

NANOCRYSTALLINE GRAPHITE AS A MATERIAL FOR ELECTROCHEMICAL SUPERCAPACITORS

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Introduction

The aim of this work is to investigate electrochemical properties of carbon nanowalls grown by plasma enhanced chemical vapour deposition (PECVD) method in dc glow discharge. A electrochemical capacity was measured before and after electrochemical oxidation of grown carbon nanowalls. It was shown that measured capacity achieves up to 200 F/g. Contribution of redox processes to electrochemical capacity was investigated as well.

Experimental

Carbon nanowalls were grown on grassy carbon substrates by using PECVD method in dc glow discharge in mixture of hydrogen and methane. Area of the substrates was 0.8 cm². No any catalysts were used during the carbon nanowalls deposition. Substrates were placed on anode. Duration of films deposition was, approximately, 25 minutes. Details of experimental parameters are described in our previous work [1]. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used for nanowalls morphology investigation. Structural properties of the nanowalls were studied by Raman spectroscopy method with using of 532 nm wavelength laser with power 30 mW.

Electrochemical potentials E were measured with respect to the reversible hydrogen electrode in an aqueous solution of 0.5 M H₂SO₄ at temperature 19 ± 1° C. Sulphuric acid «Merck Suprapur» and purified by Millipore system water were used for preparation of the electrolyte. High purity argon (99.99%) was used for blowing of electrolyte solution. Cyclic voltammograms (CVs) were measured for as-grown carbon nanowalls in a range of 0-1000 mV with scan rates 10, 50, 100, 200 mV/s. Further oxidation of nanowalls was made by means of scan range extension from 0 to 1600 mV with scan rate 100 mV/s. CVs were measured repeatedly after process of oxidation with the same scan rates in a range of 0-1000 mV. Comparative analysis of experimental results was made for investigation of functional groups effect on a value of the electrochemical capacity.

Results and Discussion

SEM study of grown film shows that it predominantly consists of nanowalls normally oriented towards to the substrate (Fig. 1). Average height of the nanowalls is 1 μm and width is 0.5-1 μm.

Fig. 1 (inset) shows Raman spectrum of the grown nanowalls. The fact of presence of D and G lines in Raman spectrum indicates that the nanowalls may be presented as aggregate of domains with linear size approximately equal to 10 nm [2]. TEM study (not presented) revealed that average thickness of the nanowalls is about 6 nm.

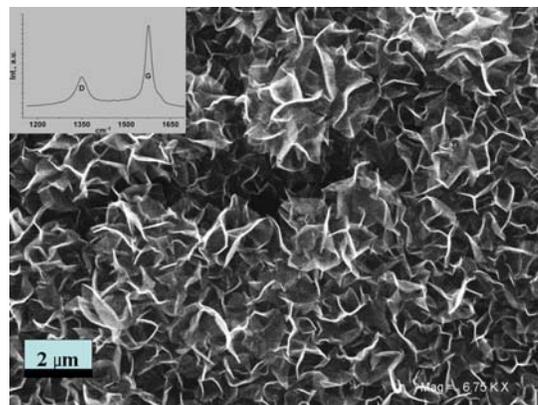


Fig. 1 SEM image of as-grown carbon nanowalls, inset – Raman spectrum.

Taking into account geometrical parameters of the nanowalls, their areal density and density of graphite total mass of grown film may be estimated as 3 × 10⁻⁶ gr/cm².

Results of electrochemical measurements with different scan rates for as-grown nanowalls are presented in Fig. 2. As it could be seen each of presented CVs has shape which corresponds to charge of the traditional electrochemical double-layer. Taking into account estimated mass we have calculated specific capacity of the film C_M as 150-165 F/g in

accordance with expression $C_M = \frac{\int_0^{t_0} Idt}{MU}$. Here M is films mass, U is scan range and I is total current of charging.

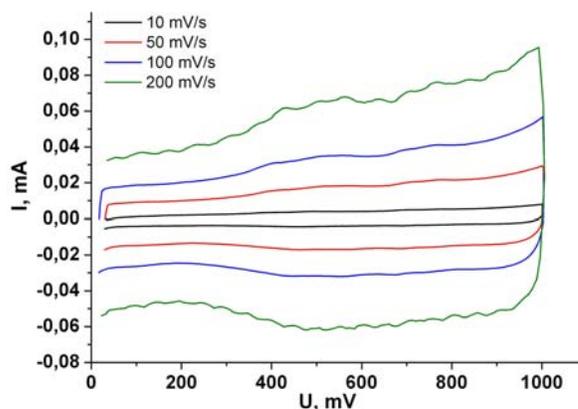


Fig. 2 Measured with different scan rates CVs of the as-grown carbon nanowalls.

