Effects of Nitric Acid Activation on Textural, Surface, and Supercapacitive Properties of Ultra-Small Carbon Nanospheres

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Chemical activation of carbon materials is critical to modify their textural and surface properties in an effort to optimize their supercapacitive performance as electrode materials for supercapacitors. This present work investigates the effects of nitric acid activation on the textural, surface, and supercapacitive properties of ultra-small carbon nanospheres with a uniform size of 24 nm synthesized through a unique catalytic emulsion polymerization strategy. Nitric acid activation has been undertaken at different temperatures for various time. The effects of these two activation parameters have been systematically examined, with some important correlations established. The optimum activation conditions for achieving the best supercapacitive performance in different aqueous electrolytes have been identified.

Keywords carbon nanospheres, chemical activation, nitric acid, supercapacitors

Introduction

Porous carbon-based supercapacitors have received enormous research attention in recent years due to their valuable properties for energy storage, such as fast charging-discharging, high power density, and ultra-long cyclic stability compared to batteries.^[1] However, carbon-based supercapacitors still face the challenges of low energy density and poor rate performance at high currents, restricting their broader applications. While tuning textural properties of the porous carbons (such as surface area, pore length, and pore size distribution) is a common way to improve their supercapacitive properties, surface functionalization of carbon materials with functional groups containing foreign atoms such as oxygen, nitrogen, boron, and phosphorous can also efficiently improve their supercapacitive performances.^[2] Methods to introduce foreign atoms to carbon materials include chemical oxidation, electrochemical oxidation, cold plasma treatment, and gaseous oxidation. Among them, chemical oxidation is most common to improve the supercapacitive performance by enhancing energy and power densities.^[3]

Commonly used chemical oxidation agents include nitric acid, sulfuric acid, potassium hydroxide, etc. In particular, nitric acid is often used as a strong oxidant to introduce some functional groups to the surface of carbon materials.^[4] These groups can improve the wettability of the electrode materials to enhance the utilization of the surface area and can also provide pseudocapacitive properties caused by redox reactions of carbonyl-type surface oxygen groups. These changes may also affect the specific surface area and pore structure of the carbon materials, and lead to a notable improvement of the specific capacitance and the cyclic performance.^[5] Nitric acid activation is usually conducted at a moderate temperature (25–80 °C), and easily introduces oxygen functional groups, albeit sometimes at the sacrifice of the morphology and textural characteristics of the carbon materials.

A large variety of carbon materials obtained from different precursors/strategies have thus far been investigated for nitric acid activation, with significant improvements in specific capacitance yielded. These include char- and biowaste-derived carbon materials,^[6–7] ordered mesoporous/macroporous carbons by both hard and soft templating,^[8–15] graphene,^[16] calcium carbide derived carbon,^[17] and carbon spheres.^[18]

Our group has recently developed a catalytic emulsion polymerization technique for the convenient, tailored synthesis of ultra-small carbon nanospheres (CNSs) with uniform, tunable ultra-small sizes within 10–50 nm.^[19] In this technique, tightly cross-linked polymer nanospheres of 1,3-diethynylbenzene (DEB) were firstly produced *via* catalytic emulsion polymerization. The polymer nanospheres were carbonized to render well-defined carbon nanospheres. Activated CNSs obtained by KOH activation showed superior supercapacitive performance with high specific capacitance and high rate performance at high currents.^[19] Nevertheless, the as-produced CNSs without undergoing activation are featured with restricted hydrophobic surface area (550 m²·g^{−1}), though having some micropores, and thus limited supercapacitance. Different from our previous study, to improve their supercapacitive performance, the CNSs are herein activated with concentrated nitric acid as the activation agent. A systematic study on the effects of activation parameters on the textural/surface properties and supercapacitive performance of the resulting nitric acid activated CNSs in different electrolytes has been undertaken. The correlations between the acidic activation and supercapacitive performance of this range of CNSs provide important guidelines for their proper usage as electrode materials in supercapacitors.

Experimental

Materials

Chemicals, including 1,3-diethynylbenzene (DEB, 97%, Al-

drich), sodium dodecyl sulphate ($\geq 98.5\%$, Aldrich), palladium acetate (98%, Strem Chemicals), α, α' -bis(di-*tert*-butylphosphino)-*o*-xylene (97%, Strem Chemicals), methanol (ACS reagent, Fisher Scientific), methanesulfonic acid (99.5%, Aldrich), dichloromethane (HPLC grade, Aldrich), nitric acid (69.3 wt%, Fisher Scientific), sulfuric acid (96.9 wt%, Fisher Scientific), potassium hydroxide (reagent grade, 90%, flakes, Aldrich), titanium foil (99.95%, Aldrich), nafion solution (5 wt% in lower aliphatic alcohols, Aldrich), platinum wire (0.5 mm in diameter, 99.95%, Strem Chemicals), and conducting carbon (acetylene black 100%, Soltex) were used as received without any additional purification. Deionized (DI) water was purified by a Barnstead-Synbron Nanopure II purification system.

Synthesis of CNS from polyDEB polymer nanospheres by catalytic emulsion polymerization

Cross-linked polyDEB nanospheres of a size of 24 nm were prepared by Pd-catalyzed emulsion polymerization, followed with a subsequent hydrothermal treatment. A typical procedure is as follows. Sodium dodecyl sulfate (0.8 g) was dissolved in deionized water (15.6 g) in a round-bottom Schlenk flask. DEB (1.86 g, 14.74 mmol) was then added under nitrogen protection. The solution was sonicated for 15 min and was vigorously stirred in a water bath set at 60 °C for 5 h to achieve a stable emulsion. In the meantime, palladium acetate (3.31 mg, 14.74 μmol) and α, α' -bis(di-*tert*-butylphosphino)-*o*-xylene (17.45 mg, 44.40 μmol) were dissolved in a mixed solvent containing 0.54 mL of dichloromethane and 0.06 mL of methanol in a small vial. The mixture was sonicated at room temperature for 10 min until all the solids were dissolved. The catalyst mixture was then injected into the polymerization flask under stirring at 450 rpm and 60 °C, followed with the addition of three drops of methanesulfonic acid to generate catalytically active cationic Pd species to start the polymerization. The emulsion polymerization lasted overnight, rendering a dark brown emulsion dispersion.

