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Full Length Article

Preparation and performance evaluation of Carbon-Nano-Sphere for electrode double layer capacitor

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ABSTRACT

We report on preparation of Carbon-Nano-Sphere (CNS), by facial sublimation of Formosa (1,7,7-trimethyl-bicycloheptan, $C_{10}H_{16}O$, camphor), to integrate directly as an efficient electrode medium with superior value of specific capacitance, C_{SP}. The synthesized CNS were subjected to Raman, UV–vis spectroscopy, BET and electron microscopy to reveal the structure-property relationship. In analysis, CNS consisted of hetro-structured sp^2 carbon ~ 1–3 nm, embedded within the sp^3 network. They formed 3D interconnected network of spheres having higher surface area, S_A, ~ 791 m^2g^{-1} with electron rich surface environment. The cyclic voltammetry (CV) measurements were performed in 1 M HCl electrolyte for different scan rates. The estimated value of the C_{SP} was 540 Fg^{-1} at 10 mVs^{-1} with cyclic stability maintained ~ 97% at 1000 cycles. The Galvanostatic charge-discharge (CD) measurements, carried out at 1 Ag^{-1}, indicated the value of C_{SP} ~ 551 Fg^{-1} with energy, E_D, and power density, P_D, 20 $Whkg^{-1}$ and 250 Wkg^{-1}, respectively. The process of fabricating active electrode material was simple, environmentally compatible, time and cost effective to achieve effective electrochemical parameters. The double layer charge storage mechanism and nearly no presence of any redox reaction, made CNS suitable candidate for rechargeable supercapacitor application. Details are presented.

1. Introduction

Globally, the current ecological system is experiencing a critical constraint to obtain electric energy from the naturally available resources. Both, the conventional and the non-conventional routes are capable to supply energy in the range of few hundreds to thousands of megawatts. However, the requirement to be fulfilled for the future energy demand is of the order of terra watts and increasing, annually, by 10–15% [1]. To satisfy this, in recent years, supercapacitors are emerging as a promising candidate for energy storage systems. They are having superior performance characteristics in terms of life cycles, environment stability, pulsed power generation, etc., over traditional energy storage devices [2]. Broadly, there are three types of supercapacitors, namely, electric double-layer- (EDL), pseudo- and hybrid-capacitor. In EDLC, *supercapacitance action* is achieved by the carbon-based electrodes to separate charges at the interface between electrode/electrolyte to form the Helmholtz double layer. Wherein pseudo-capacitors, various reactions (redox, charge-transfer and intercalation) are the basis to achieve such action using the metal oxide and/or the conducting polymer electrodes. In hybrid capacitors, one electrode acts as an electrostatic and other as an electrochemical electrode, showing both the characteristics [3]. Among them, EDLC is advantageous due to their interfacial charge dynamics, electrode surface area (S_A), cyclic stability, easy handling, good reliability and compactation. In design and construction of EDLC, the choice of an active electrode material is a crucial component. It offers efficient charge dynamics due to high S_A which has implications on their electrolytic parameters such as specific capacitance (C_{SP}), power (P_D) and energy density (E_D) [4].

Due to its large abundance, remarkable physical and chemical properties nano-carbon makes it suitable to be integrated as an active electrode for EDLC. In literature, several routes have been reported for the fabrication of nano-carbon by different methods including bio-precursors to obtain C_{SP}, E_D, and P_D, ranging from ~ 74–400 Fg^{-1}, ~ 10–55 $Whkg^{-1}$, ~ 0.56–78.5 $kWkg^{-1}$ respectively [5–7]. However, in the current study we have focused on the properties of nano-carbon electrode obtained by the Formosa (1,7,7-trimethyl-bicycloheptan, $C_{10}H_{16}O$, camphor). Table 1 shows comparison of parameters for nano-carbon, specifically, obtained from the camphor in which, electrode fabrication has been realized with the help of additives and treatments.

In current communication, we demonstrate the application of nano-carbon, obtained by facile synthesis route, as an efficient

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Table 1
Electrochemical parameters for nano-carbon electrodes.

Additives and treatments	S_A (m^2g^{-1})	C_{sp} (Fg^{-1})	E_D ($Whkg^{-1}$)	P_D ($kWkg^{-1}$)	Cyclic stability	Measurements done at	Electrolyte	Ref no.
Graphene nano sheet/MWCNTs	169.2	274.0	86.4	0.7	93% (10000)	1 A g^{-1}	1 M Et4NBF4	[8]
Polymer (P123)	30.0	484.0	–	–	76% (1000)	2Ag^{-1}	1 M H2SO4	[9]
Activated with KOH	79.6	77.0	1.4	0. 6	100,000	1 $mAcm^{-2}$	0.1 M H2SO4	[10]
Methanol, NiO nanowires	106.0	1950.0	83.0	75.0	85–90% (2000)	100 mVs^{-1}	1 m NaOH	[11]
Reduced Graphene Oxide	376.0	438.0	–	–	76% (1000)	2Ag^{-1}	1 M H2SO4	[12]
MnO_2 powder, Methanol	40.0	450.0	26.0	6.0	88% (1000)	0.5 mA	0.1 M KOH	[13]
Carbon xerogels, Nickel oxide, activated with phosphoric acid.	215.0	151.0	–	–	–	2.5 Ag^{-1}	1 M H2SO4	[14]
Ferrocene	40.8	1.0	0.3	–	83%	100 mVs^{-1}	Na2SO4	[15]
Methanol, Lithium Nickel Manganese oxide powders	30.0	154.0	–	–	83% (200)	–	–	[16]
MnO_2 nanowires, titanium foils	50.0	483.0	96.0	32.0	10000	1 mA	0.1 M KOH	[17]
Methanol, lithium titanate spinel (LTO)	–	200.0	0.3	2.8	4000	0.5 mA	1 M LiPF6	[18]
Current work	791.0	560.0	78.0	2.8	97% (1000)	10mVs^{-1}	1 M HCl	

