

Bioinspired peptide nanotubes as supercapacitor electrodes

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Abstract Bioinspired materials offer new routes in nanotechnology. These materials are composed from chemically synthesized biomolecules and inspired by natural biological structures. They are self assembled into highly ordered nanostructures (nanotubes, nanospheres, etc.) from elementary building blocks of biological origin such as peptide and proteins. We developed a new technique of physical vapor deposition of peptide nanotubes (PNT) and applied it to electrochemical energy storage devices—supercapacitors (SC). In this work, aligned and homogeneously distributed diphenylalanine PNT have been used to modify carbon electrodes for SC devices. Electrochemical properties of PNT coatings of different density and height, modifying carbon electrodes have been studied. We have found that aligned PNT arrays significantly increase the double layer capacitance of the carbon electrodes. The found enlargement of the PNT-modified electrode capacitance has been ascribed to increasing of usable electrode surface area of the carbon electrodes coated by PNT. We show that the critical factor of the accumulation process of the electrolyte ions at the PNT-modified electrode surface is a wetting process of the PNT nanoscale hydrophilic channels by aqueous electrolyte.

Introduction

The biodecorated surface may own exceptional properties, which promote its use in numerous fields such as medical implants, tissue engineering, biosensors, and bioelectronics [1–4]. Different surfaces can be decorated with almost any kind of biological material. The biological material can be a biological building blocks, such as single amino or deoxy/ribonucleic acids, proteins, DNA chains, and phospholipid membranes, or even biological supra-structures as cells and living tissue.

New emerging generations of materials are bioinspired materials. These materials are composed of chemically synthesized biomolecules and inspired by natural biological structures. Bioinspired nanomaterials possess unique physical and chemical properties that cannot be achieved by using simple biological entities [5]. They have successfully been used in several fields at nanotechnology [6] and medical regeneration [7]. One type of the most common biological molecules for this kind of inspiration is proteins. Proteins have diverse properties and architectures at nanoscale. An interesting example of a protein architecture is the fibrous formation, similar to amyloid fibrils. In 2003, Reches and Gazit [8] showed that a peptide, which is composed of two phenylalanine residues (FF), can self-assemble into peptide nanotubes (PNT) due to spontaneous growth from aqueous or organic solutions [8, 9]. This small FF dipeptide was inspired from the minimal fibril formation core recognition motif of the amyloid- β protein, which is the building block of the amyloid fibrils of the Alzheimer's disease.

Recently, we developed a new technique for the deposition of PNT by physical vapor deposition technique, which is compatible with microelectronic technology [10, 11]. The PNT demonstrate diverse physical properties such

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as wettability [10], piezoelectric [12, 13], optical [14], and electrochemical [10] properties. The found electrochemical properties allowed us to demonstrate a great advantage of PNT-modified carbon electrodes for supercapacitors (SC), which are one of the rapidly developed technologies of energy storage devices. It is important to note that even after 10,000 cycles there was no apparent damage to the PNT electrodes [10].

Energy storage technology is a key element for alternative environmentally clean energy. At the forefront of these devices are batteries and electrochemical double layer capacitors, also called SC. Although batteries are a common device in almost all industries, low current delivery and limited cycle life remain their critical drawback. Unlike batteries, SCs can operate at high charge/discharge rates over an almost unlimited numbers of cycles, due to the negligible chemical charge transfer reactions that are involved [15–17]. The energy storage mechanism in SCs is based on electrostatic attraction between charges, along the double layer, which are formed at the high surface area interface of the electrode and the electrolyte. However, SCs have a considerably lower energy density than batteries. As a consequence, the challenge in the field of SCs-based devices focuses on the improvement of the energy density. The most direct route to increase the energy density is to develop electrode material with higher surface area.