The resulting emulsion was diluted in DI water, and placed into an autoclave for hydrothermal treatment. In the hydrothermal treatment, the autoclave containing the mixture was heated to 220 °C in an oven overnight (about 15 h) and was then allowed to cool down to room temperature naturally. The resulting hydrothermally treated polymer was collected by filtration, washed with a large amount of deionized water, and then dried under vacuum at 60 °C for 48 h.

The CNS sample was obtained by carbonizing the hydrothermally treated polymer nanospheres in a tube furnace to 800 °C at a heating rate of 10 °C·min⁻¹ in a N₂ atmosphere and held at 800 °C for 1 h.

Nitric acid activation of CNS

In a typical activation process, 100 mg of CNS was dispersed in 10 mL of concentrated nitric acid (69.3 wt%) and was stirred with a magnetic stirrer (at 450 rpm) in a preheated oil bath set at a prescribed temperature. Several nitric acid-activated CNS samples were prepared by varying the temperature (25, 50, 80, or 100 °C) and activation time (2 or 4 h). The activated products were washed with a large amount of deionized water until a pH of ~ 7 was reached, further washing three times with ethanol, the product was finally dried under vacuum. Nitric acid activated CNS samples were termed correspondingly as A-CNS-xCyh with prefix A-CNS noting activated carbons, x noting nitric acid activation temperature (in °C), and y noting activation time (in h).

Characterizations and measurements

The polymer emulsion obtained following the catalytic

emulsion polymerization was characterized with a Malvern Instruments Nanosizer S90 dynamic light scattering (DLS) instrument for the size distribution of polymer nanospheres. Transmission electron microscopy (TEM) measurements of the polymer and carbon nanospheres were taken on a JEOL 2010F field emission electron microscope operated at 200 keV. Fourier-transform infrared (FTIR) spectroscopic characterization of the A-CNS samples was performed on a Thermo Scientific Nicolet 6700 Analytical FTIR spectrometer. Thermogravimetric analysis (TGA) of the A-CNS samples was carried out on a TA Instruments Q50 TGA. Measurements were performed in a nitrogen atmosphere. The samples were first heated to 100 °C at a rate of 10 °C·min⁻¹, held at 100 °C for 10 min, and then heated to 800 °C at a heating rate of 10 °C·min⁻¹.

The surface area, pore volume, and pore size distribution of the carbon samples were measured using a Micromeritics ASAP 2020 physisorption analyzer by N₂ sorption at 77 K. The specific surface area was calculated from the Braunaummett-Teller (BET) method. Non-local density function theory (NLDFT) model was used to obtain both micropore size distribution and mesopore/macropore size distribution from N₂ desorption. All carbon samples were degassed at 200 °C for 30 h before each sorption analysis.

Electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed on a Metrohm Autolab PGSTAT100 electrochemical instrument in both 2 and 3-electrode cells. In 3-electrode tests, a coiled platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode, with 2 M KOH or 1 M H₂SO₄ aqueous solution as the electrolyte.

For electrochemical testing in KOH, working electrodes were prepared with nickel foam (1 cm²) as the current collector. To prepare the electrode, the carbon sample (80 wt%), conducting carbon (10 wt%), and Nafion (10 wt%) were dispersed in ethanol under sonication in a small vial. The dispersion was evenly coated on two pieces of nickel foam by drop casting. Subsequently, both pieces of nickel foam were dried in an oven at 100 °C for ca. 2 h and pressed together under 2 tons of pressure to a thickness of ~ 0.5 mm. The loading of active material on each electrode is about 2.5 mg at a density of 2.5 mg·cm⁻². The electrode was then soaked in KOH electrolyte for 4 h under vacuum. CV curves were obtained between -1 and 0 V (vs. SCE) at different scan rates (200, 100, 50, 25, 10, 5 mV·s⁻¹, respectively). GCD measurements were performed at current densities of 30, 20, 10, 5, 3, 2, 1 and 0.5 A·g⁻¹, respectively, within -1 and 0 V (vs. SCE). EIS measurements were conducted at the open circuit potential between 0.01 Hz and 10 kHz with an AC perturbation of 10 mV.

The specific capacitance (C_{sp} in F·g⁻¹) was calculated from the CV curves through the following equation:^[19,20]

$$C_{\text{sp}} = \frac{1}{m\Delta V} \int i dV \quad (2.1)$$

where i and V are the current and voltage, respectively, in the CV curves, $\int i dV$ is the integration of the current loop over the whole voltage range, m is the mass of the active carbon, and ν is the scan rate. The specific capacitance was also calculated from the GCD discharge curve through the following equation:^[19,20]

$$C_{\text{sp}} = \frac{Q}{m\Delta V} \quad (2.2)$$

where i is the discharge current, m is carbon mass, and dV/dt is calculated as the slope of the discharge curve within the voltage range following the end of Ohmic drop to the end of the discharge curve. In all CV and GCD measurements, the cell was cycled until negligible changes were observed (*ca.* 10 cycles) prior to recording the data for calculation. The measurements in 1 M H₂SO₄ electrolyte were done similarly except within the voltage window of -0.2 and 0.8 V.

A symmetric 2-electrode cell was also prepared with A-CNS-80C4h as the active carbon. The two electrodes, prepared on nickel foam in the same manner as in the 3-electrode test, were separated with a filtration paper soaked in 2 M KOH. CV, GCD, and EIS measurements were performed in the voltage range of $0-1$ V. The specific capacitance was calculated from CV and GCD data according to Equations 2.3 and 2.4, respectively:

$$C_{sp} = \frac{\int i dV}{m \Delta V} \quad (2.3)$$

$$C_{sp} = \frac{2i}{m dV/dt} \quad (2.4)$$

where i is the current, V is voltage, $\int i dV$ is the integration of the current loop over $0-1$ V, m is the mass of the active carbon material in each electrode, v is the rate of voltage scan and dV/dt is calculated as the discharge slope within the voltage range from the end of ohmic drop to the end of the discharge curve.

