



## Composite material for supercapacitors formed by polymerization of aniline in the presence of graphene oxide nanosheets

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### H I G H L I G H T S

- ▶ The composites of polyaniline with graphene oxide were analyzed.
- ▶ The graphene oxide is reduced partially in the process of polymerization.
- ▶ The specific capacitance of the composite in 1 M H<sub>2</sub>SO<sub>4</sub> was found to be 547 F g<sup>-1</sup>.

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### A B S T R A C T

The composite material was obtained by the polymerization of aniline in the presence of graphene oxide nanosheets. The resulting composite containing polyaniline (72%) and graphene oxide nanosheets (28%) was investigated by XPS, TGA, Raman and IR spectroscopy. A partial reduction of graphene oxide was observed in the process of polymerization. The specific capacitance of the polyaniline/graphene oxide composite electrode in H<sub>2</sub>SO<sub>4</sub> (1 M concentration), corresponding to its discharge from 0.700 to 0.052 V, was found to be 547 F g<sup>-1</sup>.

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## 1. Introduction

The number of publications concerning the study of different materials used as new electrodes for supercapacitors has been growing rapidly. Recently discovered carbon nanostructures provide high specific surface area and high conductivity and could improve the performance of these devices.

Carbon nanomaterials show good mechanical properties. Manifold charge–discharge cycles do not affect their specific capacity, which is not high enough, unfortunately [1]. On the contrary, conducting polymers are characterized by high specific capacity but are unstable under cycling. Among the conducting

polymers, inexpensive polyaniline (PANI) shows high conductivity and can be easily synthesized. Composites of PANi with carbon nanomaterials show the best of the intrinsic characteristics of each of the components. For example, the PANi composite with carbon nanofibers shows a specific capacitance (SC) equal to 264 F g<sup>-1</sup> [2]. The value of SC for single-walled carbon nanotubes is 350–485 F g<sup>-1</sup> [3–5], and that of multi-walled carbon nanotubes is 322–606 F g<sup>-1</sup> [6,7]. For the composite of PANi with graphene oxide or with reduced graphene oxide, the situation is much more favorable and the value of SC according to the literature data is in the range from 210 to 1130 F g<sup>-1</sup> [8–20].

In this work we have studied the chemical composition and structure of the composite material obtained by polymerization of aniline in the presence of graphene oxide nanosheets (GONS). The specific capacity of this composite material is equal to 547 F g<sup>-1</sup>. This value is in the range of specific capacities published in the

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literature for similar materials. However, the value is higher than those of PANi ( $115 \text{ F g}^{-1}$ ) and GONS ( $183 \text{ F g}^{-1}$ ) [12]. GONS used in the composite material were not reduced previously since it was supposed that GONS would be reduced directly during polymerization [12]. The main goal of our research was to study the interaction of the components in the composite material and to understand the reason of the high dispersion of the SC values for different PANi–GONS composites.

## 2. Experimental

### 2.1. Synthesis of graphite oxide

Graphite oxide was synthesized by a modified Hammer's method as described in Ref. [21]. To prepare an aqueous suspension of graphene oxide nanosheets, 300 mg of graphite oxide was mixed with 400 ml of distilled water and the mixture was treated in an ultrasonic bath for 1 h. The resulting suspension was centrifuged for 15 min at 3000 g to remove large particles. The elemental composition of GONS after drying at  $60^\circ\text{C}$  was: C (52.99), O (45.4) and H (1.68) (wt. %). According to the Fischer method of water analysis, the composition of GONS was  $\text{C}_6\text{O}_{3.45}\text{H}_{1.35}(\text{H}_2\text{O})_{0.44}$ .

### 2.2. Synthesis of PANi and PANi–GONS composite material

Aniline sulfate (1.07 g) was dissolved in 50 ml of distilled water. The suspension of GONS was added to the solution with stirring. Concentrated sulfuric acid was added in the reactor to reach the value of  $\text{pH} = 2$ . The mixture was cooled down to  $-2 \pm 2^\circ\text{C}$  in an ice bath. Then, 50 ml of aqueous solution of ammonium persulfate was slowly added dropwise to the mixture. The reaction proceeded for 4 h at the above temperature range. The resulting precipitate was centrifuged and repeatedly washed with distilled water to form a dark green pasty mass. The samples for electrochemical studies were prepared by deposition of this dark green substance on a glassy carbon plate of  $0.5 \times 0.5 \times 4 \text{ cm}$  in size, followed by drying in air at  $60\text{--}70^\circ\text{C}$ . According to elemental analysis, the dried composite material contained: C (55.69), O (28.03), N (7.92), S (4.39) and H (4.04), in wt.%. The content of graphene oxide in composite **1** was  $26.5 \pm 1.5 \text{ wt.}\%$ .

The PANi itself was synthesized using a similar procedure but without adding the suspension of GONS to the reaction mixture. According to the chemical analysis, PANi contained: C (53.4), O (24.85), N (10.2), S (6.8) and H (4.88), in wt.%, and the general formula (without the balance of hydrogen) was  $\text{C}_6\text{N}_{0.98}(\text{H}_2\text{O})_{0.95}(\text{H}_2\text{SO}_4)_{0.29}$ .

