1.96–2.98 wt%) based on elemental analysis.
The surface area and total pore volume of the NPC materials were evaluated by the N\textsubscript{2} sorption analyzer. The Figure 4a–c represented the N\textsubscript{2} uptake isotherm and corresponding pore sizes of the NPC materials. Table 1 represents the NPC material’s surface area, pore volume and pore size. The N\textsubscript{2} sorption curves of the NPC materials possess type-I isotherms that steeply climb in the low-pressure range (P/P\textsubscript{0} = 0–0.10), suggesting that micropores were dominant [45]. In the high-pressure range (P/P\textsubscript{0} = 0.40–1.00), there were decent increases in the adsorption in all samples and a slight hysteresis loop between the sorption curves, which revealed that mesopores were also present in the materials. The surface area and total pore volume of the NPC\textsubscript{500–700} materials is nearly equal to 273, 287, 289, 296 m\textsuperscript{2}/g and 0.18, 0.20, 0.22, 0.22 cm\textsuperscript{3}/g correspondingly (see Table 1).

### Table 1. Surface and porous properties of the NPC samples.

| Sample     | I\textsubscript{D}/I\textsubscript{G} | \(S\textsubscript{BET}\) \(^a\) (m\textsuperscript{2}/g) | \(V\textsubscript{total}\) \(^b\) (cm\textsuperscript{3}/g) | \(V\textsubscript{micro}\) \(^c\) (cm\textsuperscript{3}/g) | Pore Size (nm) | \(\text{CO}_2\) uptake \(^d\) (mmol/g) (wt %) |
|------------|-----------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|---------------|-----------------------------------------------|
| NPC\textsubscript{500} | 0.92                             | 273                                             | 0.18                                            | 0.09 (50)                                        | 0.75, 1.4, 2.1–3 | 2.85 (12.54)                                  |
| NPC\textsubscript{550} | 0.98                             | 287                                             | 0.20                                            | 0.091 (45)                                       | 0.75, 1.4, 2.1–3 | 1.20 (5.28)                                  |
| NPC\textsubscript{600} | 1.01                             | 289                                             | 0.22                                            | 0.094 (42)                                       | 0.75, 1.4, 2.1–3 | 1.24 (5.46)                                  |
| NPC\textsubscript{700} | 1.07                             | 296                                             | 0.22                                            | 0.10 (45)                                        | 0.89, 1.4, 2.1–3 | 1.71 (7.52)                                  |
| NPC\textsubscript{800} | 1.24                             | 1192                                            | 0.92                                            | 0.39 (42)                                        | 0.75, 1.4, 2.1–3 | 4.71 (20.72)                                 |
| NPC\textsubscript{900} | 1.25                             | 303                                             | 0.45                                            | 0.06 (13)                                        | 1.4, 5–10      | 2.51 (11.04)                                 |

\(^a\) \(S\textsubscript{BET}\) surface area was examined in the P/P\textsubscript{0} range of 0.01 to 0.1, which gave the best linearity. \(^b\) Total pore volume at P/P\textsubscript{0} = 0.99. \(^c\) Micropore volume (≤ 2 nm) and the values in asides are the percentage of the micropore volume relative to the total pore volume (\(V\textsubscript{micro}/V\textsubscript{total}\)). \(^d\) \(\text{CO}_2\) uptake at 273 K and 1 bar and the values in asides are weight percentage (wt%).