Carbon materials, such as activated carbons, carbon nanotubes, and porous carbon materials are widely used for SCs applications [18–20]. Carbon satisfies all the requirements for energy storage application, including a large geometrical surface area, high conductivity, and electrochemical stability. However, specific capacitance obtained from carbon materials is much lower than expected. The low capacitance is mainly attributed to low useable surface area, which partially results from the poor wettability of the carbon [17, 20, 21]. The poor wettability arises from the fact that graphite materials are hydrophobic. In 1940, Fowkes and Harkins [22] measured the intrinsic contact angle of water on graphite and found a value of 86°. As a consequence, inorganic electrolyte should only partially wet the surface. Efforts have been made to enhance the wettability of carbon by surface functionalizing. Enhancing the wettability has improved significantly the specific capacitance behavior of carbon materials. However, the cycling life of the SC tends to be limited because fabricated surface functionalized groups cause Faradaic reactions [16]. These reactions result in irreversible changes, like a progressive deterioration of the capacitance and a decrease at the electronic conductivity, which causes an increase in the self-discharge rate [19, 20].

Our previous studies [10] revealed that carbon electrode, modified with vertically aligned PNT, enlarges the SC

capacitance by more than one order of magnitude. In this paper, we show the significant contribution of PNT coatings to capacitance of SC. We further report on different height and density PNT coatings, with tunable characteristics, and their influence on the double layer capacitance of SC.

Experimental

PNT coating technique

The studied PNT were deposited by a recently developed physical vapor deposition technique. During the deposition process, the FF peptide-lyophilized powder is placed in the sample holder, which is directly connected to the heater, allowing the evaporation of the biomaterial at a temperature of ~220 °C. A carbon electrode (DropSens, Spain) is placed on the holder, approximately 2 cm above the source material. PNT height and density coats tuning was achieved by altering the deposition time and the temperature of the substrate holder.

Scanning electron microscopy (SEM)

Samples were coated with palladium–gold conductive layer and analyzed using a JSM JEOL 6300 scanning electron microscope operating at 5 kV. Images were taken to obtain a top view or rotated at 90° to allow the PNT side view. The morphology of the PNT surfaces was characterized by SEM image processing. An image-processing algorithm, using MATLAB® software, was implemented to obtain quantitative information concerning the density characteristics of the PNT coating. The information was derived from 20 top and side view SEM images of investigated PNTs samples.

Electrochemical measurements

The electrochemical measurements of carbon and PNT-modified carbon electrodes were made in electrochemical cells, using the standard method of cyclic voltammetry (CV). CV measurements were carried out using a Potentiostat/Galvanostat (EG&G Princeton Applied Research, Model 273A). Voltammetry testing was carried out at potentials between –0.25 and 0.65 V. The electrochemical units contained a basic working carbon electrode, a carbon counter electrode, and a silver reference electrode. The electrolyte was a standard inorganic solution of 0.05 M KH_2PO_4 and 0.5 M KCl. All working electrodes had an identical geometric area of 0.125 cm². The capacitance was evaluated from experimental cyclic voltammetry curves, according to the following equation:

$$C_{DL} = \frac{I}{(\Delta V/\Delta t)} \quad (1)$$

where I is the recorded electric current of the charge/discharge process, and $\Delta V/\Delta t$ is the potential sweep rate.

Results and discussion

The new vapor deposition technique [10, 11] allows us not only to achieve ordered and homogenous arrays of peptide nanostructures but also to control their spatial arrangement. The average height, thickness, and surface density of these nanotubes can be tuned by adjusting the deposition parameters in a wide range. The observed top view SEM image (Fig. 1a) demonstrates normally oriented and homogeneously distributed array of nanotubes of 40 μm thick. An analysis of the SEM image (Fig. 1a) shows that the majority of the self-assembled structures are tubes with closed ends, and only 10% of them are opened. The average outer diameter of the minority of the open nanotubes is ~ 300 nm and the average inner diameter is ~ 200 nm (Fig. 1a). The found data allows us to define a PNT wall thickness of ~ 50 nm. Figure 1b shows a side view of a PNT thick array, of 40 μm height and density of $4 \times 10^8 \text{ cm}^{-2}$. Figure 1c illustrates a side view of a PNT thin array with a height of 10 μm and a density of $2 \times 10^8 \text{ cm}^{-2}$.

