From Biomimetic Mineralization to Carbonization: Fabricating Heterostructured Porous Carbon Materials with MOF Encapsulated Bacteria

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ABSTRACT: Hierarchical porous carbons (HPCs) hold great promise in energy-related applications owing to their excellent chemical stability and well-developed porous structures. Attention has been drawn toward developing new synthetic strategies and precursor materials that permit greater control over composition, size, morphology, and pore structure. There is a growing trend of employing metal-organic frameworks (MOFs) as HPC precursors as their highly customizable characteristics favor new HPC syntheses. In this article, we report a biomimetically grown bacteria-templated MOF synthesis where the bacteria not only facilitates the formation of MOF nanocrystals, but also provides morphology and porosity control. The resultant HPCs show improved electrochemical capacity behavior compared to pristine MOF derived HPCs. Considering the broad availability of bacteria and ease of its production, in addition to significantly improved MOF growth efficiency on bacterial templates, we believe that bacteria-templated MOF is a promising strategy to produce a new generation of HPCs.

Introduction

Hierarchical porous carbons (HPC) are a class of materials that are fabricated to reach high surface area, multi-scale porosity, heteroatom doping, excellent conductivity, and outstanding stability—characteristics that are highly sought after in adsorbents, catalysis, energy conversion and energy storage.¹⁻⁷ Conventional fabrications of HPCs rely on utilizing synthetic inorganic/organic templates or chemical activation that generally require multiple steps beginning with template syntheses, followed by precursor infiltration, carbonization, and template removal to generate the desired heterogenous porosity.^{1-3,8} These tedious synthetic processes inevitably increase the complexity and cost of HPC preparation thus hindering the eventual mass production and commercialization of such promising materials. Over the previous two decades, metal organic frameworks (MOFs) have become a popular architecture for advanced materials owing to their highly customizable pore structure, composition, and straight forward synthetic strategies.⁹⁻¹¹ MOFs are also recognized as promising precursors for porous carbons. Because of their characteristic

porous nature as well as high carbon content, MOFs enable one-step conversion to porous carbons possessing high surface area with an inner-connected porous architecture.¹²⁻¹⁷

Scheme 1. Schematic illustration of various bacteria shapes and assemblies.

In recent years, templated MOF synthesis with biologically derived substrates has begun producing an ever-growing array of bio-MOF composites featuring morphology and size that are dictated, in part, by the underlying biological material used. In addition to potential benefits such as environmental friendliness, low cost, and high efficiency,¹⁸⁻²⁷ the available biomass to template MOF syntheses is extraordinarily—viruses^{22-23, 28} and yeast^{20-21, 27} have already been shown to be outstanding templates to produce core-shell systems—and researchers have only begun to explore the potential uses of biomass as homogenous and low-cost templates for new MOF architectures. Bacteria's high reproduction rate and natural abundance, make it an ideal source of cheap precursor materials—indeed our body contains at least three times more bacterial cells than human cells! In addition to its ubiquity, the diversity of shapes and assemblies (Scheme 1) can provide multiple morphological templates for biomimetic MOF syntheses.

Scheme 2. Schematic illustration of synthetic processes of CEZ8 HPC (top) and CZ8 HPC (bottom), which used *E.coli*@ZIF-8 composite and pristine ZIF-8 as precursors, respectively.

Herein, we report a bio-inspired preparation of MOF-derived HPCs driven by a robust bacterial template. A non-pathogenic non-toxic laboratory strain of *Escherichia coli* was employed to construct a thin crystalline shell of zeolitic imidazolate framework-8 (ZIF-8), a widely used MOF carbonization precursor owing to its extraordinary high surface area and stability.¹¹ Interestingly, the resultant *E.coli*@ZIF-8 (EZ8) composite possess not only well-defined micropores, but also mesopores and macropores that can be attributed to the disturbed crystal growth on the cell membrane. As anticipated, this pore hierarchy can be retained after carbonization of EZ8. The as-obtained carbonized EZ8 (CEZ8) is considerably more mesoporous compared to its parent material. The electrochemical characteristics of CEZ8 were tested in a standard three-electrode system, and we observed superior specific capacity compared to carbonized pristine ZIF-8 (denoted as CZ8).

