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Carbon spheres with hierarchical micro/mesopores for water desalination by capacitive deionization

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In this work, porous carbon spheres with hierarchical pores (denoted as hCSs) were fabricated via a sol–gel process with surfactant-directing assembly strategy and invesiaged as capacitive deionization (CDI) electrode materials for the first time. The hierarchical micro/mesopores of hCSs were demonstrated by characterizations from transmission electron microscopy and N₂ adsorption/desorption tests. The results of CDI measurements indicate that hCSs obtained at 800 °C (hCSs-800) possesses the best electrosorption performance among all hCSs samples, and exhibits a high electrosorption capacity of 15.8 mg g⁻¹ when the initial NaCl solution is 500 mg L⁻¹. Further Kim-Yoon plot analysis proves that hCSs-800 integrates the merits of both high electrosorption capacity and fast electrosorption rate, indicating the superioty of hCSs for CDI applications.

Introduction

Capacitive deionization (CDI) is an emerging desalination technology which has gained enormous interests in recent years due to its several attracting features, such as low energy consumption, high desalination efficiency and environmental friendliness.¹⁻¹⁰ Analogical to supercapacitor, CDI accumulates ions by forming electrical double layer (EDL) on the surface of porous carbons.¹¹⁻¹³ Therefore, the CDI performance of one electrode is mainly dependent on the physical properties of porous carbons, such as specific surface area, pore size distribution, and so on. Currently, porous carbons such as activated carbons, carbon nanofibers, carbon nanotubes, graphene and their hybrids have been widely applied as CDI electrode materials.¹⁴⁻²⁹ Despite the progresses achieved up to date, the transfer of science into a realistic technology has still yet to be completed. Exploring new porous carbon electrodes should still be an urgent need for the development of CDI technology.

Carbon spheres (CSs), as one kind of zero-dimensional porous carbons, have emerged as a new class of promising materials for potential applications in energy storage, CO_2 capture, and catalyst support.³⁰⁻³³ Recently, the potential of microporous CSs (mCSs) as CDI electrode material has been demonstrated in our previous work.³⁴ Although the resultant mCSs possessed a high specific surface area of 1321 m² g⁻¹, they suffered from a low capacity of only 5.81 mg g⁻¹ even in the presence of a high operation voltage (1.6 V), which is far below the theoretical prediction.³⁵ This is mainly because of

pores, so the ion storage of mCSs decreases to a much less degree than those of porous carbons reported in similar conditions by now. Notably, similar situation also happened in the electrosorption process of microporous graphene sheets³⁶ until the emergence of mesoporous graphene sheets by Xu *et al.*³⁷ Taking this into consideration, an effective solution is to endow mCSs with abundant mesopores (2 to 50 nm pore size). With the introduction of meropores into mCSs, this turn of CSs.

the presence of overlapping effect caused by micropores,

which makes the ions very difficult to diffuse into the internal

endow mCSs with abundant mesopores (2 to 50 nm pore size). With the introduction of mesopores into mCSs, this type of CSs would integrate mesopore (2 to 50 nm pore size) channels for facilitating the electrolyte ion diffusion,^{37, 38} and micropores (<2 nm pore size) for providing abundant adsorbing sites for ions.³⁹ Such a hierarchical porous structure has also been demonstrated to be the most important property for the development of an advanced CDI electrode with high electrosorption capacity and rate.^{35, 40} In general, hierarchical porous carbons can be easily prepared via using silica, metal oxides, surfactants, or other non-inorganics as templates.⁴¹⁻⁴⁴ However, to date only several kinds of hierarchical porous carbons have been reported in CDI field.⁴⁵⁻⁴⁷ The synthesis of CSs with hierarchical micro/mesopores (denoted as hCSs) has rarely succeeded.

To address this issue, herein hCSs were prepared via a solgel process with surfactant-directing assembly by using cationic surfactant cetyltrimethylammonium bromide (CTAB) as a template, resorcinol-formaldehyde as a carbon source and tetraethoxysilane (TEOS) as an assistant pore-forming agent. Due to their hierarchical porous structure, high specific surface areas and large pore volumes, hCSs exhibit a superior CDI performance.

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Experimental

Materials Synthesis

Resorcinol, formaldehyde (37 wt % solution), TEOS, CTAB, ammonia aqueous solution (28 wt %) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). In a typical synthesis, resorcinol (0.30 g) and CTAB (0.30 g) were added to a mixed solution containing ammonia aqueous solution (0.30 mL), ethanol (12 mL) and deionized water (30 mL), and stirred for 30 min. Then, TEOS (1.5 mL) and formaldehyde solution (0.42 mL) were added and stirred for 24 h at room temperature, and subsequently heated at 100 °C for 24 h. The as-prepared products were collected by centrifugation, washing and drying, and subsequently carbonized at 600, 800 and 1000 °C for 3 h under N₂ atmosphere. Finally, hCSs were obtained by immersing carbonized products into 10 wt % HF at room temperature for 24 h with a subsequent washing and drying process. Notably hCSs obtained at 600. 800 and 1000 °C are named as hCSs-600. hCSs-800 and hCSs-1000, respectively.

