Biological cell template synthesis of nitrogen-doped porous hollow carbon spheres/MnO$_2$ composites for high-performance asymmetric supercapacitors

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**Abstract**

Nitrogen-doped porous hollow carbon spheres were fabricated via hydrothermal pre-carbonization and pyrolysis carbonization using yeast cell templates. After that, the MnO$_2$ nanowires were deposited by the in-situ hydrothermal reaction. By controlling the reaction concentration, various MnO$_2$ nanostructures with different morphologies and electrochemical properties were obtained. The as-prepared sample exhibited an ultrahigh specific capacitance of 255 F g$^{-1}$ at a current density 1 A g$^{-1}$ in 1 M Na$_2$SO$_4$ electrolyte. The MnO$_2$/HCS-30 material was used as the positive electrode, and the HCS was used as the negative electrode to assemble the asymmetric supercapacitor. The maximum energy density operating at the 2.0 V voltage window is 41.4 Wh kg$^{-1}$ at a power density of 500 W kg$^{-1}$ and still maintains 23.0 Wh kg$^{-1}$ at a power density of 7901 W kg$^{-1}$. Moreover, it displayed excellent cycle stability, retained approximately 93.9% of the capacitance after 5000 cycles. This work innovatively combines biomass and energy, provides an environmentally benign strategy and new insights for the preparation of electrode materials.

**Keywords:** Asymmetric supercapacitor; Biological cell template; Carbon material; Manganese dioxide; Composite

1. Introduction

Nowadays, the exploration and utilization of renewable and sustainable energy sources such as hydropower, wind energy, tidal energy, electrochemical energy, and solar energy are greatly relieving the heavy burdens on current energy and environmental issues [1–16]. However, since the aforementioned readily available and sufficient energy sources are intermittent in nature, it is extremely urgent to develop stable electrochemical energy storage (EES) systems (such as fuel cells, supercapacitors, and rechargeable batteries) to promote the effective use of these renewable power sources [17,18]. Among these EES systems, supercapacitors have become more appealing due to their exclusive characteristics such as high power density ($>10$ kW kg$^{-1}$), long-term cycling stability ($>100$ 000 cycles), and low maintenance cost [19–21]. Asymmetric supercapacitor (ASC) has a higher energy density because the complementary potential range extends the operating voltage window to give more and more applications [22].

For ASC devices, selecting/designing material systems combining all the advantages of each material component are considered as an ingenious approach [23]. MnO$_2$ is a typical transition-metal oxide which has been widely used as a positive electrode material due to its abundant reserves, low toxicity and high theoretical specific capacitance (1370 F g$^{-1}$) [24]. The mechanism of MnO$_2$ pseudocapacitive behavior can be attributed to the single-electron transfer of Mn$^{4+}$/Mn$^{3+}$ redox system [25]. The development of MnO$_2$-based electrodes is still hindered by some inherent drawbacks, including low ionic diffusion constant ($10^{-3}$...
cm² V⁻¹ s⁻¹), poor conductivity (10⁻⁵ to 10⁻⁶ S cm⁻¹) and large volume variations which make it difficult to achieve satisfying energy storage performance [26]. Therefore, integrating MnO₂ with high conductive substrate has been devoted to improve the energy storage performance [27]. For example, many research groups combined MnO₂ with carbon-based materials (such as active carbon, carbon fibers, graphene, nanotubes and carbon fibers) and other metal oxide materials (such as NiO, Co₃O₄, NiO/Ni(OH)₂ and TiO₂) [28–30]. Among these carbon-based materials, hollow carbon spheres have received special attention due to their unique spatial morphology, high chemical and thermal stability, large voids and high specific surface area [28]. In addition, it is worth mentioning that heteroatom-doped (N, O, B and P) carbon spheres can induce the surface faradic reactions by increasing the charge mobility of negative charges on the surface of carbon material, meanwhile, high performance and long cycle life are maintained [31]. Combining the advantages of nitrogen doping and hollow carbon spheres, we have been inspired to use yeast cells as biological templates to prepare electrode materials with unique structures and environmental friendliness for superior energy storage.

