Hydrothermal synthesis of spherical carbon nanoparticles (CNPs) for supercapacitor electrodes uses

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Abstract

In this paper, hydrothermal method was used to provide stable colloidal suspension of spherical carbon nanoparticles (CNPs) with good uniformity of size and shape. XRD analyses showed the formation of crystalline structure of carbon material. CNPs Raman spectrum indicates the high quality with a low content of structural defects and high graphitic degree. The formation of CNPs is confirmed by an absorption peak at 264 nm. XPS technique showed well a significant decrease of oxygen-containing functional groups, indicating a low degree of graphite oxidation. The active surface area of CNPs was measured by BET technique. TEM images show that CNPs are nearly spherical in shape and the diameters varying between 50 and 120 nm. The CV behaviors showed that CNPs exhibit the higher specific capacitance values, and is greatly improved over that of previously reported carbon nanomaterials.

Keywords Hydrothermal · Colloidal suspension · Carbon nanoparticles · Specific capacitance

Introduction

Carbon nanoparticles are black spherical particles with an average particle size of 50–100 nm and specific surface area of approximately 15–25 m²/g, are available in passivated, high purity, coated or dispersed forms; while, nanofluids are generally defined as suspended nanoparticles in solution either using surfactant or surface charge technology [1–3]. Carbon-based materials play a vital role in energy storage technology by providing high power and cycling performances and they are of interest because of their properties like high specific surface area [4, 5]. CNPs possess a high electrically conductive and can exhibit a smaller ion-transport resistance and a shorter diffusion pathway, leading to a higher specific capacitance at a large current density which candidate electrode material for high-performance supercapacitors [6]. Supercapacitor can offer many desirable

properties compared to conventional batteries such as super-long cycle life, short charging time and high power density [7]. The properties of the electrode materials and the electrode/electrolyte interface affect directly the performance of supercapacitors [8–10]. Carbon-based electrodes for supercapacitor applications have been widely investigated because of its chemical and thermal stability and excellent electrical properties [11, 12]. Large-scale CNPs have been produced by ultrasonic exfoliation of graphene in solvents [13], electrochemical exfoliation of graphite [14, 15], chemical vapor deposition [16] and solution-based chemical reduction of graphene oxide [17]. Although these techniques propose the production of high quality of CNPs, they require high temperatures [18]. Hydrothermal reaction is very simple, less polluting and low cost in comparison to the other methods listed, and these features make it ideal for use in elaboration of CNPs. In addition, this technique uses lower temperature and has lower oxygen content. These factors make hydrothermal reaction a suitable candidate for high-quality CNPs used as electrodes for supercapacitors [19, 20].

In this paper, the major objective is to synthesize abundant electrodes for supercapacitor with stable cycling performances, high conducting and low cost. We have produced large quantities of sustainable CNPs. The as-prepared colloidal suspension is composed of highly crystalline carbon presented as spherical nanoparticles.

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Experimental

Preparation of CNPs

For the hydrothermal reaction, 20 mg of multi-walled carbon nanotubes (MWCNTs) was attacked by nitric acid (HNO_3) as reported by Sepahvand et al. [21]. This mixture was then dispersed in 20 ml of dimethylformamide (DMF) by ultrasonication for 30 min. Then, the resulting mixture was vigorously stirred for 30 min at room temperature. The mixture was then placed in separate 25 ml Teflon-lined stainless steel autoclave filled with NaOH aqueous solutions (1 M, 20 ml). The autoclave was heated in ovens to 120 °C at a heating rate of 2 °C/min and maintained at this temperature for 12 h and the cooling was done in air. Finally, the gray upper part of the container is composed of suspended CNPs (dispersed in DMF) and the dark bottom layer contained the isolated MWCNTs- HNO_3 .

Characterization methods

X-ray diffraction (XRD) study was carried using D8 Siemens Advance diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). To determine the phase structures, diffractometer is operating at 40 kV and 30 mA with 2θ angles, ranging from 20° to 70°. Raman spectra were measured using SENTERRA R200L with a 532-nm radiation from an argon ion laser as exciting light. The samples were illuminated with 5 mw of laser power and the spectral data were collected in the continuous scan mode over the region of 500–3500 cm^{-1} with two 10-s integrations. The optical transmission spectrum recorded with UV–Vis Jasco V-670 spectrometer. The specific surface area was measured by nitrogen adsorption on the basis of the Brunauer–Emmett–Teller equation using Micromeritics, Tristar II 3020 analyzer. Prior to analysis, samples were heated to 120 °C for 1 h to evaporate water and dimethylformamide (DMF) from the particle surfaces which can distort the results. Samples weights were taken as the weight prior to analysis (after drying and degassing) and the heating is accompanied with degassing by nitrogen. The particles size, shape and their chemical composition were determined using coupled SEM and EDX (Philips XL30). The accelerating voltage used for EDX elemental quantification was lowered to 5 kV which minimizes the penetration depth. To examine the size and the shape of the CNPs, transmission electron microscopy (TEM; Tecnai TF20,BFTEM at 200 kV) was used. X-ray photoelectron spectroscopy measurements were done using a K-ALPHA Thermo Scientific XPS apparatus. The XPS spectra were recorded using Al-K α radiation (1486.6 eV), pass energies of 50 eV in narrow scan. The C1s line of 284.6-eV binding energy was used as a reference to correct the binding energies for the charge shift.