Composite **2** was prepared by mixing the solution of PANi in formic acid and aqueous suspension of GONS. Polyaniline was obtained in the form of the salt of sulfuric acid and was reduced to the base state by treatment with aqueous solution of ammonia for 24 h. After washing in water PANi was dried in air at  $70^\circ\text{C}$  for 24 h. The 700 mg of PANi in base state was dissolved in 100 ml of concentrated formic acid. The suspension of GONS (250 mg/300 ml water) was slowly added to PANi's water solution. The sediment formed after mixing was repeatedly washed and neutralized with aqueous ammonia. The composite was doped by keeping it in 0.5 M  $\text{H}_2\text{SO}_4$  during the day. As a result of doping the composite **2** has changed the color to bright green. The concentration (w/w) of graphene oxide in the final composite **2** was 25%.

X-ray photoelectron spectra (XPS) were measured in a Thermo Scientific K-Alpha spectrometer using monochromatic Al K $\alpha$  radiation. The working pressure in the chamber of the spectrometer did not exceed  $4 \times 10^{-10}$  Torr. The pass energy (50 eV) was constant in all experiments. The atomic concentrations in the surface layer

were calculated from integrated intensities of the peaks, taking into account the literature data for the ionization cross sections [22].

Raman spectra were excited using a laser radiation with the wavelength  $\lambda = 633 \text{ nm}$ . The spectra were recorded using LabRAM HR systems. TGA analysis was performed in a Netzsch STA-409 instrument in the temperature range  $20\text{--}800^\circ\text{C}$  at the heating rate of  $10 \text{ deg min}^{-1}$ . Cyclic voltammetry (CV) and charge/discharge characteristics were measured in an electrochemical glass cell using 1 M  $\text{H}_2\text{SO}_4$  at room temperature in air. Working and auxiliary electrodes were separated by a porous glass membrane. Glassy carbon plate,  $1 \times 4 \text{ cm}$  in size, was used as an auxiliary electrode and an Ag/AgCl electrode was used as a reference electrode. The measurements of electrode potentials relative to the reference electrode were performed with an Elins PS-7 potentiometer.

## 3. Results and discussion

Raman spectra of the polymer and the composite material are shown in Fig. 1. The attributions of the peaks in the Raman spectrum of polyaniline can be found, for example, in Ref. [23–30]. It should be noted that the peaks at  $1620$  and  $1585 \text{ cm}^{-1}$  indicate the presence of benzoid and quinoid rings, respectively, in the investigated polymer. There are also peaks in the spectrum attributed to the sulfate groups (marked as  $\nu$ ) [31–33]. The positions of the peaks attributed to the sulfate groups are the same for the pure polymer and the composite. The presence of benzoid and quinoid rings in the spectrum of the composite cannot be determined because of the overlapping with a more intense G band ( $1593 \text{ cm}^{-1}$ ) from graphene oxide. However, almost complete coincidence of the bands in the low-frequency parts of the spectra of the samples being compared leads to the assumption that the structure of the polymer in the composite is similar to that of the pure polymer. It should be noted that in both spectra there is no band at  $1678 \text{ cm}^{-1}$ , a characteristic of partially degraded polyaniline [34].

The presence of graphene oxide in the composite material is confirmed by the detection of D and G bands in the spectra. The positions of these bands for the composite material ( $1335$  and  $1593 \text{ cm}^{-1}$ , respectively) are different from those in the original graphene oxide ( $1374$  and  $1611 \text{ cm}^{-1}$ , respectively). This difference could be the result of chemical interaction of GONS with the polymer. On the other hand, we do not see any shifts of the polymer bands in the composite material in comparison with the pure

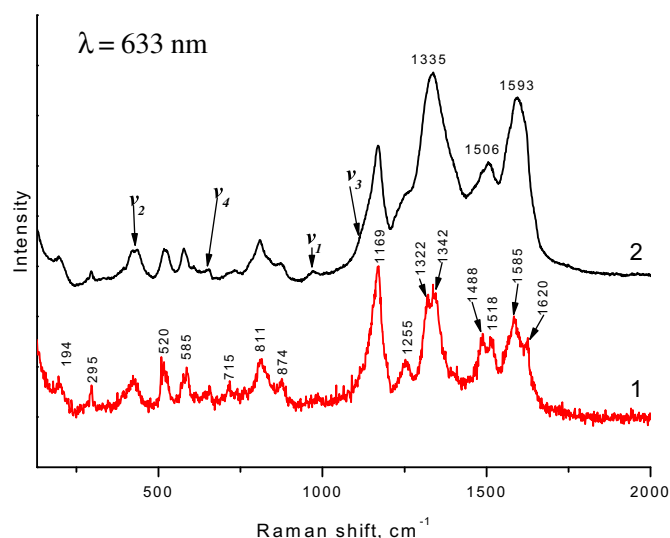


Fig. 1. Raman spectra of the polymer (1) and the composite material (2).

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