Yeast cells are common unicellular microorganisms with a spherical shape, and are widely used in wine, food, medicine, feed, cosmetics and other fields [32]. In recent years, the annual production of yeast has exceeded 3 million tons with the increase in the connection between the yeast industry and human life [33–35]. It is worth noting that the yeast-rich eutrophic wastewater is becoming an inevitable problem affecting the development of the fermentation industry [36]. With the exploration of organic wastewater separation technology (such as membrane separation, chemical precipitation, concentration and centrifugation, etc.), the ingenious combination of yeast wastewater and new energy is a sensible way to solve environmental pollution while developing new types of energy storage materials [37]. The treated yeast formed a carbon sphere material having an amorphous structure, a hollow porous morphology and self-doping of heteroatoms [38–42]. However, its application for supercapacitor electrode has not been studied and its practical applications as a two-electrode electrode has not been reported yet.

In this work, yeast cells were selected as biological templates to synthesize nitrogen-doped porous hollow carbon spheres. Yeast templates are known to be inexpensive and easy to produce, and the numerous functional groups on the cell membrane make them possible to be used as templates [43]. Based on these, the MnO₂/nitrogen-doped porous hollow carbon sphere composites were synthesized by in-situ hydrothermal deposition. The specific capacitance reached 255 F g⁻¹ at the current density of 1 A g⁻¹ in a three-electrode system. For ASC, the maximum energy density operating at the 2.0 V voltage window is 41.4 Wh kg⁻¹ at a power density of 500 W kg⁻¹ and still maintains 23.0 Wh kg⁻¹ at a power density of 7901 W kg⁻¹. In addition, it is worth mentioning that the prepared electrode material is prepared from a renewable biological template under an environment-friendly atmosphere, which represents a simple, low-cost and green storage device production route.

2. Experimental section

2.1. Materials

The yeast powder was purchased from Angel Yeast Co., Ltd., China. All chemical reagents, including glucose, potassium permanganate (KMnO₄), glutaraldehyde (50%) and ethanol are analytical grade.

2.2. Synthesis of nitrogen-doped porous hollow carbon spheres

Nitrogen doped porous hollow carbon spheres were synthesized by a modified method according to the literature [40]. Briefly, the yeast powder (1 g) was firstly incubated in 0.2 M glucose aqueous solution at a constant temperature of 38 °C for 30 min in order to activate and disperse yeast. Then the activated yeast was washed with deionized (DI) water and ethanol. Subsequently, the washed yeast cells were dispersed in 60 ml 5% glutaraldehyde aqueous solution by sonication. In the hydrothermal pre-carbonization process, the above solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 5 h. The resulting product was vacuum filtered, washed three times with DI water and ethanol, and thoroughly dried at 60 °C to obtain a brown powder. Finally, the dried brown powder was carbonized at 850 °C for 2 h under nitrogen flow (200 mL min⁻¹) with a heating rate of 5 °C min⁻¹ to synthesize hollow carbon spheres. The resultant sample was named as HCS.

2.3. Synthesis of MnO₂/N-porous hollow carbon spheres

A simple one-step hydrothermal method was used to prepare the MnO₂/carbon sphere hollow structure. Firstly, 60 mg as-prepared HCS was ultrasonically dispersed in 40 mL of 20 mM KMnO₄ aqueous solution. Then, this aqueous solution was transferred to a Teflon-lined stainless-steel autoclave and heated at 160 °C for 3 h. The reaction in the hydrothermal process is as follows [25]:

\[
4\text{KMnO}_4 + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{K}_2\text{CO}_3 + 2\text{KHCO}_3
\]

After the reaction, the Teflon autoclave was cooled down to room temperature. The product was vacuum filtered, washed three times with DI water and ethanol, and thoroughly dried in an oven at 60 °C. The product was labeled as MnO₂/HCS-20. In the subsequent experiments, the products obtained with different reaction concentrations of KMnO₄ were labeled as MnO₂/HCS-30, MnO₂/HCS-40, respectively. The flow chart of the sample synthesis process was illustrated in Fig. 1.

2.4. Materials charaterizations

Scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (HRTEM, JEM-2100, Japan) were used to characterize the structures and morphologies. X-ray diffraction (XRD) measurement was carried out by an X-ray diffractometer (Shimadzu-7000X, Japan) with Cu Kα radiation operated at 40 kV and 30 mA. Raman spectra were collected on Raman spectrometer (Thermo Nicolet NEXUS 670, USA) using 532 nm laser excitation. Fourier transformation infrared (FT-IR) spectra of the samples were measured from KBr sample pellets on a
Shimadzu IR Prestige-21 (Japan). The thermogravimetric analyses (TGA) were performed on a thermogravimetric analyzer (Netzsch STA449 F3, Germany) at a heating rate of 10 °C min⁻¹ under air atmosphere (air flow rate: 200 mL min⁻¹, sample mass: 10 mg). Nitrogen adsorption–desorption and pore size distributions were conducted by physisorption analyzer (Micromeritics ASAP 2020, USA) at 77 K. The surface elemental spectra were acquired by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi, USA) with Al Kα radiation used as the excitation source.