### 3.2 Porous Property and \(\text{CO}_2\) Uptake of NPC Materials

The textural properties of these NPC materials were evaluated by the N\textsubscript{2} sorption analyzer. The Figure 4a–c represented the N\textsubscript{2} uptake isotherm and corresponding pore sizes of the NPC materials. Table 1 represents the NPC material’s surface area, pore volume and pore size. The N\textsubscript{2} sorption curves of the NPC materials possess type-I isotherms that steeply climb in the low-pressure range (P/P\textsubscript{0} = 0–0.10), suggesting that micropores were dominant [45]. In the high-pressure range (P/P\textsubscript{0} = 0.40–1.00), there were decent increases in the adsorption in all samples and a slight hysteresis loop between the sorption curves, which revealed that mesopores were also present in the materials. The surface area and total pore volume of the NPC\textsubscript{500–700} materials is nearly equal to 273, 287, 289, 296 m\textsuperscript{2}/g and 0.18, 0.20, 0.22, 0.22 cm\textsuperscript{3}/g correspondingly (see Table 1).
while the relative current change (Figure 4c), while there are mesopores around 2.1–3 nm, which specifies the occurrence of mesopores in the NPC materials (Figures S8–S13). While the NPC900 materials show a lesser surface area (303 m$^2$/g), pore volume (0.45 cm$^3$/g) indicates framework shrinkage and fragmentation throughout the high-temperature carbonization process. The total pore volume of NPC800 material has a better percentage than the NPC500–700 and NPC900 materials. It is noted that the NPC800 material reached 42% of micropores, whereas, the percentage of $V_{\text{micro}}/V_{\text{total}}$ decreased significantly to 13% in the NPC900 sample. CO$_2$ sorption is investigated for the NPC materials at 273 K at 1 bar (Figure 4d). NPC800 demonstrated a higher CO$_2$ capture of 4.71 mmol/g than NPC500 (2.85 mmol/g), NPC550 (1.20 mmol/g), NPC600 (1.24 mmol/g), NPC700 (1.71 mmol/g) and NPC900 (2.51 mmol/g) at 273 K and 1 bar. Such a micro-mesoporous structure of NPC800 material provides a fast diffusion of CO$_2$ into the inner pores material. NPC800 material showed CO$_2$ capacity value closely matches/ greater than those of the carbon-related materials (see Table S1).

3.3. Comparisons Voltammetric Behavior of Various SPCE/NPC Modified Electrode in FeCN

CV analysis was executed to study the electrochemical behavior of SPCE and SPCE/NPC$_T$ modified electrodes in 5 mM FeCN under a potential window from $-0.2$ to $+0.6$ V. As can be seen in Figure 5, bare SPCE exhibit a well-defined reversible redox peak at $E^o = +193$ mV with a peak to peak potential difference ($\Delta E_p = E_{pa} - E_{pc}$) value of 126 mV, which is the characteristic peak for Fe$^{2+}$/Fe$^{3+}$ interconversion [46,47]. After SPCE/NPC$_T$ modification, relatively higher/lower redox current responses were noticed with a $\Delta E_p$ value of about 561, 235, 125, 112, 137 and 140 mV, while the relative current change ($\Delta I$) was recorded for SPCE/NPC$_{500}$, SPCE/NPC$_{550}$, SPCE/NPC$_{600}$, SPCE/NPC$_{700}$, SPCE/NPC$_{800}$, SPCE/NPC$_{900}$ of about $-99$, $-88$, $-29$, $-12$, $+83$ and $+113$ $\mu$A, respectively.

Figure 4. (a,b) N$_2$ sorption analysis at 77 K, (c) NLDFT pore size distribution profile and (d) CO$_2$ sorption isotherm at 273 K and 1 bar of NPC materials.
The observation is due to the semiconductor Zn moieties existing up to a carbonization temperature of 700 °C that results in a decrease in FeCN signal. In contrary, carbonization at 800 and 900 °C produced relatively smaller Zn moieties with NPC and hence an increase in signal. This result suggests that the semiconductor Zn content decreased with increasing carbonization temperature. In other words, the FeCN current response is inversely proportional to the Zn content. The obtained results coincide with the elemental analysis, ICP-MS and PXRD results.

Figure 5. Cyclic voltammetric response of SPCE and SPCE/NPC\textsubscript{T} in 5 mM ferric cyanide solution.