Characterization

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The surface morphology and structure of hCSs were investigated by scanning electron microscopy (SEM, JEOL JSM-LV5610) and transmission electron microscopy (TEM, CM200). Pore properties of hCSs were investigated by N2 physical adsorption measurement conducted at 77 K on ASAP 2010 Accelerated Surface Area and Porosimetry System (Micrometitics, Norcross, GA). Disorders and graphitization degrees of hCSs were investigated by Raman spectra (RenishawinVia microscope) with a He-Ne laser (633 nm) used as the light source for excitation. Electrochemical performances (Autolab PGSTAT 302N electrochemical workstation) of hCSs were investigated in a three-electrode system by using cyclic voltammetry (CV) measurements in 1 M NaCl solution. A standard calomel electrode and a platinum foil were used as reference electrode and counter electrode, respectively. The specific capacitance (C, $F g^{-1}$) can be obtained from CV curves using the following equation:

$$C = \widetilde{i} / (v \times m) \tag{1}$$

where \tilde{i} is the average current (A), v is the scan rate (V s⁻¹) and m is the mass of electrodes (g).

CDI tests

Electrode preparation: Each CDI electrode was prepared by pasting a mixture of the sample with polymeric binder, polyvinylpyrrolidone (PVP)/polyvinyl butyral (PVB) onto graphite paper. In detail, each electrode was composed of the sample, 1.5 wt.% PVP and 6.0 wt.% PVB. The mixtures were pressed onto graphite papers and dried in vacuum oven at 60 °C overnight. Additionally, the mass of each electrode is ~65 mg.

Batch-mode CDI tests: All experiments were carried out in NaCl solution (~100 mg L^{-1}) with a volume of 20 mL, and the solution temperature and flow rate were kept at 298 K and 27 mL min⁻¹, respectively. A direct voltage of 1.2 V was applied on the opposite electrodes and an ion conductivity meter at the

outlet of the unit cell was used to monitor and measure the concentration variation. In our experiment, the electrosorption capacity (Γ , mg g⁻¹) was defined as follows:

$$\Gamma = \frac{(C_0 - C_c) \times V}{m} \tag{2}$$

where C_0 and C_e are initial and final NaCl concentrations (mg L⁻¹), V is the volume of NaCl solution (L) and m is the total mass of the electrodes (g).

Charge efficiency $(\Lambda)^{48}$ was calculated according to the following equation:

$$1 = \frac{\Gamma \times F}{\Sigma} \tag{3}$$

where **F** is the Faraday constant (96485 C mol⁻¹), **f** is the electrosorption capacity (mol g⁻¹) and **S** (charge, C g⁻¹) is obtained by integrating the corresponding current.

Kim-Yoon plot, which was firstly proposed by Yoon et al,⁴⁹ and further developed by Suss. et al,¹ has been used to evaluate the electrosorption performance of porous carbon materials. In detail, the electrosorption capacity at $t \min(\Gamma_t, \text{mg g}^{-1})$ of the electrode materials was calculated according to the following equation:

$$\Gamma_{\rm t} = \frac{(C_0 - C_{\rm t}) \times V}{m} \tag{4}$$

where C_t are the concentration at t min. The corresponding mean electrosorption rate (v_t , mg g⁻¹ min⁻¹) of the electrode materials was calculated according to the following equation:

$$v_t = \frac{\Gamma_t}{t} \tag{5}$$

where *t* is the time of electrosorption process.

Results and discussion

Fig. 1 shows SEM images of hCSs-800. Notably, the morphologies of hCSs-600 and hCSs-1000 (not shown here) are similar with that of hCSs-800. As shown in Fig. 1a, hCSs-800 exhibits uniform spherical structures with rough surfaces. The particle size of hCSs-800 is around 300 nm. Further observation by enlarged SEM image (Fig. 1b) proves the porous surfaces of hCSs-800. Additionally, the pores within hCSs-800 were investigated by TEM measurements. As shown in Fig. 2a and b, enormous pores can be clearly seen from hCSs-800, due to the removal of template. Such a porous structure is beneficial for providing more sites for ion accommodation.