2.5. Electrochemical measurements

The electrochemical properties of the prepared electrodes were tested in 1 M Na₂SO₄ electrolyte using a three-electrode system. The nickel foam (1 × 2 cm²) containing active material, acetylene black and polyvinylidene fluoride (PVDF) (8:1:1 wt.%) was used as the working electrode. The active material coating on nickel foam is approximately 3 mg. The platinum plate and saturated calomel (SCE) were used as the counter electrode and reference electrode, respectively. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were measured by a CHI 660E (Shanghai) electrochemical workstation. EIS measurements were performed with a frequency range from 100 kHz to 0.01 Hz at an open circuit voltage.

2.6. Assembly of ASC device and electrochemical measurements

The ASC device was assembled by using MnO₂/HCS-30 as the positive electrode. HCS as the negative electrode and Na₂SO₄ as the electrolyte. The positive and negative electrodes were prepared as described in Section 2.5. The mass loading rate of the positive and negative electrodes was determined according to the Eq. (2) [23]:

\[
\frac{m_+}{m_-} = \frac{C_+ \times \Delta E_+}{C_- \times \Delta E_-}
\]

where \(C_\) represents the specific capacitance, \(\Delta E\) represents the potential range of each electrode and \(m\) represents the mass loading of the active material in the electrode. The subscripts + and - represent the positive and negative electrodes, respectively.

The specific capacitances were calculated based on GCD curves according to Eq. (3) [28]:

\[
C_\text{s} = \frac{I \times \Delta t}{m \times \Delta V}
\]

where \(I\) (A) is the discharge current, \(\Delta t\) (s) is the discharge time, \(\Delta V\) (V) is the discharge voltage range. In three-electrode system, \(m\) (g) is the mass loading of active material in a single electrode. In two-electrode system, \(m\) (g) is the total mass loading of active materials based on two electrodes.

The energy density \((E, \text{Wh kg}^{-1})\) and power density \((P, \text{W kg}^{-1})\) were calculated according to Eq. (4) and Eq. (5) respectively [28]:

\[
E = \frac{1}{2} C \text{Δ}V^2 \times \frac{1}{3600}
\]

\[
P = \frac{E}{\Delta t} \times 3600
\]

Fig. 2. SEM images of (a, b) HCS, (c) MnO₂/HCS-20, (d, e and f) MnO₂/HCS-30, (g, h) MnO₂/HCS-40, (i) EDS mapping images of C, N, O and Mn of Fig. 2e.

3. Results and discussion

3.1. Characterization of materials

SEM images of HCS and composites are shown in Fig. 2. It is noted in Fig. 2a that most of the original carbonized yeast cells exhibit a regular elliptical sphere shape. This result can be attributed to the effect of hydrothermal pre-carbonization, which coordinates the hydrolysis and carbonization speed of the cell membrane and avoids cell rupture due to direct carbonization. In addition, glutaraldehyde can be used as a protective agent in the hydrothermal pre-carbonization process to form a covalent bond between the amino group and the hydrolysis product of the polysaccharide in the cell wall, to prevent the collapse of the hollow structure and to control the integrity of the elliptical morphology [40]. The SEM image of HCS (Fig. 2b) presents an ellipsoid with a width of 2 μm and a length of 2.5 μm. As shown in SEM image of MnO₂/HCS-20 (Fig. 2c), after the hydrothermal reaction, HCS is covered by sparse MnO₂. There are still some HCS in the original state because of the lower concentration of MnO₂. The MnO₂/HCS-30 is covered with uniform MnO₂ nanowires as shown in Fig. 2d&e. From the SEM image of the broken yeast composites in Fig. 2f, it can be clearly seen that the composite has a shell hollow structure with a thickness of 100–200 nm. As shown in Fig. 2g&h, the surface of MnO₂/HCS-40 is covered by uniform MnO₂ particles. However, excessive deposition of MnO₂ may have an adverse effect on the electrical conductivity. Fig. 2i is an elemental distribution image of Fig. 2e, which demonstrates the presence and distribution of C, N, O and Mn and the results are consistent with the XPS analysis.