Results and Discussion

Synthesis and characterization of CNS

The CNS studied herein is obtained by convenient carbonization of highly cross-linked polyDEB nanospheres as the polymer precursor. The polymer nanospheres are synthesized by direct Pd-catalyzed emulsion polymerization of DEB as a difunctional acetylenic monomer.^[19] This unique method for synthesis of CNSs was firstly developed by our research group. For the emulsion polymerization, DEB is firstly emulsified (with the use of an anionic surfactant, SDS) in a continuous phase of water to form oil-in-water emulsion. The subsequent addition of a diphosphine-ligated Pd(II) catalyst system renders effectively the cross-linked polyDEB nanospheres stabilized by SDS.^[19] During the polymerization, DEB is incorporated through one of its two alkyne groups, rendering a pendant alkyne group that can be subsequently enchain to render a cross-linked structure.^[21,22] DLS characterization was undertaken on the resulting polymer emulsion to determine the average particle size and particle size distribution of the polymer nanospheres. Figure 1a illustrates the particle size distribution, which shows a single narrow peak with Z-average size of *ca.* 24 nm and the polydispersity index (PDI) of 0.074. Such a low PDI suggests that the polymer nanospheres have very uniform sphere size and are well dispersed in water.

Subsequently, the resulting polymer nanosphere sample was hydrothermally treated at 220 °C and then carbonized under N₂ to render CNS. During the hydrothermal treatment, surfactant SDS degrades and polymer nanoparticles aggregate together to generate hierarchical intersphere mesopores and macropores.^[19] The originally clear emulsion became cloudy with the presence of visible big particles with sizes in the millimeter scale. The FTIR spectra of the polymer samples before

and after hydrothermal treatments are shown in Figure 1b. Five characteristic bands (1591, 2107, 2856, 2926, and 3295 cm⁻¹) are observed in the spectra. In particular, peaks found at 3295 and 2107 cm⁻¹ correspond to $\nu_{\text{C}=\text{C}-\text{H}}$ band and $\nu_{\text{C}=\text{C}}$ bands of the pendent, unreacted triple bonds. Those around 1591 cm⁻¹ are characteristic of the stretching vibrations of the conjugated double bonds, and peaks at 2856 and 2926 cm⁻¹ indicate the presence of C—H single band.^[22] In the hydrothermally treated sample, the triple bond peaks disappear completely, indicating the degradation and/or further cross-linking reaction of the pendant triple bonds during the hydrothermal treatment.

Figure 1 (a) DLS size distribution of the polymer nanospheres in the as-produced emulsion; (b) FTIR spectra of as produced PDEB nanospheres and the hydrothermally treated sample.

The direct carbonization of the hydrothermally-treated polymer nanosphere sample at 800 °C for 1 h under N₂ protection renders the CNS sample. A TEM image of the unactivated CNS is shown in Figure 2a. Uniform nanospheres with an average sphere size of about 24 nm are observed, which is in good agreement with the DLS size found above for the polymer nanospheres. The mesopores and macropores resulting from packing/aggregation of the nanospheres are also clearly seen. N₂ sorption isotherm and mesopore/macropore size distribution curve for the CNS sample are shown in Figures 2b and 2c, respectively. Figure 2b shows a type IV isotherm, with a slight uptake in the low relative pressure range ($P/P_0 < 0.1$) and a

Figure 2 (a) TEM image; (b) N₂ sorption isotherm, (c) mesopore size distribution (determined with NLDFT model), and (d) micropore size distribution (determined with NLDFT model) of CNS.

Table 1 Results from N₂ sorption and contact angle measurements

Carbon Sample	Surface Area ^a / (m ² ·g ⁻¹)			Pore Volume ^b / (cm ³ ·g ⁻¹)			Average Pore Size ^c / (Å)		Contact Angle/ (°)		
	S _{BET}	S _{d>20Å}	%S _{d>20Å}	V _{total}	V _{d>20Å}	%V _{d>20Å}	d _{meso}	d _{micro}	Water	1 M H ₂ SO ₄	2 M KOH
CNS	591	252	43%	1.81	1.66	92	429	6.8	134	116	119
A-CNS25C2h	493	243	49%	1.81	1.70	94	425	8.1			
A-CNS25C4h	482	244	51%	1.94	1.83	94	426	8.3	133	116	119
A-CNS50C2h	487	235	48%	1.67	1.55	93	430	7.0			
A-CNS50C4h	512	238	46%	2.00	1.88	94	417	8.0	118	114	109
A-CNS80C2h	470	230	49%	1.59	1.48	93	400	8.2			
A-CNS80C4h	532	238	45%	2.00	1.87	94	429	7.7	102	125	97
A-CNS100C2h	596	275	46%	2.00	1.86	93	432	n.d.			
A-CNS100C4h	0.23			0							

^a Surface area of mesopores/macropores ($S_{d>20\text{ Å}}$) determined with *t*-plot method. The percentage data denote the percentage of surface area of mesopores relative to the total surface area. ^b Total pore volume (V_{total}), mesopore/macropore volume ($V_{d>20\text{ Å}}$) determined with *t*-plot method. The percentage data denote the percentage of mesopore/macropore volume relative to the total pore volume. ^c Average mesopore/macropore size (d_{meso}) determined from the N₂ desorption data with NLDFT model. Average micropore size (d_{micro}) determined with NLDFT model.

sharp intense uptake at the high relative pressure end ($0.8 < P/P_0 < 1$) with a distinct H1 type hysteresis loop characteristic of the packing/aggregates of uniform spheres in a regular manner.^[19] Its specific BET surface area (S_{BET}) is 591 m²·g⁻¹, with 57% of the surface area originating from micropores. Its total pore volume is high at 1.81 cm³·g⁻¹ and its micropore volume is, however, low at 0.18 cm³·g⁻¹ arising from intra-sphere micropores. These N₂ sorption results are summarized in Table 1. These data suggest the presence of abundant inter-sphere mesopores/macropores resulting from packing and aggregation of the nanospheres. From Figure 2c, CNS has a broad mesopore/macropore size range primarily from 20 nm to 63 nm, with the average size of ca. 43 nm. Figure 2d shows its micropore size distribution, with the majority of micropores less than 6 Å and a small portion within 10–12 Å.

