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High surface hierarchical carbon nanowalls synthesized by plasma deposition using an aromatic precursor

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ABSTRACT

Hierarchical carbon nanowalls (CNW) are synthesized by plasma-enhanced chemical vapor deposition using *p*-xylene as a complex precursor. In contrast to ordinary CNW, synthesized with short-chained carbons, hierarchical CNW show a unique multi-scale pore structure, made up of micro- and mesopores connected by tubular macropores, offering higher surface area and surface accessibility. Their morphology, graphitic structure, surface area and accessibility are verified by transmission and scanning electron microscopy, gas sorption and impedance spectroscopy. Focused ion beam scanning electron microscopy tomography demonstrates the presence of macropores ensuring pore connectivity down to the substrate. Nitrogen/krypton physisorption confirms the micro- and mesoporous structure contributing extensively to the surface area. The impedance spectra are evaluated according to standard RC and transmission line models. The sample deposited for 60 min, with a structure height of 4.75 μm, features a volumetric capacitance of 2.6 F cm^{-3} and a response time of 25 ms. Hierarchical CNW exhibit a two to six times higher volumetric capacitance than CNW of similar proportions, reported in literature. Hierarchical CNW offer a promising way to realize high power and energy density requirements in electrochemical energy systems, like supercapacitors, due to their good conductivity, high surface area and open pore structure.

1. Introduction

The accessibility and amount of active surface area for reactants and electrolytes are two factors strongly controlling the performance of electrochemical energy systems such as electrochemical double layer capacitors [1,2]. Research has demonstrated that the surface accessibility can be increased considerably by adjusting the materials pore size distributions [3–9]. Well conducting electrode materials with micropores among interconnected meso- and macropores exhibit high performance due to shortened ion path length and largely decreased diffusion resistance [10–12].

In this regard, carbon has become one important material in the field of energy conversion and storage. Besides the fact, that carbon is cheap and abundant, the attention owes to an immense diversity in the available carbon nanostructures of various dimensions and shapes, like fullerenes (zero dimensional, 0D), nanotubes (1D) and graphene sheets (2D) [13], as well as 3D structured carbon architectures and assemblies, like hierarchical nanowalls [14], fibers [15] or foams [7,16,17]. In addition, carbon materials have exceptional properties, such as high chemical and mechanical stability and adjustable electrical conductivity [18].

Electrode nanostructuring is highly important for applications in electrochemical double-layer capacitors (EDLC). In an EDLC, the surface area determines the energy density, while the pore sizes strongly influence the power density [19]. Nanostructures used in EDLC usually form a randomly ordered network, which limits the control over the spatial pore assembly, impeding high power densities. The alignment of 1D and 2D nanostructures offers short pathways and inhibits agglomeration, thereby theoretically enabling a high power and energy densities at the same time. However, the structures do not usually exhibit a high energy

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density, because of the high distance in-between the nanostructures and thereby high porosity [20].

By offering short ion and electron pathways combined with high surface area, hierarchical nanostructures containing interconnected micropores, mesopores and macropores can best satisfy the morphological requirements for EDLC electrodes [21]. The pores are classified as suggested by the IUPAC, according to which micropores are pores smaller than 2 nm, mesopores range between 2 and 50 nm and macropores between 50 and 1000 nm [22]. In this context hierarchical electrodes based on vertically oriented 1D or 2D nanocarbons, like tubes [23,24] or sheets [15] have recently gained much attention. They create a hierarchical pore assembly in which micropores are connected to mesopores which in turn are connected to macropores. Compared to other hierarchical assemblies, which exhibit statistically ordered pores, fractal arrangement of pores in terms of pore connectivity and electrode continuity, offer the shortest possible pathways deep inside the electrode and efficient use of the complete electrode volume [25]. Carbon nanowalls (CNW) or vertical graphene, represent the spatial alignment of 2D nanostructures. The CNW are grown directly on the substrate under formation of tubular pores with a width bigger than 50 nm resulting in a high surface area and pore connectivity [26,27]. Direct growth on the substrate advantageously allows a good contact between the CNW and the current collector, making any use of organic binders obsolete. The network density, flakes morphology and surface area of CNW can be regulated through variation of different deposition parameters. CNW offer a high number of exposed sharp edges, non-stacking morphology and high surface to volume ratio. Emerging applications of CNW are field emitters [28], atmospheric nanoscale corona discharges [29], sensors [30], supercapacitors [31], lithium-ion batteries [32], fuel cells [33] and transducers [34]. Additionally, the structure of CNW makes them ideal templates for synthesizing nanocomposites to improve CNW performance even further [35].

