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REVIEW

Preparation and performances of carbon aerogel microspheres for the application of supercapacitor

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Abstract Carbon aerogel (CA) microspheres were successfully synthesized by an inverse emulsion polymerization routine. Morphology and physical properties of the CA microspheres were characterized by scanning electron microscopy, N_2 sorption isotherm, and transmission electron microscopy. The results showed that the CA microspheres were all fine spheres with diameters about 4 μm, and the CA microsphere was a typical mesoporous material with ordered mesoporous nano-network structure. The maximum capacitance of the electrode obtained from cyclic voltammetry was 187.08 F/g and the capacitance of the supercapacitor resulted from galvanostatic charge–discharge tests was up to 45.98 F/g. The supercapacitor using CA microsphere as electrode material presented a long cycle life, high charge–discharge efficiency, and low R_s of 0.70 Ω in 6 M KOH electrolyte.

Keywords Carbon aerogel microspheres · Inverse emulsion polymerization · Supercapacitor · Electrochemical performance

Introduction

Electrochemical capacitor or supercapacitor is a type of energy-storage device with features intermediate between conventional dielectric capacitors and batteries. In recent years, great attention has been focused on electrochemical supercapacitor energy-storage systems on account of the application to electric vehicles, pulse power, and backup sources [1, 2]. The energy storage of supercapacitors based on double layer is the accumulation of ionic charges which occur at the electrode/electrolyte interface, so the high-specific surface area and large pore volumes of the electrode active material are the basic requirements to achieve high-specific capacitance [3]. Double-layer capacitor electrodes have been fabricated using activated carbon, mesoporous carbon, carbon fiber, carbon black, aerogel particulates, and carbon cloth [4–6]. In order to meet the request of new applications, the carbon materials to be prepared must have much higher energy density per weight and volume than that of the conventional ones [7]. Among various high surface area carbon materials for supercapacitors, spherical carbon aerogels represent a promising and innovative material [8].

Recently, carbon aerogel microspheres have attracted considerable attention for their various technical applications such as catalyst supports, deionization devices, or battery and supercapacitor due to their high porosity as well as their adjustable pore and particle size [9–13]. In general, spherical carbons offer several advantages such as high-electrical conductivity, good liquidity, and special pore properties over other carbon powders of flake or irregular shape in practical electrochemistry. Because of their high taping density, much more electrode material can be loaded in supercapacitors such that a higher volumetric energy density can be achieved [14].

Carbon aerogels can be synthesized by the sol–gel polycondensation of resorcinol with formaldehyde in a slightly basic aqueous solution, followed by alcohol or carbon dioxide supercritical drying and pyrolysis in an inert atmosphere [15, 16]. However, the product is difficult to be

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taken out from the reaction container and the supercritical drying step is very complex, expensive and dangerous. If carbon aerogels can be synthesized in the form of microspheres using a simple drying technique, it will become much easier to handle in many applications. Several methods have been developed for preparation of carbon aerogels microspheres. In our previous works [2, 17], we have developed an ambient preparation technology for carbon aerogel without supercritical conditions and studied its application for supercapacitors. Yamamoto et al. [18] succeeded in preparing monodisperse carbon cryogel microspheres through the membrane emulsification. Inverse emulsion polymerization is an important particle-formation process that is in wide use in the production of foods, cosmetics, pharmaceuticals, paints, etc. [18]. Generally, micro- or nano-emulsions can be easily obtained by mechanical mixing of a water phase with an oil phase in the presence of a suitable surface-active agent in the emulsification process. CA microspheres can be synthesized by inverse emulsion polymerization using a non-ionic surfactant (SPAN 80) as an emulsifier [15]. In this paper, CA microspheres were prepared by an inverse emulsion polymerization followed by drying at ambient temperatures and pyrolysis in an inert atmosphere. The prepared CA microspheres were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 sorption isotherm. Furthermore, the electrochemical behaviors of CA microspheres used as electrodes for supercapacitor were investigated by cyclic voltammetry, galvanostatic charge–discharge tests, and electrochemical impedance spectroscopy.