Fig. 1 a XRD pattern of as-prepared CNPs and graphite sheet, b Raman spectra

Fig. 2 UV–vis absorption spectrum of CNPs taken in colloid state

Fig. 3 XPS spectrum of CNPs: C1s peak was fit to three components at 282.4 eV, 284.8 eV, and 285.5 eV. Insert image: XPS survey

Table 1 XPS surface atomic percentages using the peak area subtraction method

Elements	Wt%	At%
C	92.19	91.18
O	4.63	5.24
N	3.18	3.58
Total	100	100

Fig. 4 **a, b** SEM with EDX element map of CNPs deposited on pure Ti substrate. **c** Chemical analysis on Ti substrate

Electrochemical measurements

Cyclic potentiodynamic polarization apparatus (PGP 201 Potentiostat/Galvanostat) equipped with a cell containing the conventional three electrodes was used. To prepare the working electrode, the as-prepared colloidal suspension composed of CNPs was dried under vacuum and powdered at 160 °C to eliminate DMF (boiling point 153 °C). Then, 90% of CNPs, 10% of nafion solution (5%) and iso-propyl alcohol are mixed homogeneously. The paste was then spread evenly with a metallic spatula on a stainless steel current collector and vacuum dried for 24 h. The paste is made into a film and the mass of the self-standing electrode is taken and is about 3–5 mg/cm².

For cyclic voltammetry, the counter and reference electrodes consisted of a Pt wire coil and Ag/AgCl, were used, respectively. The cyclic voltammetry (CV) curves were measured at room temperature, and the galvanostatic charge–discharge measurements were obtained over a potential range from 0 to 0.001 V in a 6.0 M KOH solution.

The specific capacitance was calculated according to the following equation:

$$C_s = \frac{2I \times \Delta t}{m \times \Delta V}, \quad (1)$$

Table 2 Percentage of each chemical elements of the CNPs deposited on pure Ti substrat

Elements	Wt%	At%	Error%
Ti	83.32	56.54	1.8
C	13.89	37.59	1.2
O	2.07	4.20	0.2
N	0.72	1.67	0.2
Total	100	100	

where I (A) is the discharge current, Δt (s) is the discharge time, m (g) is the total mass of anode and cathode materials, and ΔV (V) is the potential window.

The specific energy density of the SCs was calculated as follows:

$$E_t = \frac{C_t \times (\Delta V)^2}{2 \times 3.6}, \quad (2)$$

where E_t (Wh kg⁻¹) is the specific energy density, and C_t (F g⁻¹) is the specific capacitance of the total SC, which is $C_s/2$.

Results and discussion

Figure 1a shows XRD pattern of the as-synthesised CNPs and a sheet of graphite. The diffraction patterns exhibit three different peaks at $2\theta = 26.5^\circ$, 45° , and 54.8° . The spectra of the two samples are not identical, where we note the absence of the second pick around 45° . The peaks around 26.5° can be assigned to the (002) peak of graphite [22]. The line broadening of X-ray diffraction peaks is primarily due to the small particle size of CNPs [23]. The average crystallite size obtained by classical Scherrer equation with a geometric factor of 0.9 over (002) reflection is 52.5 nm and the interplane distance is 0.335 nm, which is characteristic of graphite [24, 25]. The peak at around 45° can be assigned to a convolution of the (100) and (101) peaks [26]. This peak is attributed to (100) and (101) reflections of carbon nanocrystallites [27]. The diffraction peak (004) is the second diffraction of the diffraction peak (002) according to layer spatial arrangement rules of microcrystals [28].