3.4. Detection of H\textsubscript{2}O\textsubscript{2} at SPCE/NPC\textsubscript{T}

The surface area and porous defective sites have an important role in the electrochemical sensors. Therefore, H\textsubscript{2}O\textsubscript{2} sensing applicability was tested for SPCE/NPC\textsubscript{500}, SPCE/NPC\textsubscript{550}, SPCE/NPC\textsubscript{600}, SPCE/NPC\textsubscript{700}, SPCE/NPC\textsubscript{800}, SPCE/NPC\textsubscript{900}, respectively. Figure 6 shows electro catalytic reduction CVs of H\textsubscript{2}O\textsubscript{2} at various SPCE/NPC\textsubscript{T} electrodes. CV measurements were done in 0.1 M, pH 7.4 PB solution under the potential sweeping from 0 to −1.2 V at a scan rate of 100 mV s\textsuperscript{−1}. During the cathodic segment, H\textsubscript{2}O\textsubscript{2} reduction peak [48] was noticed at ~−0.7 V for SPCE and for SPCE/NPC\textsubscript{T} the same reduction peak was noticed with lower over potential (~−0.4 V). Among the various electrodes, detection response are clearer and more explicit at SPCE/NPC\textsubscript{600}. These results evidently exposed that the SPCE/NPC600 electrode exhibited better electrocatalytic H\textsubscript{2}O\textsubscript{2} reduction than other electrodes. Therefore, SPCE/NPC\textsubscript{600} was chosen for further studies.
evidently exposed that the SPCE/NPC600 electrode exhibited better electrocatalytic $\text{H}_2\text{O}_2$ reduction than other electrodes. Therefore, SPCE/NPC600 was chosen for further studies.

**Figure 6.** Cyclic voltammetric detection of $\text{H}_2\text{O}_2$ in 0.1 M, pH 7PB (a) SPCE, (b) SPCE/NPC$_{500}$, (c) SPCE/NPC$_{550}$, (d) SPCE/NPC$_{600}$, (e) SPCE/NPC$_{700}$, (f) SPCE/NPC$_{800}$ and (g) SPCE/NPC$_{900}$, respectively. (h) Their corresponding current verses concentration plots.

### 3.5. Flow Injection Analysis (FIA) Detection of $\text{H}_2\text{O}_2$ at SPCE/NPC$_{600}$

The above observation was further utilized for amperometric FIA analysis of $\text{H}_2\text{O}_2$. The $\text{H}_2\text{O}_2$ reduction current increased linearly with increasing concentration, in which $\text{H}_2\text{O}_2$ was electrochemically reduced at $-0.4$ V by applying a potential, and thus yielded quantitative current responses corresponding to the content of $\text{H}_2\text{O}_2$ (Figure 7). A wide linearity range between 100 µM and 10 mM with a $R^2$ value of 0.9865 and a limit of detection (LOD) 27.5 µM were obtained. In order to access the repeatability of a SPCE/NPC$_{600}$ modified electrode, 12 repeated injections of 0.5 mM $\text{H}_2\text{O}_2$ were performed and a RSD value of 4.13% was obtained. Compared to a few other Zn based $\text{H}_2\text{O}_2$ sensors (Table S2), the present method exhibited a wide linear range along with a specific sensitivity of 108.7 µA mM$^{-1}$ cm$^{-2}$. 
Author Contributions: K.S. and C.-H.L. conceived and designed the experiments; K.S. and M.T. performed the porous properties where characterized by PXRD, SEM, TEM, Raman spectroscopy, ICP-MS, elemental analysis, and 77 K N₂ sorption isotherms. Pristine MOF pore size was tuned to the porous carbon material, such as a unique ultramicropore, micropore, and mesopore combined in unique material and interaction between ZnO to NPC to give the pathway to synthesize the effective electrochemical property and CO₂ sorption materials. These combinations in NPC₆₀₀ exhibited a higher CO₂ uptake of 4.71 mmol g⁻¹ compare to other NPC₇ materials. NPC₆₀₀ displayed a good electrochemical reduction towards H₂O₂. Under optimal conditions, our sensor exhibited linearity that ranged from 0.1–10 mM, which confirmed its sensitive response to H₂O₂ over a wide range of concentrations. The detection limit was determined to be 27.5 µM (S/N = 3).

4. Conclusions

Herein, we reported the synthesized NPC materials at various carbonization temperatures at a constant time under a N₂ atmosphere. NPC materials surface, morphology, chemical composition, porous properties where characterized by PXRD, SEM, TEM, Raman spectroscopy, ICP-MS, elemental analysis, and 77 K N₂ sorption isotherms. Pristine MOF pore size was tuned to the porous carbon material, such as a unique ultramicropore, micropore, and mesopore combined in unique material and interaction between ZnO to NPC to give the pathway to synthesize the effective electrochemical property and CO₂ sorption materials. These combinations in NPC₆₀₀ exhibited a higher CO₂ uptake of 4.71 mmol g⁻¹ compare to other NPC₇ materials. NPC₆₀₀ displayed a good electrochemical reduction towards H₂O₂. Under optimal conditions, our sensor exhibited linearity that ranged from 0.1–10 mM, which confirmed its sensitive response to H₂O₂ over a wide range of concentrations. The detection limit was determined to be 27.5 µM (S/N = 3)