Experimental

Materials

All the materials and chemical reagents were of analytical grade, which were obtained from commercial sources and directly used without any pretreatment. Resorcinol, sodium carbonate, and potassium hydroxide were purchased from Guangdong Guanghua Chemical Factory Co., Ltd., China. Formaldehyde and acetone were obtained from Changsha Antai Fine Chemical Co., Ltd., China. Hexamethylene and SPAN 80 were provided by Research Institute of Guangfu Fine Chemical, Tianjin, China. The water was distilled water.

Preparation of CA microspheres

CA microspheres were prepared by the sol–gel polycondensation of resorcinol and formaldehyde using an inverse emulsion polymerization, followed by drying at ambient temperature and pyrolysis in an inert atmosphere. The molar ratio of formaldehyde to resorcinol was held at a constant value of 2. Here, sodium carbonate (Na_2CO_3) (C) was used as the basic catalyst, the molar ratio of resorcinol to catalyst (C) was set at R/C=200. After the reactant and catalyst were dissolved in distilled water by stirring them for less than 30 min, homogeneous resorcinol-formaldehyde (RF) solution was obtained, the mass percentage of the reactants in solution was set at RF=40%. Then, the solution was poured into hexamethylene containing surfactant SPAN 80 and an inverse emulsion was formed. The volume ratios of surfactant to hexamethylene and RF solution to hexamethylene were 0.01 and 0.3, respectively. The emulsion was stirred at 353 K until the dispersed RF particles were gelled. The obtained RF hydrogel microspheres were separated from the hexamethylene by filtration and washed. Then acetone was selected as the drying solvent for ambient drying because of its low surface tension and its low boiling point which reduces the shrinkage of RF hydrogel microspheres during drying. Finally, the spheres were dried at ambient temperatures. The CA microspheres were obtained by carbonization at 1,073 K for 3 h under Ar atmosphere.

Measurement techniques of structural characterization

1. Scanning electron microscopy (SEM) (JSM-6610, JEOL) was used to study the morphology and surface structure of the samples.

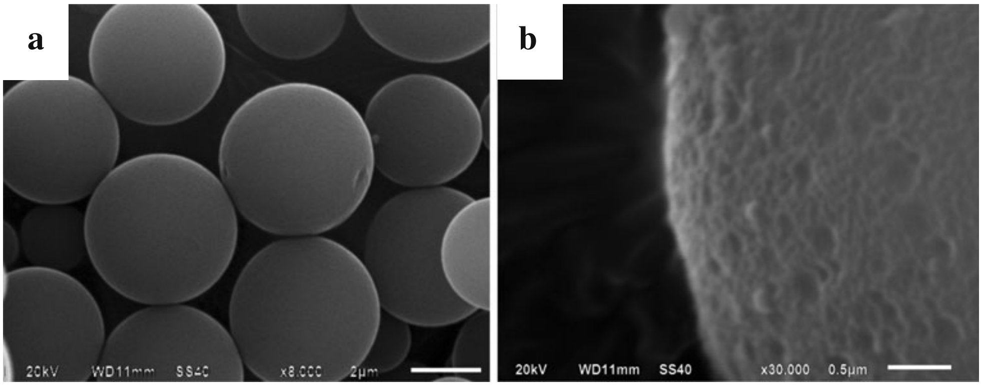


Fig. 1 **a**, **b** SEM images of the obtained CA microspheres

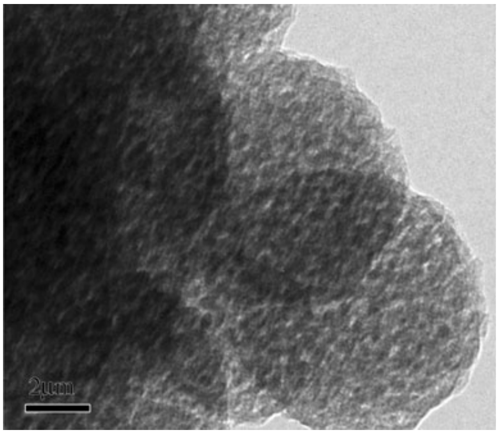


Fig. 2 TEM images of the obtained CA microspheres

2. Specific surface areas and pore size distributions of carbon aerogels microspheres were determined by N_2 gas adsorption at 77 K on a Quantachrome NovaWin2 autosorb automated gas sorption system.
3. The transmission electron microscopy of the carbon aerogels microspheres was performed using a FEI Tecnai G2 microscope at 200 kV.