Composed nearly exclusively of carbon, the unactivated CNS sample is highly hydrophobic. From the contact angle measurements on a thin film of CNS coated on carbon-coated aluminum foil as the substrate, the contact angle of DI water, 1 M H₂SO₄ solution, and 2 M KOH solution on the CNS film is 134°, 116°, and 118°, respectively (see Table 1). The latter two solutions are commonly employed as the aqueous electrolytes for porous carbon-based supercapacitors. Such a highly hydrophobic nature prevents the sufficient wetting of the surface with the aqueous electrolyte. Along with the low surface area, this feature renders the CNS with poor supercapacitive performance in aqueous electrolytes (such as KOH and H₂SO₄) with low specific capacitance even at low current densities as shown below, despite the expected short micropore length arising from its ultra-small nanosphere sizes.

Nitric acid activation of CNS and characterizations

CNS is activated herein in concentrated nitric acid (69.3 wt%) at various temperature (25–100 °C) for different time (2 or 4 h). The resulting A-CNS samples have been thoroughly characterized for their spectroscopic feature, and textural/surface properties. The effects of the activation parameters (temperature and time) on these properties have been examined. Figure S1 in Supporting Information shows the N₂ sorption isotherms of the various A-CNS samples (A-CNS25C2h, A-CNS25C4h, A-CNS50C2h, A-CNS50C4h, A-CNS80C2h, A-CNS80C4h, A-CNS100C2h), which resemble very well that of the unactivated CNS with the distinct type IV isotherm and H1 type hysteresis loop. This indicates the very well retained

nanosphere structures and textures in the nitric acid-activated samples within the activation condition range (*i.e.*, temperature ≤ 80 °C and time ≤ 4 h; up to 2 h at 100 °C) despite the surface oxidation. At the highest activation temperature of 100 °C, a complete collapse of the nanosphere structure, however, occurred with negligible N₂ sorption observed when the activation time was extended beyond 2 h. This indicates the severe harsh oxidation of the carbon material by nitric acid at 100 °C. The results (surface area, pore volume, average pore size) obtained from the N₂ sorption analysis are summarized in Table 1.

The mesopore/macropore and micropore size distributions of the various A-CNS samples are shown in Figures S2 and S3, respectively, in Supporting Information. Except the activated sample at 100 °C for 4 h that shows negligible surface area/pore volume, only insignificant marginal changes with the textural parameters are observed at the activation conditions ($T \leq 80\text{ °C}$ and $t \leq 4\text{ h}$; $t \leq 2\text{ h}$ at 100 °C). This differs from chemical activation with KOH as the activation agent, which leads to the significant enhancements in both surface area and pore volume by creating more pore structures.^[19,21] Herein, minor decreases in the surface area are instead noticed after nitric acid activation, which possibly result from some minor structural collapse after the activation and/or the occlusion of some micropores due to the generation of surface functionalities. A decrease in surface area was also seen with other carbons following nitric acid activation.^[12]

Though having only marginal effects on textural properties, nitric acid activation has been found to be highly effective in introducing surface functionalities onto the resulting activated carbons. Spectroscopic characterizations have been undertaken to monitor chemical composition changes on the surface of the carbon samples before and after nitric acid modification. Figure 3a shows the FTIR spectra of CNS, A-CNS25C4h, A-CNS50C4h, and A-CNS80C4h. A broad peak at around 3432 cm⁻¹ is observed in all the four samples, which is mainly caused by the O–H stretching vibration of the adsorbed water.^[8] Another broad band is observed at 1239 cm⁻¹, which should be caused by the stretching vibration of the C–O–C bonds.^[8] In addition, the C=O stretching vibrations related to carbonyl and/or carboxyl groups can be found at around 1733 cm⁻¹.^[8] The spectra of the nitric acid activated samples are similar to that of the unactivated CNS, except with significantly more intense bands at 1733 cm⁻¹ and 1239 cm⁻¹. This indicates the presence of more oxygen-containing functional groups on the surface of the activated samples. Moreover, with the increase of

Figure 3 (a) FTIR spectra, (b) TGA thermograms, and (c) XPS survey spectra of unactivated and nitric acid-activated carbon samples; (d) TEM image of A-CNS50C4h; (e) images of droplets of different solutions on thin films of different carbon materials for contact angle determination.

the activation temperature from 25 to 80 °C, the intensity of these two bands increases gradually.

Figure 3b compares TGA curves of unactivated CNS and the three activated samples. The weight loss in TGA can be roughly considered as the amount of surface functional groups present on nitric acid activated samples.^[16] For unactivated CNS, there is nearly no weight loss by 500 °C, showing a relatively clean porous carbon surface. For the activated samples, the weight loss at 500 °C increases with the increasing activation temperature. In particular, the weight loss for A-CNS80C4h at 500 °C exceeds 15%. The TGA results also confirm the increasing quantity of surface functional groups with the increase of activation temperature.^[23]

Figure 3c shows the XPS survey spectra of unactivated CNS and three activated samples, A-CNS25C4h, A-CNS50C4h, and A-CNS80C4h. Carbon and oxygen are the two predominant elements in these carbon samples, with only trace amounts of N, P, and Pd. Relative to unactivated CNS (oxygen atomic content: 4.4%), the three activated samples show enhanced oxygen atomic content (8.6%, 10.0%, and 14.8%, respectively), which increases with the increase of the activation temperature from 25 to 80 °C. This further confirms the increasing quantity of oxygen-containing surface functionalities upon the increase of nitric acid activation temperature. Figure S4 in Supporting Information shows the C_{1s} and O_{1s} spectra of the various samples. Deconvoluted XPS peaks attributable to oxygen-containing functionalities, including C—O, C=O, and OH, can be noted. Figure 3d shows a TEM image of A-CNS50C4h as a representative activated sample, which verifies the well retained nanosphere morphology.