For this report, CNW were synthesized by plasma enhanced chemical vapor deposition (PECVD) on selected substrates at varied deposition times using aromatic *p*-xylene precursor. A synthesis approach with aromatic *p*-xylene as carbon precursors enables new ways to manipulate the structural and electrochemical properties of a carbon material. A general discussion of the nanostructure formation in plasma environments was done by Ostrikov et al. [36] and a *p*-xylene specific approach was discussed in a previous work. Therein, it was found out, that the aromatic precursor shows two different growth mechanisms, with sheet growth dominating at low precursor supply being process driven and graphitic fibers dominating at high precursor supply rates being precursor driven. In present case, both processes are believed to occur in tandem creating a hierarchical structure [15,37].

The structural investigation of CNW synthesized in this work was performed by high resolution transmission electron microscopy (HR-TEM), scanning electron microscopy (HR-SEM) and combined focused ion beam (FIB). The crystallinity and graphitic character of the deposited CNW was investigated by HR-TEM. To prove the pore connectivity and to study the macropore size distribution, CNW were filled with zinc oxide by atomic layer deposition and the resulting structure was examined by FIB SEM, while the pore morphology of the nanostructure was studied on non-filled CNW. To determine the extent and size distribution of micro- and mesopores in CNW, N_2/Kr physisorption was performed. Additionally, the accessibility of the surface and the surface area was investigated by electrochemical impedance spectroscopy using RC and transmission line model. An extensive investigation into the CNW pore-structure, as was presented in this paper, has not been published before. The results show a new type of CNW with a micro- and mesoporous layer covering vertical aligned graphitic sheets forming hierarchical CNW.

2. Material and methods

2.1. Synthesis

The CNW were synthesized using an inductively coupled plasma enhanced chemical vapor deposition (IC-PECVD) process. *p*-xylene was used as carbon precursor and fed into the reactor at 0.5 ml h^{-1}. The carrier gas was argon and introduced at 10 sccm. The synthesis was performed at a pressure of 4.7 Pa and at a substrate surface temperature of up to 450 °C, resulting from the plasma, which was set at 150 W. Note: No external preheating of the substrate was used, the heating up to 415 °C results from the plasma and occurs at the first minutes of the deposition time. A detailed description of the setup can be found in Lehmann et al. [15] The CNW were synthesized on glassy carbon substrates ($1.0 \times 1.0 \times 0.1$ cm) for impedance spectroscopy measurements, on steel foil ($15.0 \times 2.8 \times 0.01$ cm) for N_2 and Kr physisorption measurements and on silicon wafer ($1.0 \times 1.0 \times 0.1$ cm) coated with a TiN layer (300 nm in thickness) for morphology investigations. Before deposition, the substrates were cleaned with ethanol and subsequently flushed with pure water. The deposition time was varied between 20 and 60 min and the samples are named CNW-20 CNW-40 and CNW-60 depending on the deposition time used for the synthesis.

2.2. Electron microscopy

HR-TEM measurements were done at the TU Berlin using a FEI Tecnai G^2 20 S-TWIN operated at 200 kV. HR-SEM investigations (top view of the sample surface as well as cross-sections) were accomplished using a Hitachi SU8220 FEG-SEM operated between 5 and 10 kV. For tomography studies, the cross-sections were prepared and studied using a FIB SEM Auriga 60 dual beam from Zeiss operated at 30 kV acceleration voltage and 20 pA beam current. To enhance the contrast in the SEM cross-sections, the CNW were coated with a ZnO film of approx. 100 nm in thickness by allowing diethyl zinc and water to react in a cyclic manner in a vertical-flow hot-wall reactor (OpAL, manufactured by Oxford Instruments) as described in Ref. [38]. From the SEM images of filled cross-sections, the macropore Pore-Size-Distributions (PSD) were determined using a purely geometrical method, where spheres are fitted tightly into the pore space. The spheres may overlap, however larger spheres overwrite smaller spheres. The resulting distribution of partial spheres determines the volumetric distribution of pore diameters. The method is implemented in the software GeoDict® [39].

2.3. Physisorption

The physisorption experiments were carried out on a Quantachrome Autosorb 1C at 77 K with nitrogen or krypton. Prior measurement, the samples were degassed for 24 h under vacuum at temperatures between 100 °C and 150 °C. The overall surface area of the CNW was determined by means of the multipoint BET Method applied both for N_2 and Kr physisorption data in a P/P_0 range which was determined by the Rouquerol-Method [40]. The PSD was determined using the QSDFT Model for N_2 at 77 K for carbon with slit/cylindrical pores.

2.4. Electrochemical investigations

Electrochemical impedance spectroscopy (EIS) measurements were carried out with a Solartron SI 1260 impedance/gain-phase