Evaluation of electrochemical properties

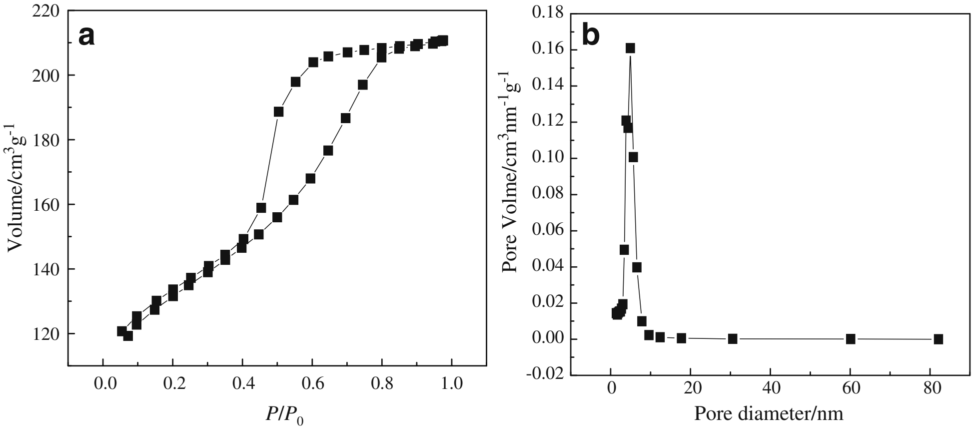
The mass ratio of carbon aerogel microspheres/graphite was 8:1, the appropriate amount of 10 wt.% of polytetrafluorethylene aqueous suspension (60%) as a binder was added and mixed well in *N*-methyl-2-pyrrolidone until it formed the slurry with proper viscosity, and then the slurry was uniformly coated on a disk-like nickel foam by dipping (served as a current collector), dried at 353 K for 12 h, and then pressed at 15 MPa for 1 min in order to assure a good electronic contact. So, the working electrode was well prepared. The mass of mixture on electrode is determined by the mass discrepancy of nickel foam before and after its coating. So the mass of carbon aerogel microspheres is equal to the mass of mixture multiplied by 0.8. The electrochemical properties of the obtained materials were studied with a typical three-electrode test cell consisting of a working electrode, a nickel sheet counter electrode, and a Hg/HgO reference electrode. The electrolyte was 6 M KOH. Electrochemical performances of carbon aerogel microspheres as electrode materials in supercapacitors were characterized using cyclic voltammery (CV), electrochemical impedance spectroscopy, and galvanostatic charge–discharge test. The cyclic voltammogram and electrochemical impedance spectroscopy were performed by means of electrochemical analyzer systems, CHI660 (CH Instruments, USA) with three-electrode system. The galvanostatic charge–discharge and cycle life tests were carried out by potentiostat/galvanostat (BTS6.0, Neware, Guangdong, China) on button cell supercapacitors. The symmetrical button cell supercapacitors were assembled according to the order of electrode–separator–electrode. All the measurements were carried out at room temperature.

Results and discussion

Material characterization

Carbon aerogels microsphere is a kind of novel mesoporous carbon materials with high electrical conductivity, good liquidity, and other interesting properties. The SEM image of a typical CA sphere sample is shown in Fig. 1a. It can be seen that the as-prepared CA particles are all fine spheres with diameters about 4 μm, look like the spherical CA prepared by the CO_2 supercritical drying technique [19]. The magnified SEM image of the surface structure of the CA spheres is shown in Fig. 1b. There are a lot of nanopores on the surface of the microspheres. The nanopores provide numerous channels inside the active material and facilitate the fast penetration of the electrolyte. So the existence of nanopores will ensure the high utilization of

Fig. 3 Nitrogen adsorption isotherms at 77 K (**a**) and pore size distributions (**b**) of CA microspheres