Raman spectra of CNPs and the graphite sheet are presented in Fig. 1b. Four characteristic bands are observed in the spectra: D-band at 1331 cm^{-1} , G-band at 1591 cm^{-1} , 2D-band at 2697 cm^{-1} and 2G-band at 2914 cm^{-1} . These bands are related to the graphite lattice vibrations [28]. D-band attributed to defects or structural disorder in graphite, which is not observed in perfect graphite sheets or in graphite single crystals. G-band gives an idea about the crystalline structure of CNPs [28]. The intensity

Fig. 5 a TEM image of the as-prepared CNPs, b DLS determination of particle sizes, c BET plots of CNPs compared to the graphite sheet using points collected at the relative pressure range 0.05–0.3, d pore diameter distributions

ratio of D-band to G-band (ID/IG) is an indicator used to evaluate the defect density of carbon materials [29]. ID/IG for graphite sheet is 2.2, while is only 0.17 for CNPs, indicating the high quality of CNPs with a low content of structural defects and high graphitic degree. The position and the form of 2D and 2G peaks are a measure to determine the number of graphite layers per each flake. By decreasing the number of layers in graphitic materials, 2D and 2G peaks become more symmetric and shift to lower wavenumbers as well [30, 31]. There are no characteristic peaks or bands of any impurities observed from Raman spectroscopy and XRD analysis; suggesting that high quality of CNPs was obtained.

Absorption spectrum was taken in the UV/Vis region to characterize the as-prepared colloidal suspension of CNPs using an UV–Vis Jasco V-670 spectrometer. The spectrum is presented in Fig. 2. The insert image shows picture of sample vial. The spectrum exhibits a peak in the UV region at about 264 nm. This peak is due to the collective π – π^* electronic transition of the condensed aromatic rings in the graphene sheet [32]. This single absorption peak in the UV region is observed due to the linear dispersion of Dirac electrons in nano-graphitic carbon [32].

In Fig. 3, the XPS spectrum of C1s from CNPs can be deconvoluted into three peaks (dashed lines), which can be attributed to the following functional groups: C=C (sp² bonded carbon, 284.67 eV), C–O (epoxy/hydroxyl, 286.27 eV) and C=O (carbonyl, 287.7 eV) [33–35]. A low degree of graphite oxidation is observed. In addition to the carbon peaks, Ca, F, N and Zn peaks were also detected. The source of these elements might be from the hydrothermal reaction.

To determine XPS surface elemental composition, Eq. (1) is used [36].

$$n_i(\%) = 100 \times \frac{I_i/\sigma_i K}{\sum (I_i/\sigma_i K)}$$

I is the peak area of element i , σ is the photoionization cross section of peak i and K depends on an instrumental constant and the measurement parameters. The determined XPS measured surface atomic percentages for CNPs are given in Table 1. XPS is a reliable quantification tool for determining surface elemental compositions [36].

The as-prepared CNPs deposited on titanium substrate were investigated by scanning electron microscope (SEM) coupled with energy-dispersive X-ray (EDX) to characterize the morphology, size and elemental distribution of the

samples. Figure 4a, b presents the SEM–EDX micrograph of CNPs which clearly shows the non-uniform size spherical particles. The as-prepared spherical particles are in a size range between 50 and 120 nm in diameter but most of the particles are about 100 nm in diameter. Figure 4c shows the EDX elemental analysis spectrum of the prepared materials. It indicates the presence of pure carbon without any contaminated substances in detectable limit ($\pm 0.01\%$). EDX measurements exhibit three peaks at 0.5, 4.6 and 4.9 keV, characteristics of Ti. Two slight intensity peaks at 0.2 and 0.6 keV also appear in the EDX spectrum are associated to C and O, respectively. The percentage of each element is summarized in Table 2.

TEM measurements were performed to characterize the size and morphology of CNPs. As can be seen from the Fig. 5a, CNPs show a fine spherical shape with the mean diameter of about 100 nm. Figure 5b presents the DLS determination of particle sizes. The X axis shows particle diameter and the Y axis the normalized counts. As seen in this figure, the obtained CNPs are practically polydispersed with a range of sizes varied from 60 to 120 nm. These results illustrate that the CNPs are in quasi-spherical shape and quite uniform. The BET plot of CNPs and the graphite sheet collected at the pressure range of 0.05–0.3 is shown in Fig. 5c. The specific surface areas as calculated using Brunauer–Emmet–Teller equation [37] are listed in Table 3. CNPs exhibit a large specific surface area compared to graphite sheet which improves practically the performance of the supercapacitor electrodes. Figure 5d shows the pore diameter distributions of mesoporous of CNPs and graphite sheet. Graphite sheet possessed bigger pore diameter and larger pore volume than CNPs, respectively, [$D_{pCNPs} = 9.4$ nm, $D_{pGraphite\ sheet} = 11.8$ nm], [$V_{pCNPs} = 1.56$ ml/g, $V_{pGraphite\ sheet} = 1.68$ ml/g].

