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Short communication

A step forward into hierarchically nanostructured materials for high performance micro-supercapacitors: Diamond-coated SiNW electrodes in protic ionic liquid electrolyte

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ABSTRACT

Silicon nanowires (SiNWs) were successfully coated by uniform, adherent and homogenous ultra-thin crystalline diamond films through microwave enhanced chemical vapor deposition (MWCVD). The as-grown functionalized nanowires were employed as electrodes in a symmetric micro-supercapacitor (MSC) using a protic ionic liquid electrolyte [triethylammonium bis(trifluoromethylsulfonyl)imide; Et_3NH TFSI]. The electrochemical performance of the device delivered a specific capacitance of 1.5 mF cm^{-2} and a power density of 25 mW cm^{-2} using an enlarged cell voltage of 4 V. Furthermore, a remarkable cycling stability was evaluated after $1 \cdot 10^6$ galvanostatic cycles at a high current density of 10 mA cm^{-2} with an excellent capacitive behavior. These results confirm that diamond-coated SiNW micro-supercapacitors exhibit very promising performances dealing with MSCs based on CVD-grown SiNWs.

1. Introduction

In recent years, the rapid and growing demand of portable miniaturized electronic devices in a wide range of technological fields, such as biomedicine (e.g., medical implants), micro-electronics (e.g., smart cards) or aeronautics (e.g., autonomous sensors for satellites), has triggered the need of finding reliable high performance energy storage units of small dimensions. Micro-supercapacitors (MSCs), as a novel family of electrochemical double layer capacitors (EDLCs), have emerged as alternative micro-electrochemical energy storage units due to their excellent properties in terms of high volumetric power density, ultra-fast charge–discharge rate and long lifetime, which make them promising candidates for their integration into such systems [1]. Presently, the main investigations in this domain are devoted to the research of new electrode materials, electrolytes and design of advanced device architectures, which will play a crucial role in order to improve the properties of micro-supercapacitors.

From the electrode material perspective, intensive efforts have currently been focused on using nanostructured carbonaceous materials with high surface-to-volume ratio as for example onion-like carbon [2,3], graphene [4], carbon nanotubes [5], carbide-derived carbon [6] or diamond [7]. Precisely, diamond-based nanostructures have attracted a great attention in the field of supercapacitor devices [8,9]. Thus, the enormous interest of this carbonaceous material in the field of energy storage results from its chemical inertness, high overvoltage and very wide electrochemical windows (7.3 V), which may enhance the electrochemical properties related to energy and power densities [10]. Thereby, an important variety of architectures such as diamond nanowires [11], diamond foams [12,13], porous diamond [14], honeycomb diamond [10,15] or nanocrystalline diamond [16] have been demonstrated to be excellent capacitive materials. In this way, boron-doped diamond nanostructures based on foams exhibited a high volumetric power density of 807 W cm^{-3} at a ultra-high discharge rate of 1000 V s^{-1} [12]. More recently, functionalized diamond nanowires by metallic hydroxides [$Ni(OH)_2$] provided a mass specific capacitance and power density values of 1601 F g^{-1} and $3 \cdot 10^5$ W kg^{-1} respectively

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[11]. These works reported by C. Nebel and his coworkers demonstrate the great potential of diamond materials for supercapacitor devices.

In this regard, the use of other attractive supercapacitive materials such as nanostructured silicon (e.g., silicon nanowires SiNWs) has recently also awakened a special attention in the field of energy storage devices [17]. Specifically, SiNW-based micro-supercapacitors have been proven to be promising devices owing to their excellent capacitive behavior, high maximal power density (225 mW cm^{-2}) and an extraordinary stability (millions of cycles) using aprotic ionic liquid electrolytes [18–20]. Within this context, we reported recently the synergistic potential of diamond-coated silicon nanowires in a 3-electrode cell configuration employing an optimized $PYR_{13}TFSI$/PC mixture (40:60 *v*/*v*) as electrolyte [21]. Accordingly, the single electrode showed a specific capacitance of 105 μF cm^{-2} with a remarkable stability over 10 000 cyclic voltammetry curves.

Herein, we report originally an alternative approach dealing with the performance of a symmetric micro-supercapacitor device based on diamond-coated SiNW electrodes using triethylammonium bis(trifluoromethylsulfonyl)imide (Et_3NH TFSI) protic ionic liquid, which was proven as an excellent electrolyte for EDLCs due to its excellent properties in terms of wide electrochemical window and high temperature stability in the field of SiNWs and carbon [22–24]. In addition, interesting properties in terms of viscosity (48.6 cp) and conductivity (5.12 mS cm^{-1}) at 25 °C were found. The obtained results in this study reflect a clear enhancement of the electrochemical properties compared with our previous works, evidencing the potential of this innovative device as an alternative to carbon-based conventional EDLCs.

2. Experimental

2.1. Materials and reagents

Highly p-doped Si (111) substrates (doping level: $5 \cdot 10^{18}$ doping atoms cm^{-3}) and resistivity less than 0.005 Ω cm were used as the substrate for SiNW growth. Triethylammonium bis(trifluoromethylsulfonyl)imide (Et_3NH TFSI) was purchased from IOLITEC (Ionic Liquids Technologies GmbH, Germany) and used without further purification. The water content of ionic liquid was determined by Karl-Fischer titration (122 ppm) (Metrohm 795 KFT-Titrino).