Supplementary Materials: The following are available online at http://www.mdpi.com/xxx/s1,
Figure S1. SEM image of (a) NPC₅₀₀ and (b) NPC₅₅₀. Figure S2. SEM image of NPC₇₀₀ (a,b). Figure S3. SEM images of NPC₆₀₀ (a–d). Figure S4. SEM image of NPC₆₀₀ (a–d). Figure S5. SEM image of NPC₉₀₀ (a–d). Figure S6. Raman spectra of the obtained NPC materials. (a) NPC₅₀₀, (b) NPC₅₅₀, (c) NPC₆₀₀, (d) NPC₇₀₀, (e) NPC₉₀₀ and (f) NPC₉₀₀. Figure S7. Relative atom percentage at different carbonization temperature (600–900 °C). Figure S8. NLDFT pore size distribution profile for NPC₅₀₀. Figure S9. NLDFT pore size distribution profile for NPC₅₅₀. Figure S10. NLDFT pore size distribution profile for NPC₆₀₀. Figure S11. NLDFT pore size distribution profile for NPC₇₀₀. Figure S12. NLDFT pore size distribution profile for NPC₉₀₀. Figure S13. NLDFT pore size distribution profile for NPC₉₀₀. Table S1. Comparison of CO₂ uptake with previously reported carbon related materials and MOF-derived carbon materials at temperature 273K in 1 bar. Table S2. Comparison of Zn electrode-based H₂O₂ sensors with previously reported ZnO/carbon related materials.

Author Contributions: K.S. and C.-H.L. conceived and designed the experiments; K.S. and M.T. performed the experiments, analyzed the data; K.S., M.T., and S.P. wrote the paper; C.-H.L. contributed reagents/materials/analysis tools. All authors have read and agreed to the published version of the manuscript.

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Figure 7. (a) Detection of H₂O₂ by FIA method at SPCE/NPC₆₀₀, (b) FIA responses of 12 continuous injections of 0.5 mM H₂O₂.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Jiang, H.L.; Liu, B.; Lan, Y.Q.; Kuratani, K.; Akita, T.; Shioyama, H.; Zong, F.Q.; Xu, Q. From Metal-Organic Framework to Nanoporous Carbon: Toward a Very High Surface Area and Hydrogen Uptake. *J. Am. Chem. Soc.* 2011, 133, 11854–11857. [CrossRef] [PubMed]

2. Yang, S.J.; Kim, T.; Im, J.H.; Kim, Y.S.; Lee, K.; Jung, H.; Park, C.R. MOF-Derived Hierarchically Porous Carbon with Exceptional Porosity and Hydrogen Storage Capacity. *Chem. Mater.* 2012, 24, 464–470. [CrossRef]

3. Khan, I.A.; Badshah, A.; Khan, I.; Zhao, D.; Nadeem, M.A. Soft-template carbonization approach of MOF-5 to mesoporous carbon nanospheres as excellent electrode materials for supercapacitor. *Microporous Mesoporous Mater.* 2017, 253, 169–176. [CrossRef]

4. Chaikittisilp, W.; Ariga, K.; Yamauchi, Y. A new family of carbon materials: Synthesis of MOF-derived nanoporous carbons and their promising applications. *J. Mater. Chem. A* 2013, 1, 14–19. [CrossRef]

5. Ling, P.; Hao, Q.; Lei, J.; Ju, H. Porphyrin functionalized porous carbon derived from metal–organic framework as a biomimetic catalyst for electrochemical biosensing. *J. Mater. Chem. B* 2015, 3, 1335–1341. [CrossRef]

6. Proietti, E.; Jaouen, F.; Lefevre, M.; Larouche, N.; Tian, J.; Herranz, J.; Dodelet, J.P. Iron-based cathode catalyst with enhanced power density in polymer electrolyte membrane fuel cells. *Nat. Commun.* 2011, 2, 416. [CrossRef]

