

# Fabrication of nitrogen and sulfur co-doped hollow cellular carbon nanocapsules as efficient electrode materials for energy storage



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## ARTICLE INFO

### Keywords:

Metal–organic frameworks  
Nanocapsules  
Carbons  
Doping  
Supercapacitors

## ABSTRACT

Hierarchical hollow carbon materials are attracting considerable attention because of their unique structural characteristics, extraordinary electrical and thermal properties. Here, we present the fabrication of N and S co-doped hollow cellular carbon nanocapsules with high surface area and pore volume from a metal–organic framework composite by a facile external template-free method. The unique nanocapsules feature large internal hollow cores, hierarchical porous cellular shells with ultrathin walls of a few nanometers thickness, and uniform N and S co-doping, which enable an efficient supercapacitor behavior by enhancing the diffusion of electrolyte ions and providing large accessible active surface. The combination of the optimal pore structure and surface functionality of the resulting materials affords an excellent capacitive performance with high specific capacitances and energy densities in both aqueous and non-aqueous media.

## 1. Introduction

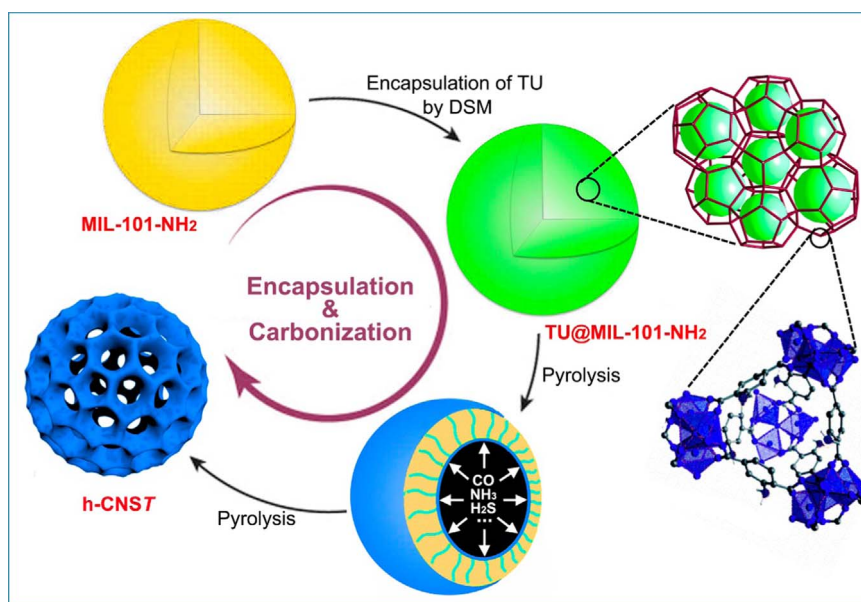
Development of open porous carbon nanostructures with controllable morphology and functionality is of great significance for their promising electrochemical applications [1–5]. Hollow carbon nanocapsules (HCNCs), emerging as a new class of porous carbon materials, could be superior to their conventional counterparts in some aspects due to their fascinating features such as high porosity, encapsulation ability, improved permeability, and excellent chemical and thermal stabilities [6–15]. Taking advantage of these great advances, HCNCs could be utilized as a promising electrode materials of supercapacitors for energy storage, where both the hollow macroporous cavities and the mesopores of the shells can act as ion-buffering reservoirs and minimize the diffusion distance for the electrolyte ions to the micropores in the shells, resulting the outstanding high-rate capacitive performance [13–15]. Traditional synthesis of HCNCs usually involves the use of either hard or soft external templates as well as complex synthetic procedures [6,9,10]; however, the facile and external template-free methods are still lacking [16,17]. Besides, the shells of most HCNCs reported previously are nonporous or microporous, which

significantly limits the utilization of their internal matrix.

Metal–organic frameworks (MOFs), which are constructed from metal ions (or clusters) and organic ligands, are known as a class of the most prospective crystalline porous materials with tunable compositions and diverse structural topologies [18–24]. By virtue of their structural features, MOFs can act as outstanding starting materials to strategically create various functional nanostructures via a pyrolysis process [25–29]. Owing to the large specific surface areas, adjustable pore structures and abundant functionality of the MOF-derived nanostructures, they have a wide range of applications in supercapacitors, batteries, fuel cells, heterogeneous catalysis, gas storage, and so on [30–49]. However, the thermal conversion of MOFs is commonly accompanied by a partial or complete collapse of their original morphologies due to the high pyrolysis temperatures. Very recently, some impressive MOF-derived nanostructures with controllable morphologies and corresponding enhanced performance have been reported [24,50–60]. Particularly, the synthesis of hollow carbon spheres with micropore-dominated shells has been accomplished by templated thermal activation of the core–shell MOFs [61–64]. However, the efficiency of mass transport through the porous struc-

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**Scheme 1.** Schematic representation of the encapsulation of TU into MIL-101-NH<sub>2</sub> by DSM and subsequent formation of the N and S co-doped hollow cellular carbon nanocapsules (h-CNST).

tures is quite restricted by the type and diameter of the pores. Consequently, the integration of the hollow cores and the hierarchical porous shells may create more advantages for a wider range of applications of the hollow carbon nanocapsules through the collective behavior, which is still a great challenge.