To investigate the effects of nitric acid activation on the surface wetting properties by different electrolytes, the contact angles of the different carbons towards three aqueous solutions (DI water, 2 M KOH, and 1 M H_2SO_4) were measured (see Table 1; Figure 3e). Such surface wetting properties revealed by contact angle data should affect supercapacitive properties of these carbon materials.^[24] Due to the enhanced content of hydrophilic oxygen-containing surface functionalities, the surface wetting properties of the activated samples show significant improvement towards water and 2 M KOH solution. The contact angles of DI water and 2 M KOH solution on the thin films of the activated carbon samples all show a clear trend of decrease with the increase of activation temperature. The unactivated CNS shows contact angles of 134° and 119° for DI

water and 2 M KOH solution, respectively. Upon nitric acid activation, the water contact angles for A-CNS25C4h, A-CNS50C4h, and A-CNS80C4h are 133°, 118°, and 102°, respectively; the corresponding values for 2 M KOH solution are 119°, 109°, and 97°, respectively. These indicate the enhanced surface wetness of the carbon material by DI water and 2 M KOH solution following nitric acid activation, which should be beneficial to the improvement in supercapacitive properties in 2 M KOH electrolyte due to the improved infiltration of the electrolytes into the pores for better wetting. On the contrary, relative to the value of 116° for the unactivated CNS, the contact angle for 1 M H_2SO_4 solution shows an opposite trend of change (116, 114, and 125°, respectively) with instead a slight increase upon the increase of activation temperature, suggestive of the deterioration in surface wetting by 1 M H_2SO_4 solution upon activation. This leads to our expectation of their deteriorated supercapacitive properties in 1 M H_2SO_4 electrolyte upon the enhanced surface activation at the elevated temperature. These contact angle data also indicate that the surface acidity on the activated carbon materials affects the surface wetting properties of the carbon materials, with enhanced wetting noted with the basic 2 M KOH solution and deteriorated wetting with the acidic 1 M H_2SO_4 solution.

Supercapacitive performance of activated CNS in 2 M KOH electrolyte

The supercapacitive properties of the A-CNS samples were firstly evaluated in a 3-electrode cell with 2 M KOH as the aqueous electrolyte by CV, GCD, and EIS measurements. The working electrodes were prepared by loading the carbon samples on nickel foam. The measurements were all undertaken within a voltage range of −1.0 to 0 V (vs. SCE).

Figure 4a shows the CV curves of all activated samples and unactivated between −1.0 and 0 V (vs. SCE) at the scan rate of 10 $mV \cdot s^{-1}$. Figure 4c shows the CV curves of A-CNS80C4h at different scan rates from 10 to 200 $mV \cdot s^{-1}$. While the unactivated CNS shows a quasi-rectangular curve (see Figure 4a), the activated samples generally show weak but broad redox peaks absent in the unactivated CNS, which should result from the redox reactions of the oxygen-containing functionalities on the surface of the activated carbon materials. The specific capacitance data calculated from the CV curves are listed in Table 2. At 10 mV/s, it increases by following the order: CNS (71 $F \cdot g^{-1}$) < A-CNS25C2h (118 $F \cdot g^{-1}$) $\approx$ A-CNS25C4h (118 $F \cdot g^{-1}$) < A-CNS50C2h (131 $F \cdot g^{-1}$) < A-CNS50C4h (141 $F \cdot g^{-1}$) $\approx$

Figure 4 (a) CV curves (at 10 mV s^{-1}) and (b) GCD curves (at 0.5 A g^{-1}) of the various carbon samples; (c) CV curves at various scanning rates and (d) GCD curves at various current densities of A-CNS80C4h; (e) capacitance retention (relative to 0.5 A g^{-1}) of various samples at different current densities; (f) Nyquist plots of various samples. All measurements were undertaken in a 3-electrode cell in 2 M KOH.

A-CNS80C2h (140 F g^{-1}) < A-CNS100C2h (144 F g^{-1}) $\approx$ A-CNS80C4h (144 F g^{-1}). This order follows very well the decrease in contact angle, or the increased surface wetness, for 2 M KOH solution observed above upon nitric acid activation. It indicates the direct correlation between electrolyte contact angle/surface wetting and the specific capacitance. Among all carbon samples, A-CNS80C4h appears to have the highest specific capacitance at all CV scanning rates. All the activated samples, except that collapsed at 100°C , thus have significantly enhanced specific capacitance relative to unactivated CNS of hydrophobic surface, showing the positive effects of the activation given the modification of the surface properties of the carbon materials due to the enhanced content of the surface functionalities for pseudocapacitance and improved surface wetting.

A similar trend of change is observed at other scan rates. This trend of change reflects the effects of activation temperature and time on the specific capacitance. At a given activation time (2 or 4 h), the increase of activation temperature from 25 to 80°C leads to consistent, appreciable increases in the specific capacitance; however, a further increase from 80 to 100°C leads to a slight decrease in specific capacitance possibly due to the collapse of some pore structure at the harsh condition of 100°C . At the lowest temperature of 25°C , extending the activation time from 2 to 4 h has negligible effects on the specific capacitance due to the low reactivity at this temperature. At the highest temperature of 100°C , extending the time from 2 to 4 h leads to complete collapse of pore structures. At any intermediate temperature (50 or 80°C), increasing the activation time leads to appreciably enhanced specific capacitance. In particular, the combination of 80°C and 4 h appears to be the optimum activation condition given the highest specific capacitance of A-CNS80C4h among all samples in all the CV measurements.