7. Liu, B.; Shioyama, H.; Jiang, H.; Zhang, X.; Xu, Q. Metal-organic framework (MOF) as a template for syntheses of nanoporous carbons as electrode materials for supercapacitor. *Carbon* 2010, 48, 456–463. [CrossRef]

8. Khan, I.A.; Badshah, A.; Nadeem, M.A.; Haider, N.; Nadeem, M.A. A copper based metal-organic framework as single source for the synthesis of electrode materials for high-performance supercapacitors and glucose sensing applications. *Int. J. Hydrog. Energy* 2014, 39, 19609–19620. [CrossRef]

9. Khan, I.A.; Qian, Y.; Badshah, A.; Nadeem, M.A.; Zhao, D. Highly Porous Carbon Derived from MOF-5 as a Support of ORR Electrocatalysts for Fuel Cells. *ACS Appl. Mater. Interf.* 2016, 8, 17268–17275. [CrossRef]

10. Khan, I.A.; Badshah, A.; Nadeem, M.A. Single step pyrolytic conversion of zeolitic imidazolate to CoO encapsulated N-doped carbon nanotubes as an efficient oxygen reduction electrocatalyst. *Catal. Commun.* 2017, 99, 10–14. [CrossRef]

11. Wang, L.; Xu, Q.; Xu, J.; Weng, J. Synthesis of hybrid nanocomposites of ZIF-8 with two-dimensional black phosphorus for photocatalysis. *RSC Adv.* 2016, 6, 69033–69039. [CrossRef]

12. Wei, X.; Zhang, Z.; Qiu, L.; Dai, J. Template-free preparation of yeast-derived three-dimensional hierarchical porous carbon for highly efficient sulfamethazine adsorption from water. *J. Taiwan Inst. Chem. E* 2018. [CrossRef]

13. Wei, L.; Tian, K.; Jin, Y.; Zhang, X.; Guo, X. Three-dimensional porous hollow microspheres of activated carbon for high-performance electrical double-layer capacitors. *Microporous Mesoporous Mater.* 2016, 227, 210–218. [CrossRef]

14. Li, Y.; Xu, R.; Wang, X.; Wang, B.; Cao, J.; Yang, J.; Wei, J. Waste wool derived nitrogen-doped hierarchical porous carbon for selective CO2 capture. *RSC Adv.* 2018, 8, 19818–19826. [CrossRef]

15. Estevez, L.; Barpaga, D.; Zheng, J.; Sabale, S.; Patel, R.L.; Zhang, J.-G.; McGrail, B.P.; Motkuri, R.K. Hierarchically Porous Carbon Materials for CO2 Capture: The Role of Pore Structure. *Ind. Eng. Chem. Res.* 2018, 57, 1262–1268. [CrossRef]

16. Zhang, Y.; Li, B.; Williams, K.; Gao, W.Y.; Ma, S. A new microporous carbon material synthesized via thermolysis of a porous aromatic framework embedded with an extra carbon source for low-pressure CO2 uptake. *Chem. Commun.* 2013, 49, 10269–10271. [CrossRef]

17. Oschatz, M.; Antonietti, M. A search for selectivity to enable CO2 capture with porous adsorbents. *Energy Environ. Sci.* 2018, 11, 57–70. [CrossRef]

18. Liu, J.; Wang, X.; Gao, J.; Zhang, Y.; Lu, Q.; Liu, M. Hollow porous carbon spheres with hierarchical nanoarchitecture for application of the high performance supercapacitors. *Electrochim. Acta* 2016, 211, 183–192. [CrossRef]

19. Geng, W.; Ma, F.; Wu, G.; Song, S.; Wan, J.; Ma, D. MgO-templated hierarchical porous carbon sheets derived from coal tar pitch for supercapacitors. *Electrochim. Acta* 2016, 191, 854–863. [CrossRef]
20. Kim, H.R.; Yoon, T.-U.; Kim, S.-I.; An, J.; Bae, Y.-S.; Lee, C.Y. Beyond pristine MOFs: Carbon dioxide capture by metal–organic frameworks (MOFs)-derived porous carbon materials. *RSC Adv.* 2017, 7, 1266–1270. [CrossRef]