The pore properties of hCSs samples were investigated by N_2 adsorption/desorption isotherms. As shown in Fig. 3a, all hCSs samples show hysteresis loops with a combination of type I and type IV, indicating a hierarchically porous structure composed of micropores and mesopores.²⁰ The corresponding specific surface areas, pore volumes and mean pore diameters are listed in Table 1. It can be seen that hCSs-800 exhibits a high specific surface area of 1529 m² g⁻¹ and a large pore volume of 1.73 cm³ g⁻¹, higher than those of hCSs-600 (1351 m² g⁻¹; 1.64 cm³ g⁻¹) and hCSs-1000 (1281 m² g⁻¹; 1.46 cm³ g⁻¹). Furthermore, the hierarchically porous structures of hCSs

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samples were proved by Barrett-Joyner-Halenda (BJH) pore size distribution curves (Fig. 3b). Obviously, all hCSs samples display hierarchical micro/mesopore structures. As reported by previous works,^{50, 51} mesopores are favourable for enhancing mass transport and ion accommodation, and micropores are beneficial to ion accommodation. Moreover, due to the introduction of mesopores in hCSs, more micopores can be accessible for ion accommodation. Therefore, hCSs with micro/mesopore structures should be effective for CDI application.







Fig. 2 TEM images of hCSs-800.



Fig. 3 (a) N₂ adsorption/desorption isotherms and (b) BJH pore size distribution curves of hCSs samples.

Table 1	Specific	surface	areas,	pore	volumes,	mean	pore	diameters
and $I_{\rm D}/I$	_o values c	of hCSs s	amples					

ind by ig values of ness samples.					
Sample	Specific Pore		Mean pore	I_D/I_G	
	surface area	volume	diameter		
	(m² g⁻¹)	(cm ³ g ⁻¹)	(nm)		
hCSs-600	1351	1.64	4.9	1.02	
hCSs-800	1529	1.73	4.5	0.85	
hCSs-1000	1281	1.46	4.6	0.76	



Fig. 4 Raman spectra of hCSs samples.

Raman spectra were used to investigate the local structure of hCSs. As shown in Fig. 4, all hCSs samples show D and G bands centered at ~1349 and ~1598 cm⁻¹, respectively, corresponding to sp³-carbon and sp²-carbon in carbon matrix. The intensity of D-band to G-band (I_D/I_G) is representative for defective or disordered degree in carbon matrix,³⁴ and listed in Table 1. Obviously, with the increase in carbonization temperature, I_D/I_G value increases, indicating the increase of defects or disorders in hCSs, which is believed to favour ion accommodation during the electrosorption process.³⁴

CV tests were used to investigate the electrochemical performances of hCSs samples before electrosorption tests. As shown in Fig. 4, all CV curves display relatively distorted rectangular shapes. Moreover, hCSs-800 exhibits a largest current density among all samples, indicating the largest capacitance. The specific capacitances of hCSs samples calculated according to equation (1) are listed in Table 2. It can be seen that hCSs-800 shows a high capacitance of 263.6 F g⁻¹, which is much higher than those of hCSs-600 (216.8 F g⁻¹) and hCSs-1000 (175.6 F g⁻¹), possibly due to its higher specific surface area and larger pore volume, which could provide more sites for the formation of EDL. Considering the correlation between capacitance and electrosorption capacity, it should be believed that hCSs-800 should have the best electrosorption performance.



Fig. 4 CV curves of hCSs samples in 1 M NaCl solution at a scan rate of 2 mV $\mbox{s}^{-1}.$

Table 2 Specific	capacitances o	f hCSs sample:
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Sample	hCSs-600	hCSs-800	hCSs-1000
Specific	216.8	263.6	175.6

To figure out the electrosorption performances of hCSs electrodes, batch-mode CDI experiments were carried out in NaCl solution with an initial concentration of ~100 mg L⁻¹. The applied voltage was 1.2 V and the current variations were recorded simultaneously and independently at each experiment. Fig. 5 shows the NaCl concentration variations for hCSs samples. It can be seen that once the electric field is imposed, a sharp decrease of NaCl concentration can be observed and it reaches equilibrium after 45 min. The electrosorption capacities of hCSs shown in Table

3 demonstrate that hCSs-800 shows the best electrosorption performance.



Fig. 5 NaCl concentration variations for hCSs samples. Table 3 Electrosorption capacities of hCSs samples in NaCl solution with an initial concentration of ~100 mg L^{-1} .

Sample	hCSs-600	hCSs-800	hCSs-1000		
Electrosorption	5.6	8.4	6.7		



Fig. 6 (a) SEM images and (b) N₂ adsorption/desorption isotherm of mCSs-800. Inset of (b) is corresponding BJH pore size distribution curve.

In order to further highlight the superiority of hCSs, mCSs were prepared as described in the literature⁵² with a carbonization process at 800 °C (denoted as mCSs-800). The morphology and pore property of mCSs-800 were investigated by SEM and N_2

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adsorption/desorption isotherm, respectively. As shown in Fig. 6a, mCSs-800 displays uniform spherical structures with smooth surfaces. The particle size of mCSs-800 is around 500 nm. The characterization using N₂ adsorption/desorption isotherm shows that mCSs-800 displays a type-I hysteresis loop (Fig. 6b) with a BET specific surface area of 656 m² g⁻¹ and a pore volume of 0.32 cm³ g⁻¹. Obviously, these values are much lower than those of hCSs-800. Furthermore, BJH pore size distribution curve shown in the inset of Fig. 6b proves the microporous structure of mCSs-800.