The GCD curves of the various carbon samples obtained at the current density of 0.5 A g^{-1} are shown in Figure 4b. The GCD curves at different current densities for the representative

carbon, A-CNS80C4h, are shown in Figure 4d. Table 2 summarizes the specific capacitance results calculated from the GCD measurements at different current densities from 0.5 to 50 A g^{-1} . The GCD curves are generally triangle-like and show a strong dependence of discharge time on current density. The voltage drop resulting from equivalent series resistance (ESR) is favorably very small (even at high current density of 30 and 50 A g^{-1} , see the inset in Figure 4d), which is also confirmed with EIS results to be shown below.

A similar order of change, as above from CV measurements, is found with the specific capacitance data obtained from GCD measurements among the samples, with A-CNS80C4h showing the best specific capacitance nearly at all current densities (e.g., 172 F g^{-1} at 0.5 A g^{-1}). Similar to an earlier study by Lang *et al.*,^[9] even though the specific surface area and pore volume decrease slightly after nitric acid activation, the specific capacitance increase markedly in 2 M KOH electrolyte after concentrated nitric acid activation. This increase should result in part from the pseudocapacitive effects of the surface functional groups following the strong oxidation with the concentrated nitric acid. Meanwhile, the enhanced surface hydrophilicity upon nitric acid activation may also help the diffusion of the electrolyte and thus contribute to the enhanced specific capacitance.

Figure 4e shows the capacitance retention (relative to the corresponding values at 0.5 A g^{-1}) at different current densities for the carbon samples. All carbon samples have the extremely high capacitance retention of about 90% and 83% at the high current density of 10 and 50 A g^{-1} , respectively, except A-CNS100C2h with relatively lower retention values of 83% and 73%, respectively. The rate performance found here with these samples are even superior to many high-rate carbon-based electrode materials reported in the literature. In an earlier study by our group,^[21] activated carbon microparticles without hierarchical pore structures obtained from homopolymer of DEB by KOH activation has a much lower capacitance retention of only 56% at 10 A g^{-1} , where the carbon samples contain

Table 2 Specific capacitance data (in $\text{F}\cdot\text{g}^{-1}$) of various carbon samples obtained from CV and GCD measurements in 3-electrode cell in 2 M KOH

Scanning rate ($\text{mV}\cdot\text{s}^{-1}$) or current density ($\text{A}\cdot\text{g}^{-1}$)	CNS	A-CNS25C2h	A-CNS25C4h	A-CNS50C2h	A-CNS50C4h	A-CNS80C2h	A-CNS80C4h	A-CNS100C2h
CV								
200	62	98	99	99	105	101	130	110
100	68	112	110	116	124	122	145	129
50	72	120	116	125	135	134	152	142
25	73	123	119	131	141	140	152	147
10	71	118	118	131	141	140	144	144
GCD								
0.5	86	140	146	146	159	156	172	165
1	83	136	137	142	154	151	165	156
2	80	133	131	139	151	148	161	152
3	79	131	128	137	149	146	159	150
5	77	128	125	135	147	143	157	148
10	75	125	121	132	143	140	154	136
20	74	122	118	129	139	135	150	130
30	73	120	117	126	136	133	148	125
50	72	116	116	123	131	128	143	121

primarily micropores. As Zhu *et al.* mentioned, the quick decrease of specific capacitance at high current density is caused by insufficient ion transport and/or the relatively insufficient faradic redox reaction of the carbon samples under higher discharge current densities.^[8] For the carbon nanosphere samples herein with abundant large mesopores and macropores, fast transport of ions can be facilitated to render advantageously high capacitance retention at high currents.

Figure 4f shows the Nyquist plots of activated and unactivated samples, obtained from EIS measurements within the frequency range of 10 kHz to 0.01 Hz. Typical of electrical double layer capacitors (EDLCs), all carbon samples show a semicircle at high frequency and a nearly vertical line at low frequency.^[25] The expanded semicircle in the high frequency region is given in the inset. Equivalent serial resistance (ESR) can be calculated from the intercept of the semicircle at real axis (Z'), which is affected by ionic resistance of the electrolyte, internal resistance of the carbon materials and current collector, and contact resistance at the carbon material/current collector interface. Low ESR values in the range of 0.1–1.9 Ω are found with unactivated and nitric acid activated carbons, which are also reflected in the low voltage drop in the GCD curves as mentioned earlier (see Figure 4d). At the low frequencies, the Warburg-type line (with a slope of 45°) is not obvious, indicating that ion transfer within micropores occur fast in these carbons due to short micropore length and abundant mesopores/macropores.^[19]

Based on the supercapacitive results obtained from 3-electrode cell, we have subsequently fabricated a symmetric 2-electrode cell using A-CNS80C4h as the electrode material since it shows the highest specific capacitance in 3-electrode cell configuration. Electrochemical measurements were undertaken in aqueous 2 M KOH electrolyte within the voltage window of 0–1 V. Unlike those measured in 3-electrode cell, the CV curves of the 2-electrode cell at different scan rates (Figure 5a) are nearly rectangular with a specific capacitance of 121 $\text{F}\cdot\text{g}^{-1}$ at 10 $\text{mV}\cdot\text{s}^{-1}$. The GCD curves in Figure 5b exhibit a triangle-like shape and the voltage drop resulting from discharge is very small even at the highest current density of 50 $\text{A}\cdot\text{g}^{-1}$. The specific capacitance data calculated from GCD curves are 158, 139, 119, 115, and 98 $\text{F}\cdot\text{g}^{-1}$ at 0.1, 0.5, 5, 10, and 50 $\text{A}\cdot\text{g}^{-1}$, respectively (Figure 5c). The capacitance retention at 10 and 50 $\text{A}\cdot\text{g}^{-1}$ is 73% and 62%, respectively, relative to the value at 0.1 $\text{A}\cdot\text{g}^{-1}$. These percentages of capacitance retention are high,

relative to a retention of 52% at 10 $\text{A}\cdot\text{g}^{-1}$ reported by our group for a 2-electrode cell fabricated with KOH-activated carbon microparticles obtained from homopolymer of DEB.^[21] Relative to those obtained from GCD measurements in a 3-electrode cell at identical current densities, the capacitance values measured in 2-electrode cell are lower due to the heightened sensitivity of 3-electrode cell.^[26] Figure 5d shows the Nyquist plot of the 2-electrode cell with an ESR of 0.56 Ω . This ESR value is nearly twice of that (0.34 Ω) in 3-electrode cell. Figure 5e shows the cyclic stability of the 2-electrode cell over 2500 GCD cycles at 5 $\text{A}\cdot\text{g}^{-1}$. The specific capacitance is very stable with 91% of retention after 2500 cycles, demonstrating the excellent stability of the 2-electrode cell built with the activated carbon nanosphere sample.