21. He, Y.; Chen, F.; Li, B.; Qian, G.; Zhou, W.; Chen, B. Porous metal–organic frameworks for fuel storage. *Coord. Chem. Rev.* 2018, 373, 167–198. [CrossRef]

22. Lin, R.-B.; Xiang, S.; Xing, H.; Zhou, W.; Chen, B. Exploration of porous metal–organic frameworks for gas separation and purification. *Coord. Chem. Rev.* 2019, 378, 87–103. [CrossRef]

23. Du, W.; Bai, Y.-L.; Xu, J.; Zhao, H.; Zhang, L.; Li, X.; Zhang, J. Advanced metal–organic frameworks (MOFs) and their derived electrode materials for supercapacitors. *J. Power Sources* 2018, 402, 281–295. [CrossRef]

24. Wen, Y.; Zhang, J.; Xu, Q.; Wu, X.-T.; Zhu, Q.-L. Pore surface engineering of metal–organic frameworks for heterogeneous catalysis. *Coord. Chem. Rev.* 2018, 376, 248–276. [CrossRef]

25. Müller-Buschbaum, K.; Beuerle, F.; Feldmann, C. MOF based luminescence tuning and chemical/physical sensing. *Microporous Mesoporous Mater.* 2015, 216, 171–199. [CrossRef]

26. Nadar, S.S.; Rathod, V.K. Magnetic-metal organic framework (magnetic-MOF): A novel platform for enzyme immobilization and nanozyme applications. *Int. J. Biol. Macromol.* 2018. [CrossRef]

27. Torad, N.L.; Hu, M.; Kamachi, Y.; Takai, K.; Imura, M.; Naito, M.; Yamauchi, Y. Facile synthesis of nanoporous carbons with controlled particle sizes by direct carbonization of monodispersed ZIF-8 crystals. *Chem. Commun.* 2013, 49, 2521–2523. [CrossRef]

28. Aijaz, A.; Sun, J.K.; Pachfule, P.; Uchida, T.; Xu, Q. From a metal–organic framework to hierarchical high surface-area hollow octahedral carbon cages. *Chem. Commun.* 2015, 51, 13945–13948. [CrossRef]

29. Chen, J.J.; Chen, Y.T.; Senthil Raja, D.; Kang, Y.H.; Tseng, P.C.; Lin, C.H. Carbonization and oxidation of metal–organic frameworks based on 1,4-naphthalene dicarboxylates. *Sci. Technol. Adv. Mater.* 2015, 16. [CrossRef]

30. Chen, J.J.; Chen, Y.T.; Raja, D.S.; Kang, Y.H.; Tseng, P.C.; Lin, C.H. Metal-Organic Frameworks to Metal/Metal Oxide Embedded Carbon Matrix: Synthesis, Characterization and Gas Sorption Properties. *Materials* 2015, 8, 5336–5347. [CrossRef]

31. Sivasankar, K.; Devasenathipathy, R.; Wang, S.-F.; Kohila rani. K.; Raja, D.S.; Lin, C.-H. Synthesis of hierarchical mesoporous graphite oxide/Al2O3 from MIL-100(Al) for the electrochemical determination of caffeic acid in red wine samples. *J. Taiwan Inst. Chem. E* 2018, 84, 188–195. [CrossRef]

32. Sivasankar, K.; Rani, K.K.; Wang, S.F.; Devasenathipathy, R.; Lin, C.H. Copper Nanoparticle and Nitrogen Doped Graphite Oxide Based Biosensor for the Sensitive Determination of Glucose. *Nanomaterials* 2018, 8, 429. [CrossRef] [PubMed]

33. Song, Y.; Cho, D.; Venkateswarlu, S.; Yoon, M. Systematic study on preparation of copper nanoparticle embedded porous carbon by carbonization of metal–organic framework for enzymatic glucose sensor. *RSC Adv.* 2017, 7, 10592–10600. [CrossRef]

34. Bai, Z.; Dong, W.; Ren, Y.; Zhang, C.; Chen, Q. Preparation of Nano Au and Pt Alloy Microspheres Decorated with Reduced Graphene Oxide for Nonenzymatic Hydrogen Peroxide Sensing. *Langmuir* 2018, 34, 2235–2244. [CrossRef] [PubMed]

