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Electrochemical activation of carbon nanowalls

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The electrochemical oxidation of carbon nanowalls resulted in an essential improvement of the capacitance.

Increase of supercapacitor specific performances is closely related to the choice of active materials used as electrodes.[1,2] Carbon nanotubes are the best known nanostructures for supercapacitors application.[3] However, the presence of a catalyst, which is required for their growth, and the dispersion of nanotube properties creates some difficulties for CNT wide applications.[4] The films of carbon nanowalls (CNWs) grown by plasma enhanced chemical vapour deposition (PECVD) are also very attractive materials for supercapacitor electrodes due to their unique combination of electron conduction, high specific surface area and porosity.[5] However, the electrochemical properties of this material are not well studied.

Here, we report the effect of anode pretreatment of PECVD grown carbon nanowalls on their electrochemical properties, in particular, capacitive characteristics.†

The SEM study of grown carbon film shows that it predominantly consists of normally oriented CNWs towards the substrate [Figure 1(*a*)]. The average height of the CNWs is 1 μm and the width is 0.5–1 μm. The Raman spectrum of the CNWs (Figure 1) has two sharp lines at 1360 and 1580 cm^{-1}, which are typical of graphite films (co-called D and G modes, respectively).[7] It is known that D mode is caused by structural defects inside a graphene plane and its finite size (presence of boundaries). Thus, the internal structure of the CNWs may be conditionally presented as an aggregate of graphene crystallites (domains). Taking into account a ratio between the intensities of D and G modes, the linear size of domains may be estimated at 10 nm.[7] The TEM study revealed that the average thickness of the CNWs is about 6–8 nm [Figure 1(*b*)]. Gravimetric measurements of the glassy carbon substrate before and after the CNWs growth revealed that the total specific mass of the grown carbon film is about 5×10^{-6} g cm^{-2}.

Cyclic voltammograms (CVAs) with different scan rates v for as-grown nanowalls (Figure 2) have the shape that corresponds to the change in the total differential capacitance of the electrode $C_t = I/v$, where I is current, and v is the scan rate of potential.[8,9]

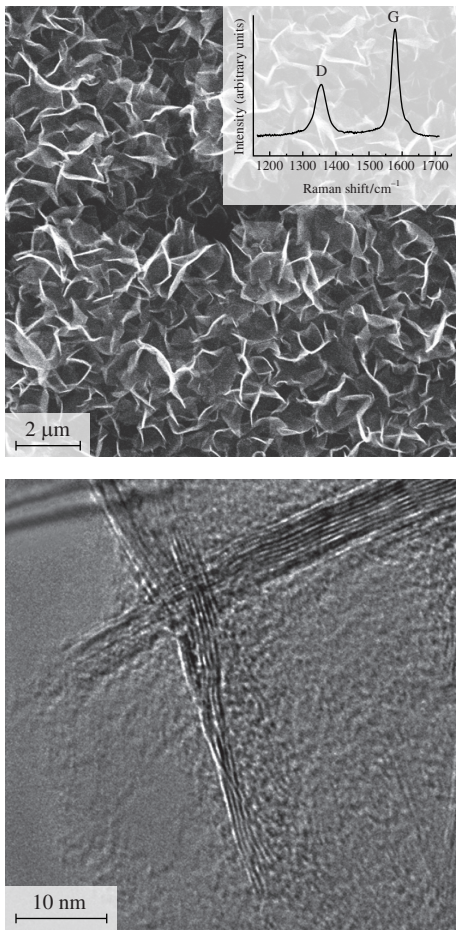

Figure 1 (*a*) SEM image of as-grown CNWs (scale bar, 2 μm), inset: corresponding Raman spectrum, (*b*) TEM image of the nanowall.

We have calculated the specific capacity of a film C_m in accordance with the following expression:

$$C_m = \int_{E_1}^{E_2} \frac{I}{v} dE \Big/ (E_2 - E_1)m$$

in a range of potentials from $E_1 = 0$ to $E_2 = 1.0$ V (m is total mass of the carbon film consisted of nanowalls). C_m weakly depended on v and was 95–105 F g^{-1}.

The oxidation of nanowalls was made by means of scan range extension from 0 to 1.6 V with a scan rate of 50 mV s^{-1} (Figure 3). It is clearly seen that the first cycle results in essential increase

† The films of CNWs were grown on glassy carbon substrates using PECVD in a dc glow discharge in a mixture of hydrogen and methane. The surface area of the substrates was 0.8 cm^2. No catalysts were used during the CNWs deposition. Substrates were placed on the anode of a dc glow reactor. The duration of film deposition was approximately 25 min. The experimental parameters were described previously.[6] Morphology and structural properties of grown carbon films were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy using a 532 nm wavelength laser with a power of 30 mW. Electrochemical measurements were carried out in an aqueous solution of 0.5 M H_2SO_4 at 19±1 °C. Potentials E are presented relative to a reversible hydrogen electrode in the same solution.