Fig.3 shows repeatedly measured CVs after several steps (< 5) of electrochemical oxidation in a range of 0-1600 mV. Peaks in a region of 580 mV may be attributed to functional groups which were attached to the nanowalls surface during process of oxidation. We assume that these groups are presented by quinone/hydroquinone. It is known that edge-plane defects in graphene have most chemical activity and are active sites for surface groups [3]. Moreover, structural imperfections inside graphene plane (i.e. edge-plane-like or Stone-Wales defects) also may be considered as active sites for bonding of chemical groups [4]. The same is valid for carbon nanotubes where edge-planes are formed by their opened ends.

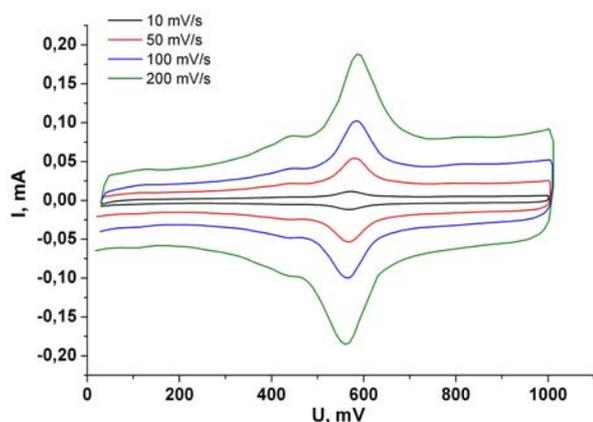


Fig. 3 Repeatedly measured CVs after process of electrochemical oxidation.

At the same time total electrochemical capacity arises from double-layer capacity which is proportional to electrodes surface area and pseudo capacity due to redox processes. However contribution of pseudo capacitance of nanowall should be more significant due to higher total length of edge-plane. Thus total values of films capacity before and after oxidation are presented in Fig.4.

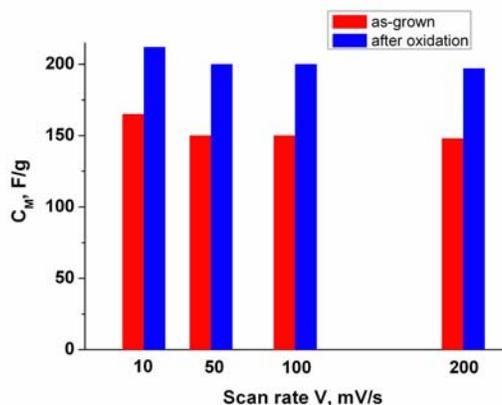


Fig. 4 Comparison of C_M measured with different scan rates before and after oxidation.

As it could be seen value of electrochemical capacity increases more than 20 % and reaches up to 200 F/g after oxidation. We believe that such increment is due to redox processes and it isn't associated with irreversible structural changes in surface area during oxidation. This assumption correlates with our Raman scattering measurements which didn't reveal any changes in Raman spectra of graphite (nanowalls) after oxidation.

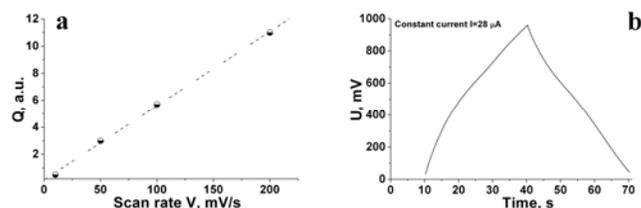


Fig. 5 Redox peaks area Q vs. scan rate V (a), charge/discharge curve at constant current 28 μA (b).

Amplitude of redox peaks area has linear dependence on scan rate (Fig. 5(a)). This indicates that charging/discharging of the capacity follows reactions on the surface of the nanowalls and doesn't depend on diffusion. Also low value of ΔE (< 25 mV at scan rate 200 mV/s) attests to high kinetic of charge transfer on the surface of the film. It should be noted that ΔE and position of redox peaks depend on both structural properties and way of oxidation (type of an electrolyte).

Typical constant current charge/discharge curve is shown in Fig. 5(b). As can be seen no IR drop was observed.

Conclusions

Electrochemical properties of the PECVD grown carbon nanowalls were studied before and after oxidation. It was shown that such structures may be considered as a perspective material for supercapacitors.

Acknowledgment. This work was financially supported by Scientific School grant No 3322.2010.2 and G.C. No 0055.

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