To study the influence of electrode surface area on the capacitance behavior, we measured the double layer capacitance using carbon substrates. The carbon surfaces were coated by aligned PNT with different thicknesses of PNT layer. Figure 2 shows voltamograms of two PNT-modified electrodes, compared to the primary carbon electrode. The current density response versus voltage for the thick PNT-modified electrode was found to be higher

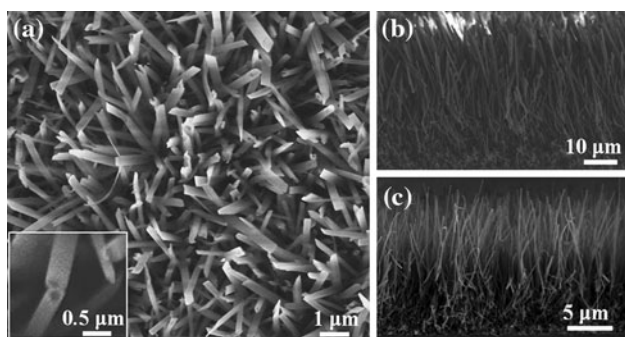


Fig. 1 **a** Top-view SEM image of the 40 μm PNTs after the vapor deposition process. The *inset* shows a high-resolution SEM image of an open PNT. **b** Side view of vertically aligned PNTs demonstrating the elongated PNTs, with a thickness of 40 μm . **c** Side view of vertically aligned PNTs demonstrating the PNT with a thickness of 10 μm

by an order of magnitude than that of an unmodified-carbon electrode. The CV curves for all tested electrodes present a quite rectangular and symmetric shape. This shape is a clear proof of a double layer capacitance charge–discharge process with no Faradaic processes [16]. The capacitance estimation for the unmodified carbon electrode was $16 \mu\text{F}/\text{cm}^2$, which imply that the carbon electrode is rather a smooth surface [23]. The capacitance estimation for the PNT-coated electrode of 40 μm layer thick was $240 \mu\text{F}/\text{cm}^2$, that is 15 times higher than that for the uncoated carbon electrode. The thin PNT-coated electrode of 10 μm layer showed capacitance of $\sim 160 \mu\text{F}/\text{cm}^2$. This shows a direct dependence of the current density on the PNT electrode surface area (Fig. 2).

Previous experimental studies found that the charge–discharge SC current density of carbon electrodes may be increased by PNT, of various origin and treatment [10, 24]. The increase was attributed to significant growth of useable electrode surface area. It should be reminded that SC electrode wettability by an electrolyte is a critical factor, providing high double layer capacitance [19].

To calculate the contribution of the PNT coating to the capacitance properties of the carbon electrode, we refer to the model of the PNT developed by Gorbitz [25–27]. Gorbitz has characterized the PNT structure, composed of linear diphenylalanine peptide, by using X-ray analysis. In this model, the inner and outer walls are either completely hydrophobic or partly hydrophobic. The model shows that the PNT walls contain numerous hydrophilic channels with a diameter of 10 \AA , which are elongated along the PNT axis. The nanotubes have a six-fold symmetry of $P6_1$, and the channels possess a hexagonal shape. Gorbitz's model describes the PNT as tubes that are open at the top. Following this model, we may assume that the outer and inner PNT walls cannot influence sufficiently the measured capacitance due their hydrophobic properties. The major

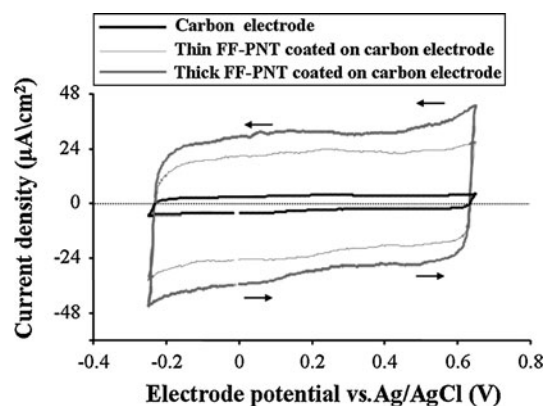


Fig. 2 Cyclic voltammetry measurements of carbon electrode (*black line*), thin PNT coated on carbon electrode (*thick grey line*) and thick PNT coated on carbon electrode (*thin grey line*)