Fig. 3 presents the TEM and HRTEM images of HCS and MnO₂/HCS-30. HCS (Fig. 3a) exhibits uniform ellipsoidal morphology, which is consistent with the SEM images. The HRTEM images of the HCS (Fig. 3b&c) present a hollow internal structure and a porous shell structure. The porous structure is caused by the decomposition of some amorphous components into monosaccharides during the carbonization and hydrolysis of polysaccharides in the cell wall [46]. As can be seen from the Fig. 3d, the surface of the HCS is uniformly covered by MnO₂ nanowires. The HRTEM image (Fig. 3f) of a nanowire shows a fringe spacing of 0.24 nm, which can be ascribed to the (006) diffraction plane in birnessite-type MnO₂ and is consistent with XRD analysis.

Fig. 4a shows the XRD patterns of different samples. For HCS,
two broad diffraction peaks at 25° and 43° can be attributed to the (002) and (100) reflections of the disordered carbon layer, indicating its amorphous state [44,45]. The five diffraction peaks at 2θ = 12.5°, 18.6°, 26.9°, 55.9° and 65.5° in the pattern of MnO2/HCS-30 can be indexed to (002), (101), (006), (301) and (119) crystal planes of birnessite-type MnO2 crystalline phase (JCPDS No. 18-0802) [46].

Table 1 lists the physicochemical properties of HCS and MnO2/HCS-30. The composition of different composites was further investigated by TGA (Fig. 4f). It can be seen that all the TGA curves can be divided into four parts. The mass loss of the first part can be attributed to the removal of physically adsorbed water below 200 °C. The weight losses of MnO2/HCS-20, 30 and 40 can be calculated to be 2.6%, 2.3% and 5.2%, respectively. The third mass loss between 300 and 450 °C can be ascribed to the crystalline water in the composites, which are 2.6%, 2.3% and 5.2%, respectively. The third mass loss between 300 and 450 °C can be ascribed to the combustion of HCS and the transformation of layered structure of MnO2 into a thermodynamically stable tunnel structure. In this process, MnO2 decomposes to Mn3O4 with the release of oxygen in MnO2. The weight losses of MnO2/HCS-20, 30 and 40 can be calculated to be 42.7%, 26.4% and 14.6%, respectively. The final mass loss above 500 °C can be attributed to the combustion of the residual HCS and the transformation of Mn3O4 to Mn2O3, which are 5.8%, 3.0% and 2.1%, respectively. Therefore, the weight percentages of MnOx in MnO2/HCS-30, 30 and 40 composites were 44.8%, 63.1% and 72.2%. In other words, the content of MnOx increases with the increase in the concentration of MnOx [25].

To obtain more abundant information of surface functional groups, XPS measurements were performed on the HCS and MnO2/HCS-30. The survey XPS spectra of HCS and MnO2/HCS-30 (Fig. 5a) reveal the presence of C, N, O and C, N, O, Mn elements, respectively. The percentages of different elements in HCS and MnO2/HCS-30 are shown in Table 1. The high-resolution C 1s spectrum (Fig. 5b) of HCS exhibits two peaks: C–C (284.6 eV) and C–N (285.7 eV) [51]. Fig. 5c shows the Cls high-resolution XPS spectrum of MnO2/HCS-30 with the curve fitted with binding energies of C–C (284.7 eV), C–O (286.1 eV), and O–C=O (288.2 eV). The high-resolution N 1s spectrum of HCS was divided into four peaks (Fig. 5d) centered at 398.2, 399.3, 400.8, and 402.2 eV, corresponding to the pyridinic (N-6), pyrrolic or pyridonic (N-5), quaternary (N-Q), and oxidized (N-X), respectively [52]. Compared to the N 1s spectrum of HCS,
MnO₂/HCS-30 (Fig. 5e) shows more diversification, which is reflected with additional \(-N=\) bond (quaternary nitrogen) at 399.9 eV in addition to the above four peaks [50]. Among these bonds, N-6 and N-5 can provide additional pseudocapacitance as electrochemically active sites. The N-Q bonds with three carbon atoms in a carbon matrix, which facilitates the electron transfer and greatly enhances the conductivity of the carbon matrix [52]. The O1s spectrum of MnO₂/HCS-30 (Fig. 5f) could be deconvoluted into four peaks at 529.8, 531.2, 531.7 and 534.1 eV. These peaks could be assigned to Mn—O—Mn, —COOH, Mn—O—H and C=O groups, respectively [53]. The presence of the Mn—O—Mn bond can be attributed to oxygen bonded with manganese in the MnO₂ crystal lattice. Furthermore, the contained Mn—O—H bond enhances the ion exchange and improves the electrochemical properties of the electrode material [54]. Fig. 5g shows the deconvoluted Mn 2p XPS spectrum for typical MnO₂ characteristics. In the MnO₂/HCS-30 sample, the two peaks appearing at 641.9 and 653.6 eV with a spin-energy splitting of 11.7 eV are severally pertained to the Mn 2p₃/₂ and Mn 2p₁/₂ orbits of Mn⁴⁺ [55].