Figure 6 presents the high-resolution transmission electron microscopy (HRTEM) measurement used to further investigate the crystal structure of the CNPs. HRTEM gives a

Fig. 6 HRTEM and SAED pattern of the as-prepared CNPs

Table 3 Specific surface areas (S_{BET}), pore diameters (D_p) and pore volumes (V_p) of CNPs and Graphite sheet

	S_{BET} (m ² /g)	D_p (nm)	V_p (ml/g)
CNPs	79	11.8	1.68
Graphite sheet	23	9.4	1.56

Fig. 7 **a** CV curves of CNPs and graphite sheet at different scan rates ($mV\ s^{-1}$). **b** Galvanostatic charge–discharge curves at $I = 0.1\ A/cm^2$ current densities. **c** The specific capacitance at various current densities

fringe spacing of 0.335 nm corresponding to the (002) lattice planes of graphite [29]. The selected area electron diffraction (SAED) pattern revealed that the diffraction rings of the as-prepared CNPs exhibited Debye–Scherrer rings assigned (002) and (004) lattice planes of graphite crystal lattice.

The CV behaviors of the graphite sheet and CNPs are tested in a three-electrode using a 6.0 M KOH solution as the electrolyte configuration in Fig. 7. As shown in Fig. 7a, the integral area enclosed by the voltammetric current of the CNPs is much larger than that of the graphite sheet. Samples possessing the larger integral area enclosed by the voltammetric current are having the excellent electric double-layer capacitive properties and its electrochemical performance is better than that possessing the smaller integral area. Similarly, the period of discharge time of the CNPs is longer than that of the graphite sheet (Fig. 7b). A

comparison in specific capacitance of the two supercapacitors at various discharge rates, calculated according to Eq. 2 for symmetric supercapacitor, is given in Table 4, highlighting that the electrochemical performance of CNPs is better than that of graphite sheet (Fig. 7c). Due to having the largest specific surface area than graphite sheet, which can effectively enhance the capacitance, CNPs exhibit the higher specific capacitance values. The capacitance retention rates at 5.0 A/cm² are 48.9% and 41.4% for the graphite sheet and CNPs, respectively, meaning that the CNPs possesses superior energy storage capability and as good rate capability as the graphite sheet. The specific energy density of CNPs is approximately of 8.4 Wh kg⁻¹ at a high current density of 50 A/cm², which is higher than that of the other sample. The specific capacitance of CNPs is greatly improved over that of previously reported carbon nanomaterials (Table 5).

Table 4 The specific capacitance values of the calculated based on the charge times at different current densities

Current densities (A/cm ²)	0.1	0.2	0.5	1	2	5
Specific capacitance, graphite sheet (F/cm ²)	95	83	79	64	53	33
Specific capacitance, CNPs (F/cm ²)	132	124	115	104	92	86

Table 5 The specific capacitance resulting from this work in comparison with other studies

Carbon material	Specific capacitance	Electrolyte	References
Carbon nanoparticles	132 (0.1 A/cm ²) 86 (5 A/cm ²)	6 M KOH	This work
Microporous carbon nanosphere	110 (2 A g ⁻¹)	6 M KOH	[38]
Graphene-carbon nanotube foam architectures	175 (0.02 A/cm ²)	6 M KOH	[39]
Graphene nanosheet	115 (0.5 A/cm ²)	6 M KOH	[40]
Multi-walled carbon nanotubes	137 (0.001 A/cm ²)	6 M KOH	[41]
Carbon nanofiber web	120 (1 A g ⁻¹)	6 M KOH	[42]

Fig. 8 Current amplitude and released charge of CNPs after different numbers of charge–discharge cycles

Table 6 Numbers of cycles resulting from this work in comparison with other studies

Carbon materials	Numbers of cycles	References
Carbon nanoparticles	10 ⁷	This work
Porous carbon	10 ³	[43]
Carbon coated negative electrode	6780	[44]

As shown in Fig. 8, after numbers of cycles, the current amplitude and the released charge vary slightly, which means that the cycling has little impact on the performance of CNPs. A comparison on the number of cycles with various reported carbon-based materials demonstrating the energy storage performance of the obtained CNPs is given in Table 6.

Conclusion

Hydrothermal technique is a promising method to produce large quantities of sustainable graphite-based nano-materials. The as-prepared colloidal suspension is composed of highly crystalline graphite presented as spherical nanoparticles and shows uniform size distribution ranging from 50 to 120 nm. XRD, XPS, Raman and UV–Visible spectroscopies show the formation of high-quality crystalline structure of carbon material with a low content of structural defects. SEM–EDX, TEM and HRTEM were also used to characterize the size and shape of nanoparticles. The carbon nanoparticles show high specific surface area and high specific capacitance.

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