Results & Discussion

Preparation of *E. coli*@ZIF-8 (EZ8)

The CEZ8 HPC was produced from core-shell structured EZ8 composite precursor, which was fabricated using direct bio-mimetic template methods that we and others have developed. This new approach differs from previous efforts to grow ZIF-8 on bacteria²⁷ in a number of important ways. In particular, the synthesis yields *E.coli*@ZIF-8 with a more homogeneous surface and thinner ZIF-8 shell (Figure 1a and c). Furthermore, our one-pot synthesis procedure is fast (30 minutes) and works at ambient conditions in a purely aqueous system without methanolic solvent, which can cause cell lysis and the breakdown of the bacteria. In a typical synthesis, purified *E. coli* (1 mg) was mixed with an aliquot of 2-methylimidazole (HMIM) aqueous solution (1600 mM) followed by an aliquot of zinc acetate aqueous solution (20 mM). The mixture was shaken for 20 s and left on the benchtop for 30 min. The as-formed EZ8 was collected by centrifugation at 4300 ×g then washed twice with ultrapure water. As shown in Figure 1, EZ8 retains the rod-like morphology of bacteria (Figure 1a), and the light/dark contrast in TEM micrograph clearly illustrates the core-shell structure (Figure 1c). High magnification TEM micrograph (Figure S1a) illustrates clearly that the shells are composed of closely packed nanocrystals. To analyze crystallinity and phase purity, EZ8 dry powder was analyzed by

powder X-ray diffraction (PXRD) (Figure 2a), and the result shows the pure sodalite crystalline phase of ZIF-8.

Figure 1. SEM micrographs of a) uncarbonized EZ8 and b) the carbonized CEZ8; TEM micrographs of c) EZ8 and d) CEZ8.

A nitrogen sorption isotherm was collected at 77 K to obtain the specific surface area and pore size distribution of EZ8 and pristine ZIF-8, as shown in Figure S3. The as-prepared pristine ZIF-8 possesses a typical type I isotherm with a sharp uptake at low relative pressure (< 0.03), indicating the presence of micropores (Figure S3a); however, in addition to the similar microporous pattern, EZ8 also contains a H3 hysteresis loop at relative pressure of 0.45 to 1.0, which typically indicates capillary condensation of adsorbate (N₂) in mesopores. The calculated BET surface area of ZIF-8 and EZ-8 are 1842 and 1209 m²/g, respectively. As shown in Figure S3b, the pore distribution analysis uncovered two intense peaks at 10.8 Å in both ZIF-8 and EZ8, while a series of lower peaks in the mesopore range (2 – 50 nm) indicate hierarchical pore characteristics in EZ8. We attributed the presence of mesopores to crystalline defects arising from the drastic crystallization on the surface of bacterial cell membranes, and we anticipated that the mesoporous characteristics of the shell can be retained after carbonization.

Figure 2. a) Powder X-ray diffraction patterns of EZ8 and CEZ8; b) Raman spectra of CZ8 and CEZ8.

Figure 3. a) N₂ sorption analysis of CZ8 and CEZ8; b) porosity distribution of CZ8 and CEZ8.

Preparation of carbonized *E. coli*@ZIF-8 (CEZ8)