### 3.2. Electrochemical measurements

The electrochemical behavior was first tested in a three-electrode set-up in 1 M Na₂SO₄ aqueous electrolyte. From Fig. 6a, we can clearly see that the curves of three samples have different integrated areas at the scan rate of 50 mV s⁻¹, indicating that the K₂MnO₄ concentration during hydrothermal reaction has an effect on the electrochemical performance of the material. The CV curves of the three composites all exhibit a nearly rectangular shape, which is a representation of the pseudo-capacitance properties of the MnO₂/HCS-30 electrode material [54]. Fig. 5g shows the deconvoluted Mn 2p XPS spectrum for typical MnO₂ characteristics. In the MnO₂/HCS-30 sample, the two peaks appearing at 641.9 and 653.6 eV with a spin-energy splitting of 11.7 eV are severally pertained to the Mn 2p₃/₂ and Mn 2p₁/₂ orbits of Mn⁴⁺ [55].

(MnO₂/HCS-30) makes it far from achieving the best electrochemical performance. The excessive deposition of MnO₂ (MnO₂/HCS-40) on the surface affects its electrical conductivity, resulting in a decreased performance. It is worth mentioning that the carbon sphere network based on the nitrogen doping can improve the wettability and electrical conductivity of the material in collaboration with a typical pseudo-capacitance material to achieve excellent electrochemical performance [56]. Fig. 6c shows the CV curves of the MnO₂/HCS-30 at scan rates from 5 to 200 mV s⁻¹. It can be seen that all the curves can still maintain approximately rectangular shape with the increase of the scan rate to 100 mV s⁻¹, indicating that the MnO₂/HCS-30 material has excellent electrochemical activity, high reversibility and a stable voltage window at 0–1 V. The curve begins to become distorted as the scan rate increases to 200 mV s⁻¹, which may be due to the fact that the internal resistance of the electrode hinders the charge collection and cation diffusion in the electrode at higher scan rates [57]. The CV curves of the MnO₂ electrode material show no peaks in the scan window, indicating that MnO₂ is charged/discharged at a pseudo-constant rate over the complete CV and is usually caused by the following two reactions:

\[
(MnO₂)_{\text{surface}} + C^{\text{+}} + e^{-} \leftrightarrow (MnOOC)_{\text{surface}}
\]  

(6)

\[
MnO₂ + C^{\text{+}} + e^{-} \leftrightarrow MnOOC
\]  

(7)