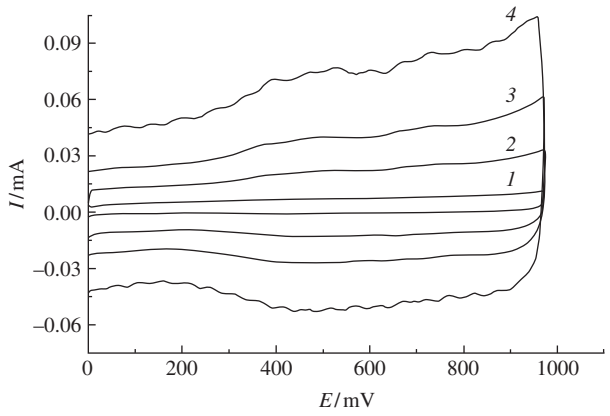

Figure 2 CVAs measured at different scan rates (v) for as-grown CNWs; v = (*1*) 10, (*2*) 50, (*3*) 100 and (*4*) 200 mV s^{-1}.

of current at $E > 1.3$ V. Comparison of first and second cycles allows us to assume that the extension of a cycling interval up to 1.6 V leads to the irreversible oxidation of the nanowalls (Figure 3). Moreover, the oxidation leads to an increase in C_m due to the appearance of well recognized and intense peaks at ≃580 mV, which may be attributed to quinone-hydroquinone functional surface groups.[10] Some increase in C_m in a range of potentials differing from potentials of quinone–hydroquinone redox reactions may be explained by a growth of the film surface area due to a 'loosening' of the oxidized material surface. Raman spectra analysis of as-grown and oxidized CNWs did not reveal any changes in their internal structure.

The presence of quinone–hydroquinone redox peaks is associated with the specific oxidation of the CNWs and depends on their structural features.

Figure 4 shows repeatedly measured CVAs in a range of 0–1 V with different scan rates after five cycles of oxidation. A small difference between the potentials of anode and cathode peaks ΔE (<25 mV at a scan rate of 200 mV s^{-1}) attests to high kinetics of charge transfer on the surface of the film. The redox current linearly depended on scan rate (Figure 4). This indicates that the charging/discharging of the capacity is determined by reactions on the surface of the CNWs and does not depend on diffusion.

Note that ΔE and the position of redox peaks depend on both the structural properties of CNWs and the way of their oxidation. Thus, CNWs fabricated by microwave PECVD[5] and by CVD in

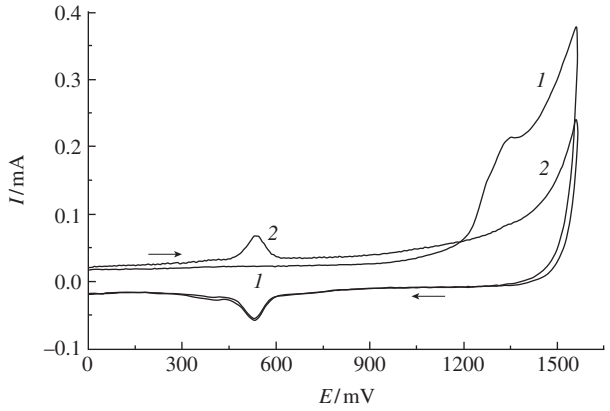

Figure 3 CVAs corresponding to two first cycles of electrochemical oxidation (scan rate, 50 mV s^{-1}, numbers correspond to the sequence of cycling).

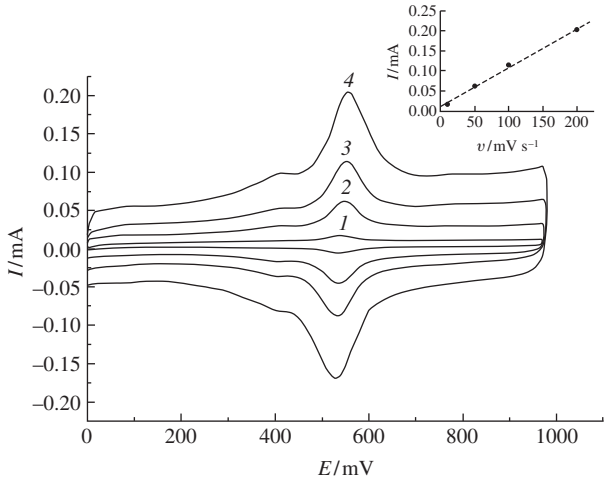

Figure 4 CVAs repeatedly measured after electrochemical oxidation; v = (*1*) 10, (*2*) 50, (*3*) 100 and (*4*) 200 mV s^{-1}. Inset: redox peaks I *vs.* scan rate v.

an electron cyclotron resonance plasma process[11] showed electrochemical properties different from those of the CNWs described above. In particular, ΔE was >80 mV.

The electrochemical capacity after oxidation is being increased by more than 20% and reaches ~120 F g^{-1} after oxidation. Moreover, the working potentials for the CNWs, as well as the total charge capacity, may be increased (Figures 2 and 3).

In conclusion, the electrochemical oxidation of the CNWs leads to a significant increase in their electrochemical capacity. Thus, the CNWs are promising electrode materials for supercapacitors. Furthermore, the presence of reversible quinone–hydroquinone redox peaks makes the CNWs suitable for the fabrication of indicated electrodes based on mediator catalysis.

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