2.2. Growth of SiNWs

Highly doped SiNW electrodes with a length of approximately 50 μm were grown in a CVD reactor (EasyTube3000 First Nano, a Division of CVD Equipment Corporation) via gold catalysis (4 nm evaporated thin gold) using an optimal deposition procedure [25].

2.3. Deposition of nanocrystalline diamond on SiNWs

The growth and doping of diamond onto SiNWs were reported in our previous work [21].

2.4. Morphological characterization

The morphology of the resulting SiNW electrodes was examined by using a ZEISS Ultra 55 scanning electron microscope operating at an accelerating voltage of 10 kV.

2.5. Fabrication and electrochemical characterization of the micro-supercapacitor device

Symmetric micro-supercapacitors were designed from electrodes made of diamond-coated SiNWs (1 cm^2) using a Whatman glass fiber paper separator soaked with the electrolyte. Cyclic voltammetry, galvanostatic charge–discharge cycles and electrochemical impedance spectroscopy (EIS) were performed using a multichannel VMP3 potentiostat/galvanostat with Ec-Lab software. All measurements were carried out in an argon-filled glove box with oxygen and water levels less than 1 ppm at room temperature.

The specific capacitance value of the device was calculated from the charge–discharge curves using the following equation $SC = i / A(dV/dt)$, where the i is the discharge current, A is the area of the electrode and dV/dt corresponds to the slope of discharging curve. The energy density (E) and power density (P) were calculated by using $E = 0.5SC(\Delta V)^2$ and $P = E/t$, where ΔV is the potential range and t is the total time of discharge.

3. Results and discussion

Fig. 1a and b displays the morphology of SiNWs grown by CVD on highly p-doped Si substrates. The density of nanowires was calculated to be $3 \cdot 10^9$ NWs per cm^2 with a diameter ranging from 20 to 200 nm according to our previous works [26]. The cross-section view shows a 50 μm SiNW length as displayed in Fig. 1b. Fig. 1c and d shows the morphology of nanocrystalline diamond on the surface of SiNWs. As can be seen a uniform, adherent and homogeneous coating was deposited along all SiNWs with a nanometric thickness of ~100 nm [21]. Additionally, the nanocrystalline grains vary from tens of nanometers to approximately 150 nm as shown in Fig. 1d. The boron-based doping and structure of crystalline diamond were confirmed by Raman spectroscopy in our recent work [21].

The electrochemical performance of a diamond-coated SiNW electrode was evaluated in a 3-electrode cell using a configuration reported previously [27]. Fig. 2a shows the CV curves of the electrode at different scan rates ranging from 0.4 to 4 V s^{-1} within a cell voltage of 4 V [−2.5 to 1.5 V vs Ag^+/Ag]. As can be seen, the profiles show a good capacitive behavior at low scan rates whereas at high scan rates a distortion of the CV curves was observed, implying faradaic processes. This behavior was also corroborated in a symmetric device configuration employing CV curves and galvanostatic charge–discharge cycles at different electrochemical windows (3, 3.5 and 4 V respectively), as displayed in Fig. 2b and c. Thus, the most accentuated behavior was reflected in the case of galvanostatic cycles (Fig. 2c). This electrochemical performance was ascribed to the presence of adsorbed carbon–oxygen functionalities and hydrogen on the surface of diamond during its doping and growing, which lead to reaction sides on the film surface [28,29]. Nevertheless, it is worth noting that the results suggest a good capacitance at a large cell voltage of 4 V. To evaluate the potential application as electrochemical micro-supercapacitor, the device was analyzed at a high current density of 10 mA cm^{-2} (Fig. 2d) at this voltage. The specific capacitance of the

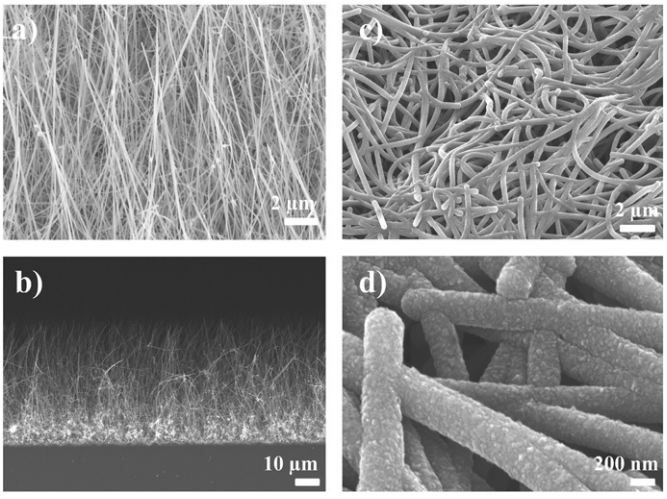

Fig. 1. a) SEM image of the morphology of SiNWs recorded at 45° tilted angle. b) Cross-sectional view of SiNWs. c) and d) Low and high resolution SEM images of diamond-coated SiNWs.