35. Selvaraj, B.; Jen-Lin, C.; Jyh-Myng, Z. Extremely Stable Copper—Polymelamine Composite Material for Amperometric Hydrogen Peroxide Sensing. *J. Polym. Sci.* 2013, 51, 1639–1646. [CrossRef]

36. Qinglin, S.; Xiujuan, Q.; Jianbin, Z. The Hybrid of Gold Nanoparticles and 3D Flower-like MnO2 Nanostructure with Enhanced Activity for Detection of Hydrogen Peroxide. *Electroanalysis* 2018, 30, 137–145. [CrossRef]

37. Wang, J.; Xu, M.; Zhao, R.; Chen, G. A highly sensitive H2O2 sensor based on zinc oxide nanorod arrays film sensing interface. *Analyst* 2010, 135, 1992–1996. [CrossRef]

38. Al-Hardan, N.H.; Abdul Hamid, M.A.; Shamsudin, R.; Othman, N.K.; Kar Keng, L. Amperometric Non-Enzymatic Hydrogen Peroxide Sensor Based on Aligned Zinc Oxide Nanorods. *Sensors* 2016, 16, 1004. [CrossRef]

39. Chaemchuen, S.; Zhou, K.; Kabir, N.A.; Chen, Y.; Ke, X.; Van Tendeloo, G.; Verpoort, F. Tuning metal sites of DABCO MOF for gas purification at ambient conditions. *Microporous Mesoporous Mater.* 2015, 201, 277–285. [CrossRef]

40. Qadir, N.U.; Said, S.A.M.; Bahaidarah, H.M. Structural stability of metal organic frameworks in aqueous media—Controlling factors and methods to improve hydrostability and hydrothermal cyclic stability. *Microporous Mesoporous Mater.* 2015, 201, 61–90. [CrossRef]
41. Tarlani, A.; Fallah, M.; Lotfi, B.; Khazraei, A.; Golsanamlou, S.; Muzart, J.; Mirza-Aghayan, M. New ZnO nanostructures as non-enzymatic glucose biosensors. *Biosens. Bioelectron.* 2015, 67, 601–607. [CrossRef] [PubMed]
42. Gong, Y.-T.; Li, B.-H.; Pei, T.; Lin, C.-H.; Lee, S. Raman investigation on carbonization process of metal-organic frameworks. *J. Raman Spectrosc.* 2016, 47, 1271–1275. [CrossRef]
43. Gadipelli, S.; Guo, Z.X. Tuning of ZIF-Derived Carbon with High Activity, Nitrogen Functionality, and Yield—A Case for Superior CO₂ Capture. *ChemSusChem* 2015, 8, 2123–2132. [CrossRef] [PubMed]
44. Zhang, C.; Fu, L.; Liu, N.; Liu, M.; Wang, Y.; Liu, Z. Synthesis of nitrogen-doped graphene using embedded carbon and nitrogen sources. *Adv. Mater.* 2011, 23, 1020–1024. [CrossRef]
45. Gomez-Gualdron, D.A.; Moghadam, P.Z.; Hupp, J.T.; Farha, O.K.; Snurr, R.Q. Application of Consistency Criteria to Calculate BET Areas of Micro- and Mesoporous Metal-Organic Frameworks. *J. Am. Chem. Soc.* 2016, 138, 215–224. [CrossRef]
46. Thiruppathi, M.; Thiyagarajan, N.; Gopinathan, M.; Chang, J.-L.; Zen, J.-M. A dually functional 4-aminophenylboronic acid dimer for voltammetric detection of hypochlorite, glucose and fructose. *Microchim. Acta* 2017, 184, 4073–4080. [CrossRef]
47. Zen, J.-M.; Tsai, D.-M.; Senthil Kumar, A. Flow Injection Analysis of Ascorbic Acid in Real Samples Using a Highly Stable Chemically Modified Screen-Printed Electrode. *Electroanalysis* 2003, 15, 1171–1176. [CrossRef]
48. Thiruppathi, M.; Lin, P.-Y.; Chou, Y.-T.; Ho, H.-Y.; Wu, L.-C.; Ho, J.-A.A. Simple aminophenol-based electrochemical probes for non-enzymatic, dual amperometric detection of NADH and hydrogen peroxide. *Talanta* 2019, 200, 450–457. [CrossRef]

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