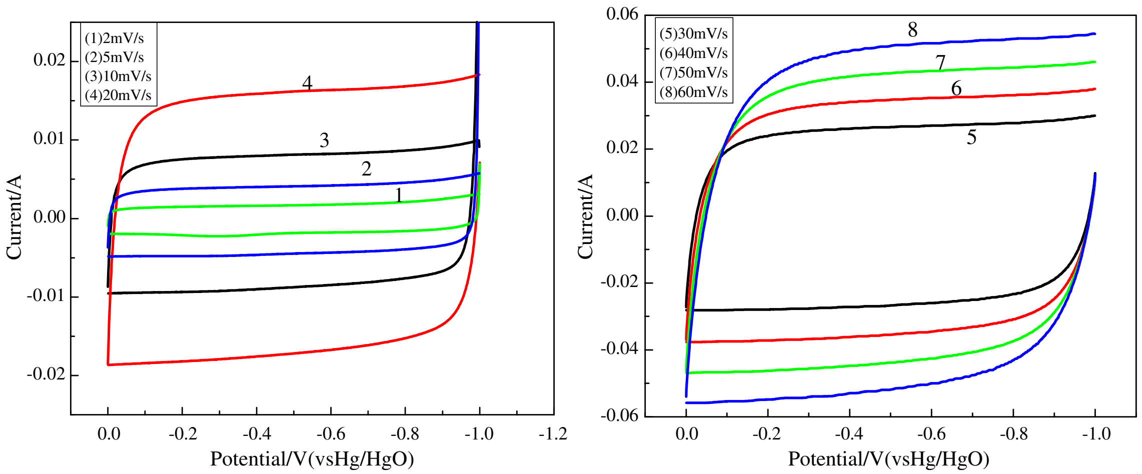


Fig. 4 Cyclic voltammograms of CA microspheres electrodes at different scan rates. (*1*) 2 mV/s, (*2*) 5 mV/s, (*3*) 10 mV/s, (*4*) 20 mV/s, (*5*) 30 mV/s, (*6*) 40 mV/s, (*7*) 50 mV/s, (*8*) 60 mV/s

electrode materials. The morphology and microstructure of the CA microspheres have also been examined by TEM as shown in Fig. 2. The CA microspheres consist of ordered mesoporous nano-network structure, thus the CA microspheres with a larger percentage of pores are more suitable to high-power supercapacitor applications.

Physical adsorption of gases was carried out in order to characterize the porous structure of samples. Adsorption and desorption isotherm of nitrogen on the CA microspheres are shown in Fig. 3a. The isotherm is of type IV recommended by the IUPAC classification, a significant hysteresis loop can be observed, which indicates the development of mesoporosity within the material, and thus the material is beneficial to electrolyte ion's movement [20]. Nitrogen sorption analysis was used for calculating-specific surface area (SSA) using the Bruauer–Emmet–Teller equation. The SSA of the CA microspheres is 602.698 m^2g^{-1}. And the pore size distribution (PSD) of CA microspheres were determined by applying Barrett–Joiner–Halenda method to the adsorption isotherm. The PSD of the CA microspheres is shown in Fig. 3b. PSD plays an important role when we choose the ideal carbon material for supercapacitor. The sample shows sharp distribution having their average pore size at around 4.95 nm in the range of mesopore (between 2 and 50 nm), which ensure the access of electrolyte into the material and cause this sample to have higher capacitance.

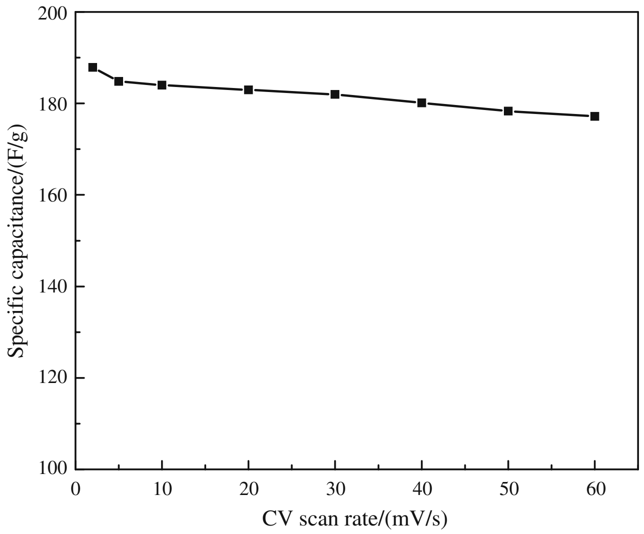


Fig. 5 Effects of CV scan rates on the specific capacitance of CA microspheres electrodes