electrode medium with effective electrochemical parameters. The carbon-nano-sphere (CNS) are obtained from the single step synthesis by complete atmospheric sublimation of Formosa. It doesn't need any additional pre- and/or post-treatment. The method is cost and time effective. The parameters achieved are superior as compared to the reported literature shown in Table 1, specifically, C_{SP}. The analysis of charge storage mechanism is presented. To the best of our knowledge, there has been no report on direct implementation of the campho-carbon as a high performance EDLC. Details are presented.

2. Experimental

2.1. Single step preparation of CNS

Formosa was taken as a starting material to grow CNS. The deposition was carried out on the surface of a commercially available alumina substrate (KETAO, advanced ceramic solution), under normal thermodynamic conditions. The production scheme of CNS deposition is shown in Fig. 1. Initially, a square substrate of dimension $5 \times 5 \times 1\ cm^3$ was cut and subjected to sonication process by immersing into acetone and, subsequently, into deionised water for a period of 10 min at room temperature. Following this, the drying process was carried out for about 20 min with the help of IR heating.

For deposition, spatula of stainless steel was mounted on a fixed platform and 1 g pellet of Formosa was kept on the circular side of the spatula. The platform was vertically moveable clamp coupled with a stand so that it can move freely in the vertical direction. By adjusting the vertical distance between the clamp and the spatula deposition of CNS on the substrate was facilitated. Substrate was clamped and brought into vicinity of the precursor pellet subjected to the flash point sublimation process at 54 °C. The complete process occurred in a period of 2–3 mins or so. The powder was deposited onto the substrate and, subsequently, collected by gentle scrubbing of the surface of substrate using razor blade and collected into the crucibles/bottles as seen in Fig. 1.

In this fashion, several pellets were subjected to combustion to obtained nano-carbon. It was found that 1 g of precursor combustion yields around 70 mg nano-carbon. It is noteworthy that, the adopted process is facile with no involvement of catalyst in reaction. In one step, the product is readily available and required no pre- or post-treatment prior to application.

2.2. Characterizations

The obtained CNS was subjected to number of characterization techniques like scanning and transmission electron microscopy including selective area electron diffraction (SAED), Raman, UV–vis spectroscopy, BET, etc.

Raman measurements were carried out, using LABRAM HR-800 model, at wavelength 457.0 nm, over 100.0–3200.0 cm^{-1}. The obtained spectra were furnished using Labspecs 5.0 software (Horiba Industries Corporation, lesulis, France). The Raleigh and florescence scattering background were best fitted for the 4th order polynomial baseline and abolished form the raw spectrum prior to peak fitting and evaluated by curve fitting in terms of spectroscopic parameters such as peak position, peak width, line shape and band intensity (i.e. Gaussian, Lorentzian or a mixture of both).

UV–vis spectroscopic measurements were performed, using Specord 210 PLUS, Analytik Jena over the range 200.0–800.0 nm for absorption, α, as a function of wavelength.

Surface morphology of CNS samples were investigated using scanning electron microscopy (FESEM; Zeiss Sigma) at beam potential of 5.0 kV with different magnification and a large number of images were recorded.

The microstructures of CNS were explored by transmission electron microscopy (HRTEM, G220STwin, Tecnai, FEI, USA), at beam potential around 300.0 kV. In addition, SAED patterns were recorded for few specimens. A number of images were taken in order to evaluate dimension, structure, and other details, a few of them are shown here.

The S_A of CNS specimen was determined by BET (Quanta Chrome Nova 1000, USA) adsorption method at low temperature nitrogen adsorption-desorption technique. Prior to measurements, samples were dried at 100 °C under vacuum conditions for about 2 h to remove the moisture contents.

2.3. Electrode preparation and electrochemical measurements

For electrochemical measurements, the fabrication process of working electrode is shown, schematically, in Fig. 2. The obtained CNS and PTFE (polytetrafluoroethylene) was mixed in a weight ratio of 9:1 to form a slurry after dispersing CNS in the ethanol solution, added by a micro-pipette. Using the drop cast technique, solution was casted onto the tip of a metal disc electrode (MDE). Following this, the electrode was positioned vertically in a force convection oven and dried at 80 °C for about 14 h. Several such electrodes were prepared and used for the electrochemical measurements. The electrochemical properties were studied, at room temperature, using CV and Galvostatic charge-discharge (CD) technique, (Ivium Technology, Vertex). The CV setup consisted of three electrodes (i) Platinum wire: counter, (ii) Ag/AgCl: reference, (iii) CNS: working electrode immersed in 1 M HCl electrolyte, as shown in Fig. 2. The CV curves were obtained at potential window of − 0.2–0.8 V at a

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