In this work, we report the synthesis of N and S co-doped hollow cellular carbon nanocapsules from a MOF composite by a facile external template-free method, which have high surface area and hierarchical pore distribution (Scheme 1). The simple pyrolysis of the MOF encapsulated with thiourea (TU) generates the unique carbon nanostructure, where TU dispersed in the pores of the MOF not only acts as the heteroatom source to achieve the homogeneous doping of N and S within the carbon matrix but also serves as structure-directing agent to regulate the in situ generation of the large internal void spaces and the porous cellular shells. Different from those reported previously, this is the first example of the hollow carbon nanocapsules having cellular shells and hierarchical macro/meso/micro multimodal porosities, which would greatly improve the charge transfer and offer more accessible surface for supercapacitor. The combination of the unique hierarchical structure and the synergetic effect between the heteroatoms renders the resulting carbon materials ideal for supercapacitor electrodes with high specific capacitance, excellent rate capability and long-term stability in both aqueous and non-aqueous media.

## 2. Results and discussion

The N and S co-doped hollow cellular carbon nanocapsules were constructed from a MOF composite by carbonization under an inert atmosphere (Scheme 1). By introducing the TU molecules into the pores of an aluminum-based MOF (i.e., MIL-101-NH<sub>2</sub> [65]), which possesses high surface area (2987 m<sup>2</sup> g<sup>-1</sup>) and large pore volume (1.825 cm<sup>3</sup> g<sup>-1</sup>) and can be very facilely and economically synthesized in high yield and large scale, via a double-solvent method (DSM) [66,67], the heteroatom-rich TU@MIL-101-NH<sub>2</sub> composite with quantitative TU loading within the hydrophilic MOF pores was obtained. The scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD) results show that the introduction of TU into the pores did not disturb the structural integrity of MIL-101-NH<sub>2</sub> (Figs. S1 and S2). The prominent decreases in surface area and pore volume further testify the encapsulation of the TU molecules in the MOF pores (Fig. S3 and Table S1). Of particular interest is that the direct pyrolysis of the TU@MIL-

101-NH<sub>2</sub> composite in inert atmosphere resulted in carbonization, affording the intriguing hollow cellular carbon nanocapsules with uniform N and S co-doping, labelled as h-CNST (where *T* is the pyrolysis temperature). We believe that the high dispersion of the guest precursors inside the MOF pores played significant roles in producing such unique hierarchical architectures and promoting the uniform incorporation of the heteroatoms. By contrast, the carbonization of MIL-101-NH<sub>2</sub> and its mixture with TU only led to the dense carbon structures of CNS900 and C900, respectively (*vide infra*). The formation principle of the hollow cellular nanocapsule structure of h-CNS900 could be attributed to the hypothesis that upon the pyrolysis, the plentiful and rapidly expanding N- and S-containing gases (e.g., NH<sub>3</sub>, H<sub>2</sub>S, H<sub>2</sub>CO, CS<sub>2</sub> and HSCN) released from the decomposition of the filled TU cause the substantial internal stresses and strains, which expand the MOF framework to form the hollow core and the porous cellular shell structures (Fig. 1a).

The intriguing hollow cellular nanocapsule architecture of the as-synthesized h-CNS900, which was unexpectedly obtained without using any additional external template, was revealed by SEM and transmission electron microscopy (TEM) analyses. The SEM images show that the material has a mean spherical diameter of ~ 350 nm (Fig. 1a and S4), consistent with particle size of the parent MOF. As shown in the inset of Fig. 1a, a typical broken nanocapsule clearly reveals its hollow nature and the cellular channels arranged radially from the hollow core to the surface. Close observation of the cellular texture at a higher magnification shows that the nanoscale cells are highly interconnected through the ultrathin cellular walls with a thickness of few nanometers (Fig. S4b). According to the nitrogen sorption results (*vide infra*), the cellular walls contain a high density of micro- and mesopores, which can be easily reached for the electrolyte ions through the short-penetrating paths. The hollow cellular structure of the nanocapsules was further evidenced by the TEM and high-annular dark-field scanning TEM (HAADF-STEM) measurements (Fig. 1b–f and S5–S7). The hollow size of the nanocapsules is estimated to be ~ 150 nm, while the shell thickness is ~ 100 nm. The radially oriented macro-/mesopore structure can also be observed from the TEM and HAADF-STEM images (Fig. 1c,e). Energy-dispersive X-ray spectroscopy (EDX) measurement and elemental mapping demonstrate that the hollow cellular carbon nanocapsules contain uniformly distributed C, N, O and S elements (Fig. 1e,f and S5), indicating the successful doping of N and S atoms in the carbon matrix. The similar hollow cellular nanocapsule structures were also found in the carbon

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