Briefly, one of these two mechanisms is the surface adsorption/desorption of electrolyte cations (C = H⁺, Li⁺, Na⁺, K⁺) on the surface of MnO₂ as shown in Eq. (6), and the other is the intercalation/deintercalation of electrolyte cations in MnO₂ as shown in Eq. (7) [58]. Fig. 6d displays the GCD curves of the MnO₂/HCS-30 at current densities from 0.5 to 20 A g⁻¹. The Cₛ are 336, 255, 236, 224, and 208 F g⁻¹, and the charge capacity of MnO₂/HCS-30 increases from 117 to 137 F g⁻¹.
216 and 176 F g\(^{-1}\) as the current densities increase to 0.5, 1, 2, 4, 8 and 20 A g\(^{-1}\), respectively. Although the \(C_s\) decreases as the current density increases, it maintains the shape of an isosceles triangle, which indicates that the MnO\(_2\)/HCS-30 sample has excellent electrochemical reversibility and high Coulomb efficiency. The interface compatibility is one of the important factors that affects the property of a supercapacitor [59]. Fig. 6e presents the Nyquist plots of different samples. A magnified view of the Nyquist plots and corresponding equivalent circuit diagram are presented in the inset of the Fig. 6e. The equivalent circuit diagram is obtained by fitting, where \(R_{\text{ESR}}, R_{\text{ct}}, \text{CPE},\) and \(Z_W\) correspond to the equivalent series resistance, charge transfer resistance, constant phase element and Warburg impedance, respectively. The illustrated curves have a similar shape, exhibiting a semicircular portion in the high-frequency region and an approximately vertical line in the low-frequency region. The cross-section semicircle reflects the values of the \(R_{\text{ESR}}\) and \(R_{\text{ct}}\). The slope of the line represents the Warburg impedance of the diffusion behavior of the electrolyte in the electrode pores and the ions in the active material [60]. The \(R_{\text{ESR}}\) values of MnO\(_2\)/HCS-20, MnO\(_2\)/HCS-30, and MnO\(_2\)/HCS-40 are 2.4, 2.2 and 2.7 Ω, respectively, and the \(R_{\text{ct}}\) values are 2.2, 1.3 and 3.1 Ω, respectively. In addition, the curve of MnO\(_2\)/HCS-30 in the low-frequency region is also closer to vertical. The results above show that the MnO\(_2\)/HCS-30 has excellent ion diffusion and distribution properties.

As shown in Fig. 6f, the \(C_s\) of MnO\(_2\)/HCS-30 can still reach 89% of the initial capacitance after 5000 cycles of GCD at a current density of 10 A g\(^{-1}\), indicating that the material has good cycle stability. It can be observed by the internal illustration that even though the decrease of charge/discharge time causes the attenuation of the capacitance, the symmetry of the curve shows only a slight change. This change may be due to the loss of the structural stability of the electrode material during the long cycle test [61]. It is worth mentioning that the Coulomb efficiency increased from 91% to 96% after 5000 cycles of charge-discharge cycle. It may be due to the electrode being more fully wetted in the electrolyte as the cycle progresses, resulting in a more complete cation adsorption/desorption and intercalation/deintercalation process on the MnO\(_2\) surface.

The excellent electrochemical properties of the prepared MnO\(_2\)/HCS-30 electrodes may be attributed to: (1) HCS can not only provide strong mechanical support but also reduce the volume

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**Fig. 7.** The electrochemical performance of ASC in 1 M Na\(_2\)SO\(_4\) aqueous electrolyte in a two electrode system: (a) The schematic diagram of the ASC. (b) Comparative CV curves of HCS and MnO\(_2\)/HCS-30 composite electrodes in a three-electrode system at a scan rate of 50 mV s\(^{-1}\). (c) CV curves of the ASC device in different operation voltage windows from 1.4 to 2.2 V at the scan rate of 50 mV s\(^{-1}\). (d) CV curves at different scan rate. (e) GCD curves at different current densities. (f) The gravimetric capacitance of the ASC device as a function of current density. (g) Nyquist plots of the ASC. (h) Cycling performance of the ASC device over 5000 cycles at a current density of 8 A g\(^{-1}\). (i) The Ragone plot of the ASC.
expansion during the charge and discharge to enhance the cycle stability. In addition, this structure facilitates the electrolyte entering the electrochemical site and provides a short diffusion path length for adsorbing ions [62]. (2) The presence of wrinkles on the surface of the HCS can produce high electron conductivity and more reaction sites for faster ion and charge transfer rates [63]. (3) A large number of nitrogen-containing functional groups form a stable nitrogen doping in the carbon matrix after high-temperature carbonization, which can improve the wettability and provide more active sites [64]. (4) The MnO2 nanowire is perfectly coated on the carbon shell, which facilitates the insertion of cations and provides a short diffusion path for electrolyte ions on the premise of minimizing the loss of conductivity.