Electrochemical characterization

Cyclic voltammetry was used to determine the electrochemical properties of the CA microspheres electrode. The CV curves at different scan rates are shown in Fig. 4. The CV curves are close to the ideal rectangular shape and they are mirror images with respect to the zero-current line. The results show a rapid current response on voltage reversal at each end potential, indicating that the electrode has better reversibility [21, 22]. Based on the CV curves, the specific capacitances were estimated on the basis of Eq. (1) [23].

$$C_{\mathrm{s.t}} = \frac{I_{\mathrm{a}} + |I_{\mathrm{c}}|}{2W(\mathrm{d}V/\mathrm{d}t)} \tag{1}$$

Where I_a, I_c, W, and dV/dt are the currents of anodic and cathodic voltammetric curves on positive and negative scans (*A*), mass of the electrode material (*g*), and the scan rate (*V/s*), respectively. $C_{\mathrm{s.t}}$ is the specific capacitance of electrode (F/g). The relationship between scan rate and the specific capacitance of CA microspheres electrodes in 6 M KOH solution are presented in Fig. 5. It can be seen that the specific capacitances have tiny decrease with the increase

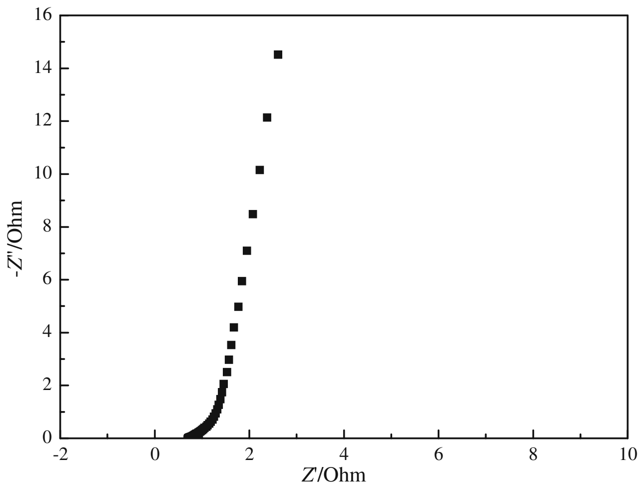


Fig. 6 Electrochemical impedance plot of the supercapacitor for the CA microspheres

of the potential scan rate and an excellent rate capability can be noted. Since CA microspheres have extensive mesopores and high electrical conductivity, the ions can easily transport into the pores of CA microspheres to form double-layer capacitance no matter whether the potential scan rate is low or high. The specific capacitance of CA microspheres electrode keeps approximately 180 F/g at different scan rates, and the maximal capacitance is up to 187.08 F/g at 2 mV/s.

The electrochemical impedance measurement of the CA microspheres supercapacitor is carried out (Fig. 6). The high-frequency intercept on the Z' axis represents the sum of the resistances (R_s) arising from the electrolyte, the intrinsic resistance of the active material, and the contact resistance between the active material and the current collector. In Fig. 6, a lower R_s of the CA microspheres supercapacitor in the aqueous system about 0.70 Ω is obtained, which is less than the reported results [16, 24, 25]. Moreover, the CA microspheres electrode exhibits a nearly vertical line at low frequency, showing an ideal capacitor behavior.

Table 1 Specific capacitance of supercapacitor at different charge/discharge currents

Current (mA)	Specific capacitance (F/g)
10	45.98
20	44.06
40	39.99
80	34.28

In order to gain further understanding on the electrochemical performances of the CA microspheres, the charge/discharge curves of electrode measured in 6 M KOH at different currents from 10 to 80 mA within a potential window (0 to 1.0 V) are shown in Fig. 7. It can be found that the capacitor voltage varies linearly with time and the curves are close to isosceles triangle, which indicates that the charging/discharging processes of the electrode are reversible and the material has a good cycling stability.