The carbonization was carried out with by temperature-programed pyrolysis for both EZ8 and ZIF-8. Materials were dried at 120 °C under dynamic vacuum overnight prior to pyrolysis in a tube furnace with a nitrogen atmosphere. The temperature was raised with a 5 °C/min ramp to 350 °C and kept at 350 °C for 2 h. We utilized this process to ablate bacterial matter without impacting the stability of the ZIF-8 shells, owing to the large thermal stability differences between *E. coli* and ZIF-8 as revealed by TGA (Figure S4). Following bacterial template ablation, the furnace was thermally ramped to 800 °C with the same rate and kept at 800 °C for 4 h. The carbonized products appeared as black powder and were washed with 2 M HCl and 10% HF, respectively, to remove residual zinc in the products. The carbonized *E.coli*@ZIF-8, denoted as CEZ8, retained rod-like morphology of EZ8, though a certain level of shrinkage (Figure 1b) was observed. TEM (Figure 1d) revealed an enhanced transparency at the inner part of CEZ8 rods. The hollowness of these rod-like structures indicates the ablation of the bacterial template. At high magnification in the TEM (Figure S1b), we observed a large number of high contrast dots on the surface of the CEZ8 rods, which can be attributed to defects or nanopores that were generated during carbonization. These observations are consistent with the hysteresis loop in the N₂ sorption isotherm (Figure 3a) and pore analysis that shows peaks in the mesoporous range (Figure 3b). The microstructure of carbonized materials was characterized by PXRD (Figure 2a). Both CEZ8 and CZ8 only contain a broad peak at about 25°, which can be attributed to the (002) peak of graphitic carbon. The content of graphitic carbon in comparison to amorphous carbon was revealed by Raman spectroscopy (Figure 2b), and the I_D/I_G values were calculated as 1.07 for CEZ8 and 1.45 for CZ8, indicating that *E.coli*@ZIF-8 composite can produce higher content of graphitic carbon than pristine ZIF-8.

Electrochemical Characterization

Owing to its high content of graphitic carbon and well-developed hierarchical porosity, we were encouraged to investigate the electrochemical properties of CEZ8 in energy storage. Therefore, a standard three electrode cell with Ag/AgCl and platinum mesh as reference electrode and counter electrode, 6 M KOH aqueous solution as electrolyte, was carried out to evaluate the capacitive behavior of CEZ8, and CZ8 as comparison. Cyclic voltammograms (Figure 4a and b) were recorded with the voltage window from -0.6 to 0.2 V, and

specific capacitance was calculated accordingly, as illustrated in Figure 4c and Table S1. We found that CZ8 contained the typical rectangular CV of electrostatic double-layer capacitors whereas the CV of CEZ8 appears to show pseudocapacitance from the carbonized bacteria substrate.²⁹ The highest specific capacitance of CEZ8 and CZ8 were obtained as 163 and 87 F/g, at scan rate of 5 mV/s, indicating a superior capacitive behavior of CEZ8. Though CEZ8 contains a lower specific surface area comparing to CZ8 (645 m²/g vs. 841 m²/g), the superior performance is attributed to its hierarchical porosity, in particular the high content of mesopores as well as its higher content graphitic carbon, which greatly improves the ion transfer efficiency. Moreover, both CEZ8 and CZ8 show excellent cyclability as they demonstrate 94.5% and 95% retention after 2000 cycles (Figure 4d), which we ascribe to their robust structural stability.

Figure 4. Cyclic voltammograms at different sweep rates of a) CZ8 and b) CEZ8; c) specific capacitance as a function of scan rate for CZ8 and CEZ8; d) cycling stability of CZ8 and CEZ8.

Conclusions

In this work, we demonstrated a new strategy to prepare hierarchical porous carbons via a straightforward and convenient biomimetic mineralization of ZIF-8 using non-pathogenic and non-toxic bacterial cells. We found that bacterial cell surfaces efficiently nucleate the rapid crystallization of ZIF-8, which produces a crystalline shell that can be carbonized into a material possessing a hierarchy of porosities. The bacterial template is thermally ablated during carbonization and contributes to a higher level of graphitization of the ZIF-8 shell during pyrolysis. The as-prepared CEZ8 possesses superior capacitive performance than carbonized pristine ZIF-8 owing to its high specific surface area, excellent conductivity, and well-developed hierarchical porosity. We believe that the size and morphological diversity of bacteria and their high reproduction rate means they hold great promise in templating and fabricating hierarchical porous carbon materials.

ASSOCIATED CONTENT

Supporting Information

Experimental procedure, characterization techniques and additional characterization results are available in supplemented file.

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