In order to further characterize the electrochemical performance of the electrode material for practical applications, the ASC devices have been assembled by using MnO2/HCS-30 and HCS as a positive electrode and negative electrode as shown in Fig. 7a. Stable CV curves (Fig. 7b) were obtained in the potential windows of −1 to 0 V for the HCS with ideal electric double-layer capacitor behavior and from 0 to 1 V for the MnO2/HCS-30 with pseudocapacitive behavior, which is also consistent with the literature [61]. As shown in Fig. 7c, the assembled ASC can remain stable within a 2.0 V voltage window. However, when the voltage window reaches 2.2 V, the high potential current drastically increases due to the oxygen and/or hydrogen evolution reaction [65]. As can be seen in the Fig. 7d, the rectangular shape of the CV curves also remained unchanged when the scan rate was increased to 200 mV s⁻¹, indicating high rate capability. Furthermore, the GCD curves (Fig. 7e) of the ASC also show perfect highly linear and low IR drop with increasing the current density, indicating low internal series resistance. As shown in the EIS curve of the three-electrode above. From the curve, it can be calculated that the interfacial resistance between the prepared electrode material and the Na₂SO₄ aqueous solution electrolyte is about 2.6 Ω, and the Rct value is 1.7 Ω, showing a low resistance. In addition, the approximately vertical line at the low-frequency region also indicates a low ion diffusion resistance [67]. As shown in Fig. 7f, the prepared ASC device exhibits an excellent cycling stability with 93.9% capacitance retention after 5000 cycles. The internal illustration shows that the ASC can light up a 2.0 V light-emitting diode (LED) after charging, demonstrating the practicability of the material and proving to be an effective energy storage material. The Ragone plot (Fig. 7i) is commonly used to characterize the electrochemical performance of a supercapacitor device. From the curves, we can see that when the ASC reaches the maximum energy density of 41.4 Wh kg⁻¹, the power density is 500 W kg⁻¹, and when the maximum power density of 7901 W kg⁻¹ is reached, the energy density value is 23.0 Wh kg⁻¹. In addition, it is worth mentioning that the use of HCS as a negative electrode instead of a commercial anode material in our device is more advantageous due to its lower cost and easier preparation.

4. Conclusion

In summary, we successfully prepared the nitrogen-doped porous hollow carbon spheres derived from the live yeast cell templates using hydrothermal pre-carbonization and pyrolysis carbonization method. During the in-situ deposition of MnO2, the HCS acted as the template, nucleating agent, and carbon source. The MnO2/HCS-30 (with a deposition thickness of 90 nm) exhibited a ultrahigh specific capacitance of 255 F g⁻¹ at current density 1 A g⁻¹ in 1 M Na₂SO₄ electrolyte. The assembled ASC employed the MnO2/HCS-30 material as the positive electrode and the HCS as the negative electrode. The maximum energy density operating at the 2.0 V voltage window was 41.4 Wh kg⁻¹ at a power density of 500 W kg⁻¹ and still maintained 23.0 Wh kg⁻¹ at a power density of 7901 W kg⁻¹. In addition, MnO2/HCS-30 also exhibited a good cycling stability of 93.9% capacitance retention after 5000 cycles. This work may pave the way for the discovery of high-performance supercapacitor electrode materials based on the use of biological templates.

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References


Table 2

<table>
<thead>
<tr>
<th>Positive/negative electrodes</th>
<th>Specific capacitance (F g⁻¹)</th>
<th>Cell voltage (V)</th>
<th>Electrolyte</th>
<th>Capacitance retention (%)</th>
<th>Cycle stability</th>
<th>Energy density (Wh kg⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO2/GO/AC</td>
<td>145 (0.5 A g⁻¹)</td>
<td>2.1</td>
<td>1 M Na₂SO₄</td>
<td>72% (0.2–5 A g⁻¹)</td>
<td>92% (1 A g⁻¹, 5000)</td>
<td>24 [22]</td>
<td></td>
</tr>
<tr>
<td>MnO2–NHCS/NHCS</td>
<td>59.5 (0.5 A g⁻¹)</td>
<td>1.8</td>
<td>1 M Na₂SO₄</td>
<td>37% (0.5–5 A g⁻¹)</td>
<td>100% (1 A g⁻¹, 4000)</td>
<td>26.8 [30]</td>
<td></td>
</tr>
<tr>
<td>MRCF/AC</td>
<td>41.3 (0.3 A g⁻¹)</td>
<td>2.0</td>
<td>1 M Na₂SO₄</td>
<td>53% (0.3–3 A g⁻¹)</td>
<td>88% (2 A g⁻¹, 1000)</td>
<td>22.9 [54]</td>
<td></td>
</tr>
<tr>
<td>MnO2/HCS–30/HCS</td>
<td>74.5 (0.5 A g⁻¹)</td>
<td>2.0</td>
<td>1 M Na₂SO₄</td>
<td>55.7% (0.5–8 A g⁻¹)</td>
<td>93.9% (1 A g⁻¹, 5000)</td>
<td>41.4 This work</td>
<td></td>
</tr>
</tbody>
</table>