Supercapacitive performance of activated CNS in 1 M H_2SO_4 electrolyte

The supercapacitive properties of nitric acid activated CNS samples were further evaluated in 1 M H_2SO_4 electrolyte in a 3-electrode cell. Electrodes were prepared by loading the carbons on Ti foil. Given the use of acidic electrolyte, the CV and GCD measurements were performed within the voltage range of –0.2 to 0.8 V (vs. SCE).

Figure 6a shows the CV curves of the electrodes made with the various carbons at the scan rate of 10 $\text{mV}\cdot\text{s}^{-1}$. Figure 6c shows the CV curves for A-CNS25C2h as a representative activated carbon at various scan rates. The CV curve of the unactivated CNS has a nearly perfect rectangular shape at 10 $\text{mV}\cdot\text{s}^{-1}$, suggesting its absence of significant surface functionalities. All the activated samples show redox peaks centered at around 0.3 (anodic mode) and 0.2 V (cathodic mode), respectively. Arising from redox reactions of the oxygen-containing carbonyl functionalities, these peaks contribute to Faradic pseudocapacitance.^[12] Table 3 lists the specific capacitance data calculated from the CV measurements. Though the activated carbons generally show enhanced specific capacitance than the unactivated one due to the pseudocapacitance resulting from the surface functionality, a very different trend of change is observed with the respect to the effects of activation temperature and time on the capacitance value in the acidic electrolyte relative to that in basic electrolyte. In 1 M H_2SO_4 electrolyte, the specific capacitance at each scan rate increases by following the general order: CNS $\approx$ A-CNS100C2h < A-CNS80C4h < A-CNS80C2h < A-CNS50C2h $\approx$ A-CNS50C4h

Figure 5 (a) CV curves at various scanning rates and (b) GCD curves at various current densities of a two-electrode cell fabricated with A-CNS80C4h in 2 M KOH; (c) plot of specific capacitance as a function of current density obtained from the GCD data; (d) Nyquist plot of the two-electrode cell; (e) cyclic stability of the two-electrode cell at $5 \text{ A} \cdot \text{g}^{-1}$ over 2500 GCD cycles.

Figure 6 (a) CV curves (at $10 \text{ mV} \cdot \text{s}^{-1}$) and (b) GCD curves (at $0.5 \text{ A} \cdot \text{g}^{-1}$) of various carbon samples; (c) CV curves at various scanning rates and (d) GCD curves at various current densities of A-CNS25C2h; (e) capacitance retention (relative to $0.5 \text{ A} \cdot \text{g}^{-1}$) of various samples at different current densities; (f) Nyquist plots of various samples. All measurements were undertaken in a 3-electrode cell in $1 \text{ M H}_2\text{SO}_4$.

$\approx$ A-CNS25C2h. While the differences in specific capacitance are only marginal and indistinct for those activated at 25 and 50°C , appreciably lower specific capacitance data are observed with those more heavily activated at 80 and 100°C . From this trend, it appears that enhanced activation at 80/ 100°C or extending the activation time reduces the specific capacitance of the activated carbon. This differs dramatically from the

results found in 2 M KOH electrolyte, indicating that the electrolyte plays an important role depending on the acidic or basic surface of the carbon materials. The trend of change is also in good agreement with the deteriorated surface wetting or enhanced contact angle data for $1 \text{ M H}_2\text{SO}_4$ solution. This indicates the dramatic effect of surface properties on the supercapacitive performance.

Table 3 Specific capacitance data (in $\text{F}\cdot\text{g}^{-1}$) of various carbon samples obtained from CV and GCD measurements in a 3-electrode cell in 1 M H_2SO_4

Scanning rate/ ($\text{mV}\cdot\text{s}^{-1}$) or current density/($\text{A}\cdot\text{g}^{-1}$)	CNS	A-CNS25C2h	A-CNS50C2h	A-CNS50C4h	A-CNS80C2h	A-CNS80C4h	A-CNS100C2h
CV	200	39	114	116	88	60	38
	100	48	129	127	116	88	48
	50	55	139	133	136	116	61
	25	63	145	137	149	137	75
	10	70	145	133	157	149	93
GCD	0.5	95	190	212	192	182	140
	1	89	180	179	183	171	107
	2	84	172	166	175	165	81
	3	81	168	162	170	161	69
	5	78	163	158	164	155	56
	10	74	157	152	154	143	41
	20	70	151	148	141	125	33
	30	68	147	146	132	110	32
	50	67	143	143	122	96	33

Figure 6b shows the GCD curves of the various carbons measured at $0.5 \text{ A}\cdot\text{g}^{-1}$; Figure 6d shows, in particular, the GCD curves of AC-NA25C2h as a representative one in 1 M H_2SO_4 electrolyte at different current densities. The voltage drop resulting from equivalent series resistance (ESR) is also very small in 1 M H_2SO_4 electrolyte even at high current densities like $50 \text{ A}\cdot\text{g}^{-1}$. Consistent with those observed in CV curves, some plateaus corresponding to redox reactions of the surface functional groups can be seen at correspondingly similar voltages in the charge and discharge curves. The specific capacitance data calculated from the discharge curves in GCD measurements are also summarized in Table 3. A similar order of the specific capacitance as that derived from CV data can be found among the various samples.