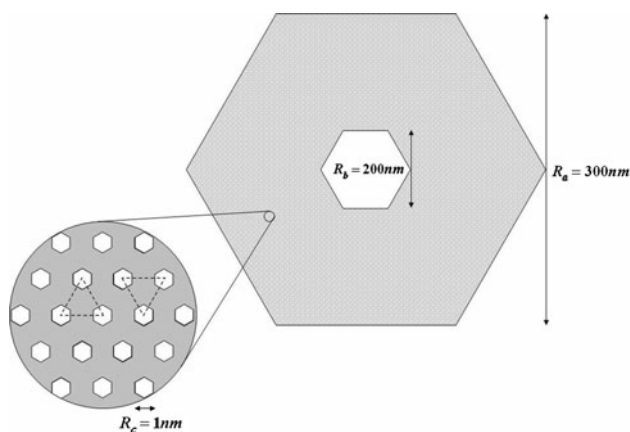


Fig. 3 Schematic representation of the arrangement of hydrophilic channels within the PNT

factor of the capacitance enlargement, which was found in our experiments with PNT coatings, is due to the contribution of the hydrophilic thin 10-Å channels. The thin nano-channels can allow transport of aqueous electrolyte liquids through them.

We calculated the useable electrode surface area coated by PNT array that may contribute to the measured capacitance. The estimations were based on the assumption that electrolyte ions accumulation process occurs only within the hydrophilic PNT 10-Å channels, which are of a hexagonal shape [25–27]. The experimentally measured parameters taken for the estimations are as follows: the inner and outer PNT average diameters (R) are of 200 and 300 nm, respectively (Fig. 1a); the average height (L) of the PNTs for thin and thick surfaces are 10 and 40 μm , respectively (Fig. 1b, c).

The model developed by Gorbitz [25] considers the cross section of a PNT wall as a network of the nanoscale channels, which create numerous repeated triangular cells (Fig. 3). Such an approach permits to estimate a number, N , of the hydrophilic channels in each PNT as $N \sim 12,500$ units. For a thin PNT surface coating of 10 μm height with a density of $2 \times 10^8 \text{ cm}^{-2}$, we received an average usable surface area of 900 μm^2 for every 1 μm^2 of plain electrode. For a thick coating of 40 μm with a density of $4 \times 10^8 \text{ cm}^{-2}$, we received an average usable surface area of 7000 μm^2 for 1 μm^2 of plain, smooth, uncoated electrode.

The estimated usable surface area of open PNT gives an increase of ~ 3 –4 orders of magnitude, in comparison to a smooth electrode. Our direct measurements showed the capacitance of PNT-modified electrode is enhanced by 15 times only. It should be stressed that the model proposed by Gorbitz [25] for PNT structure, exploited by us for the presented estimations, considers all PNTs to be open and containing nanoscale hydrophilic channels. Recently, another model was proposed for cyclo-diphenylalanine

(cyclo-PNT) [28], describing the nanotube as a fiber without any channels. Our previous study [10] showed that the ordered vapor deposited peptide coating consists mainly of cyclo-PNT (80%) and the rest is the linear-PNT (20%). Our direct experimental data, shown in this work, on PNT image analyzing gave the ratio of 10/90 between open and closed-edge, respectively. Therefore, only 10–20% of the PNT deposited by vapor deposition are open PNT and only they may contribute to the measured capacitance. Even after considering the 10/90 partition of the cyclo-PNT (closed PNT) and linear-PNT (open PNT), the estimated increase in the total usable surface area of PNT still higher than the experimental results. The inconsistency may be ascribed to a few factors such as non-full wetting of the nanoscale channels within the open PNT, or any specific features of the PNT formation, which deviate from the original model.

Conclusion

In this study, we examine the electrochemical behavior (charge–discharge properties) of electrical double layer capacitor of modified-carbon electrodes, containing PNT coatings of different density and thickness. We have found that aligned PNT arrays significantly increase the capacitance of the SC electrodes. The found enlargement of the capacitance of the PNT-modified electrode has been ascribed to increasing of usable electrode surface area of the carbon electrodes, coated by open PNT. We have showed that the critical factor for the SC capacitance is the wetted surface area of the PNT nanoscale hydrophilic channels.

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