The average specific capacitance of the supercapacitor can be calculated on the basis of Eq. (2)[26]:

$$C_m = \frac{C}{m} = \frac{I \times t}{\Delta V \times m} \qquad (2)$$

Where C_m is the specific capacitance of supercapacitor (F/g), C is the capacitance measured (F), m is the mass of active material within supercapacitor (g), I is charge/

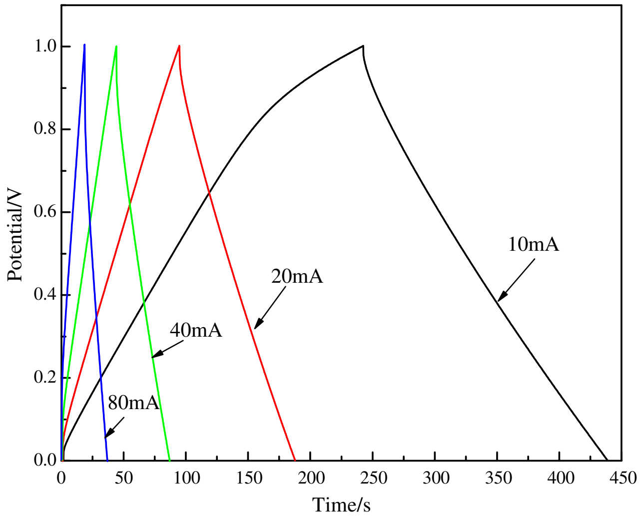


Fig. 7 Charge/discharge curves of CA microspheres supercapacitors at different charge/discharge currents

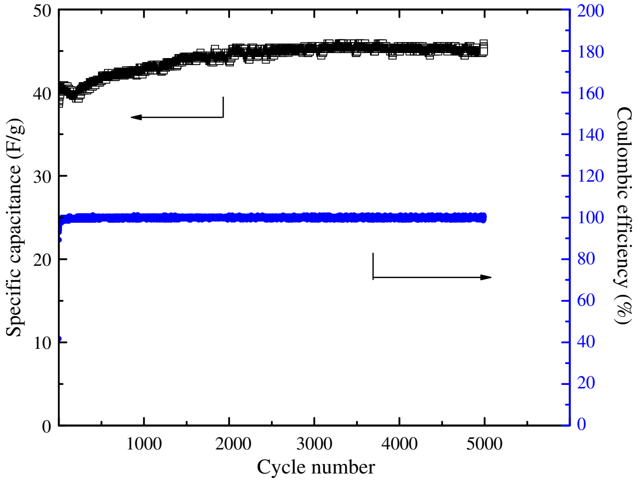


Fig. 8 Cycle life and coulombic efficiency of supercapacitor at a current of 20 mA

discharge current (A), t is the discharge time (s), and ΔV is the range of the charge/discharge (V). Based on the experimental results of Fig. 7, the specific capacitances of electrode calculated by Eq. (2) are tabulated in Table 1. It can be found that the specific capacitance decreases with the increase of charge/discharge currents, it may be caused by the internal resistance of the electrode, which leads to a large ohmic drop at large current density [3] and the ions cannot penetrate well into the inner of electrode materials due to slow diffusion at large current density. The highest capacitance of the supercapacitor is up to 45.98 F/g, which is larger than the carbon aerogel prepared using conventional method [2].

Usually, the stability of capacitors can be examined by repeated charge–discharge cycling, and the supercapacitor using carbon material as active electrode material exhibits a long cycle life. The CA microspheres supercapacitors were charged and discharged between 0 and 1.0 V at 20 mA in 6 M KOH solution. The variations of the discharge capacitance and the coulombic efficiency with cycle number are illustrated in Fig. 8. It can be found that the specific capacitance increases gradually with the increase of cycle before 2,000 cycles, then the specific capacitance keeps a stable value with shallow depth of numbers discharge till 5,000 cycles, and the coulombic efficiency (charge capacitance/discharge capacitance) remains above 99%.

Conclusions

The CA microspheres have been prepared by an inverse emulsion polymerization successfully. The as-prepared CA microspheres were typical mesoporous materials with truly spherical shape, which size were about 4 μm. The results of electrochemical measurements indicated that CA microspheres electrode had excellent electrochemical performance, high reversibility, high specific capacitance, a long cycle life, and low resistance in 6 M KOH electrolyte. The maximum capacitance of electrode obtained from cyclic voltammetry was up to 187.08 F/g. The capacitance of the supercapacitor with the CA microspheres as the electrode active materials was up to 45.98 F/g. After 5,000 cycles, the specific capacitance almost did not decrease, and the coulombic efficiency remained above 99%. Thus, the CA microspheres are an ideal electrode material for the application in supercapacitor.

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