Figure 6e shows the percentage of capacitance retention at different current densities in reference to the values at $0.5 \text{ A}\cdot\text{g}^{-1}$. In general, the capacitance retention in 1 M H_2SO_4 electrolyte is not as good as the corresponding one in 2 M KOH electrolyte. The best retention is found with A-CNS25C2h, which has about 80% of capacitance retention at $50 \text{ A}\cdot\text{g}^{-1}$, along with the unactivated CNS being the second (ca. 72% retention). Generally, with the increase of activation temperature or time, a deterioration in the capacitance retention can be observed. In particular, A-CNS100C2h has the poorest capacitance retention of only 23%. This is again in agreement with the deteriorated surface wetting by the 1 M H_2SO_4 solution noted above from the contact angle data.

Figure 6f shows the Nyquist plots of the various carbons, obtained from EIS measurements in 1 M H_2SO_4 . Again, all the carbons show the distinct parts associated with EDLCs in the plots. Similar to those in 2 M KOH, low ESR values in the range of $0.1\text{--}0.3 \Omega$ are generally found with all the activated carbons. One distinct difference is noted in the intermediate frequency range. For the unactivated and weakly activated samples (CNS, A-CNS25C2h, A-CNS50C2h, A-CNS50C4h), the Warburg line (with a slope of about 45°) in the intermediate frequency range is nearly absent with a semicircle in the high frequency followed directly with a nearly vertical line at low frequency, while a long Warburg line is observed with the other samples that are more strongly activated at 80°C (A-CNS80C2h and A-CNS80C4h). The Warburg line is ascribed to the ion movement within the micropores; a longer Warburg line corresponds to more ion diffusion resistance within the micropores.^[27] Clearly, a higher level of nitric acid activation reduces the wettability of the micropore surface toward the 1 M H_2SO_4 electrolyte, thus

restricting the ion movement and in turn reducing the specific capacitance.

Besides the electrochemical results obtained from 3-electrode cell, a symmetric 2-electrode cell was also fabricated with A-CNS50C4h as the electrode material in 1 M H_2SO_4 . Electrochemical measurements were conducted within the voltage window of $0\text{--}1 \text{ V}$. Similar to the measurement of 2-electrode cell in 2 M KOH, the CV curves of the 2-electrode cell at different scan rates (see Figure 7a) are nearly rectangular, and the GCD curves in Figure 7b exhibit a triangle-like shape and a very small voltage drop. The specific capacitance data calculated from GCD curves are 156, 128, 120, 104, and $98 \text{ F}\cdot\text{g}^{-1}$ at 0.1, 0.5, 5, 10, and $50 \text{ A}\cdot\text{g}^{-1}$, respectively (Figure 7c). The capacitance retention at 10 and $50 \text{ A}\cdot\text{g}^{-1}$ is 77% and 67%, respectively, relative to the value at $0.1 \text{ A}\cdot\text{g}^{-1}$. Figure 7d shows the Nyquist plot of the 2-electrode cell with an ESR of 0.18Ω , which is also nearly twice of that (0.10Ω) in the 3-electrode cell. From the cycling test, the capacitance retention is almost 100% after 2500 GCD cycles at $5 \text{ A}\cdot\text{g}^{-1}$ though with an initial decay followed with a gradual recovery (see Figure 7e), demonstrating the excellent stability of the electrodes built with the nitric acid activated carbon in 1 M H_2SO_4 .

Conclusions

The effects of nitric acid activation on the textural, surface, and supercapacitive properties of ultra-small carbon nanospheres (size: 24 nm) synthesized by a catalytic emulsion polymerization strategy have been systematically investigated. In general, nitric acid activation shows marginal effects on the textural properties (surface area, pore volume, pore size distribution, etc.) of the carbon material within the activation temperature range of $25\text{--}80^\circ\text{C}$ and activation time up to 4 h. However, at 100°C , a long activation for 4 h leads to the complete destruction of the carbon nanostructures. From the FTIR, XPS, and TGA characterizations, enhanced activation by increasing the temperature or extending the time leads to enhanced content of oxygen-containing surface functionalities. From contact angle measurements, enhanced activation leads to improved wetting of the surface of the carbon materials by DI water and 2 M KOH solution, but deteriorated surface wetting by 1 M H_2SO_4 solution. The activated carbon samples generally show improved specific capacitance compared to the unactivated CNS in both 2 M KOH and 1 M H_2SO_4 electrolytes due to the involvement of pseudocapacitance arising from the

Figure 7 (a) CV curves at different scanning rates and (b) GCD curves at different current densities of the symmetrical 2-electrode cell with A-CNS50C4h in 1 M H_2SO_4 ; (c) plot of specific capacitance as a function of current density obtained from the GCD data; (d) Nyquist plot of the two-electrode cell; (e) cyclic stability of the two-electrode cell at $5 \text{ A} \cdot \text{g}^{-1}$ over 2500 GCD cycles.

introduced surface functionalities following activation. In 2 M KOH electrolyte, enhanced activation by increasing activation temperature and/or time leads to improved specific capacitance due to the increased supercapacitance and improved surface wetting by the electrolyte, with A-CNS80C4h showing the best supercapacitive performance (specific capacitance and rate performance). In 1 M H_2SO_4 electrolyte, enhanced activation leads instead to deteriorated supercapacitive performance (reduced specific capacitance and deteriorated rate performance), with A-CNS25C2h showing the most optimum performance, due to the deterioration in surface wetting by the acidic electrolyte. This difference highlights the distinct surface effect on the supercapacitive performance of carbon materials. Given their ultra-small nanosphere structures with short ion diffusion lengths, the optimum activated samples in both electrolytes are noted for their superior rate performance with excellent capacitance retention at high current densities (e.g., up to 83% at $50 \text{ A} \cdot \text{g}^{-1}$ relative to $0.5 \text{ A} \cdot \text{g}^{-1}$ in 3 -electrode cell).

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