The obtained mCSs-800 was applied for constructing CDI electrodes with a similar process with hCSs-based CDI electrodes. The CDI performances of hCSs-800 and mCSs-800 were compared in a NaCl solution of ~500 mg L⁻¹ at an applied voltage of 1.2 V. The corresponding electrosorption capacities and charge efficiencies are shown in Fig. 6. Clearly, hCSs-800 exhibits a high electrosorption capacity of 15.8 mg g⁻¹ and charge efficiency of 0.78, much higher than those of mCSs-800 (6.3 mg g⁻¹ and 0.56). In addition, these values (electrosorption capacity and charge efficiency) also surpass those of other CSs-based CDI electrodes (Table 4), and hierarchical porous carbons-based CDI electrodes (0.7-9.1 mg g⁻¹)^{45, 46, 53} reported previously.



Fig. 7 Electrosorption capacities and charge efficiencies of mCSs and hCSs in a NaCl solution of ~500 mg $L^{\rm -1}.$

Table 4 Comparison of electrosorption capacities and charge efficiencies for hCSs and other CSs-based CDI electrodes in a NaCl solution of ~500 mg L^{1} .

Sample	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Electrosorption capacity (mg g ⁻¹)	Charge efficiency
mCSs ³⁴	0.59	1321	5.8	0.40
N-doped mCSs ⁵⁴	0.79	1640	13.7	0.49
Hollow CSs ⁵⁵	0.67	809	13.2	-
Hollow CSs ⁵⁶	-	618	7.2	-
N-doped hollow CSs ⁵⁷	0.70	512	10.3	0.52
mCSs- 800 (in this work)	0.32	656	6.3	0.56



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The superior electrosorption performance of hCSs-800 can be ascribed to following reasons: (i) hCSs-800 exhibits a higher specific surface area of 1529 $m^2 g^{-1}$ and a larger pore volume of 1.73 $\text{cm}^3 \text{g}^{-1}$ compared with other kinds of CSsbased materials (Table 4). As reported previously, such a high specific surface area and pore volume (1529 $m^2 g^{-1}$ and 1.73 cm³ g⁻¹) can provide more sites for ions storage,³⁵ thus improving the electrosorption performance. (ii) hCSs-800 possesses a hierarchical porous structure. This type of hierarchically porous structure integrates mesopore (2 to 50 nm pore size) channels for facilitating the electrolyte ion diffusion,^{37, 38} and micropores (<2 nm pore size) for providing abundant adsorbing sites for ions.³⁹ Therefore, the hierarchical micro/mesoporous structure of hCSs-800 is believed to not only accelerate the mass transfer, but also help to release more accessible surface area for ion accommodation.

Kim-Yoon plot model was used to further evaluate the CDI performances of hCSs-800 and mCSs-800. As shown in Fig. 8, the Kim-Yoon plot of hCSs-800 shifts towards the upper and right region compared with that of mCSs-800, indicating that hCSs-800 integrates the merits of both high deionization capacity and fast deionization rate.







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The cycle stability of porous carbon is very important for CDI application. The long-term cycle stability of the hCSs-800based CDI unit was investigated in NaCl solution of ~500 mg L^{11} at an applied voltage of 1.2 V. As shown in Fig. 9, after 50 cycles, the capacity maintains almost constant, indicating an excellent stability of hCSs-800-based CDI unit.

Conclusions

In summary, hCSs were prepared via a sol-gel process with surfactant-directing assembly by using CTAB as a template, resorcinol-formaldehyde as a carbon source and TEOS as an assistant pore-forming agent and investigated as CDI electrode materials. It is found that (i) hCSs-800 possesses a highest specific surface area of 1529 m² g⁻¹ and a largest pore volume of 1.73 cm³ g⁻¹ as well as a best electrosorption performance amongst all hCSs samples; (ii) hCSs-800 exhibits a high electrosorption capacity of 15.8 mg g⁻¹ (NaCl concentration: 500 mg L⁻¹; applied voltage: 1.2 V), much higher than those of mCSs-800 and other CSs reported previously; (iii) further Kim-Yoon plot analysis proves that hCSs-800 integrates the merits of both high electrosorption capacity and fast electrosorption rate; (iv) hCSs-800 should be promisingly applicable for CDI application.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Graphical Contents Entry



Carbon spheres with hierarchical micro/mesopores were prepared via a sol-gel process with surfactant-directing assembly strategy and applied for capacitive deionization.