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EFFECTS OF THE NATURE OF OXIDANT AND SYNTHESIS CONDITIONS ON PROPERTIES OF NANOCOMPOSITES POLYANILINE/CARBON NANOTUBES

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Abstract: Nanocomposites based on carbon nanotubes, modified with polyaniline have been obtained. Polyaniline has been synthesized by oxidative polymerization of aniline. Potassium permanganate and ammonium persulfate have been used as oxidizers. The effects of the nature of oxidant and synthesis conditions on electoconductivity and morphology of the obtained materials have been studied.

Introduction

Conductive polymers, such as polyaniline, polypyrrole, polythiophene, polyacetylene, and others are promising electrode materials for chemical power sources [1–9]. A number of studies have investigated the electrochemical properties of nanocomposites containing carbon nanotubes (**CNTs**) and conductive polymers, including polyaniline [10–32]. For the application of these materials it is necessary to find optimal conditions for synthesis of polyaniline and composites containing it. Polyaniline possesses both electronic and ionic conductivity and can be obtained using available and inexpensive reagents.

Electrochemical characteristics of polyaniline are determined by its ability to reversible redox transformations. Polyaniline macromolecules have at least three redox forms. Different acids can act as protonating agents for nitrogen atoms (HA – acid molecule). In brackets it is shown one unit of the polymer chain (Fig. 1).

Normally HA is hydrochloric or sulfuric acid. Organic sulfonic acids are also used as agents for protonation of polyaniline. We presume that forms of polyaniline with greater degree of protonation are formed under oxidative polymerization with sufficient excess of oxidant or by dissolving of polyaniline in concentrated acids. Thus, the black solution of polyaniline in concentrated sulfuric acid may contain polyaniline in maximally protonated form. It should also be understood that the above linear structures of polyaniline are idealized. Really polyaniline can also contain branched fragments and the length of polymer chains may be different. In addition to the structure of the polymer chains, electrochemical properties of polyaniline to a large extent depend on the morphology of its particles (globules and agglomerates, nanofibers, nanotubes) determined by conditions of synthesis of PANI.

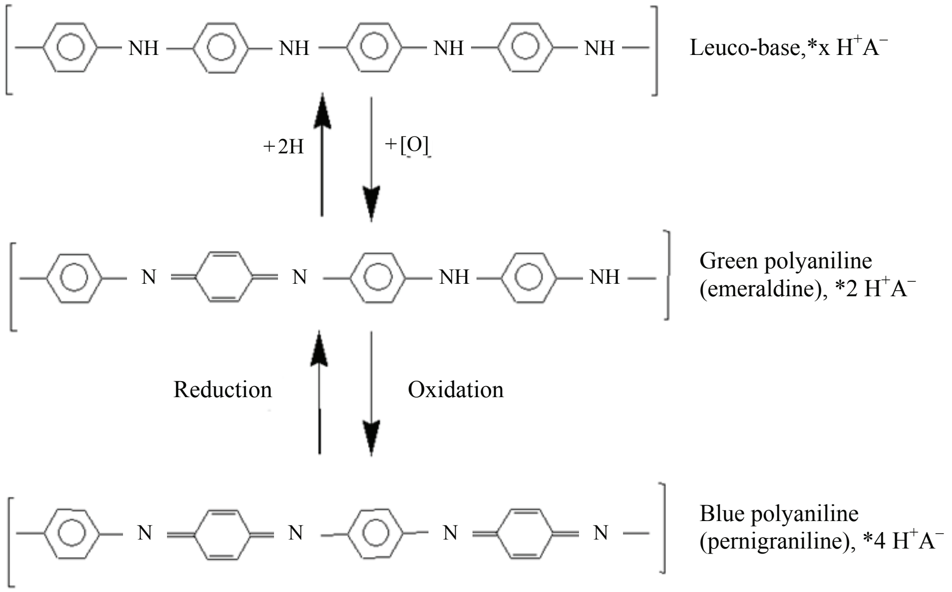


Fig. 1. Red-ox transformations of polyaniline

In particular, the degree of polymerization, morphological parameters, redox state of polyaniline and the degree of protonation, and consequently, its electrical and electrochemical properties depend on the nature of the oxidant, the ratio of oxidant to original aniline, consistency and speed of addition of reagents, acidity, temperature [33, 34]. To obtain a material with desired properties it is first necessary to determine optimal conditions of its synthesis.

The aim of this work was to investigate the influence of nature of oxidant and conditions of synthesis of polyaniline, particularly in presence of carbon nanotubes, on the yield of desired product, conductive properties of the PANI/CNTs nanocomposites and their morphological features.

Experimental

Following reagents were used: potassium permanganate $KMnO_4$ "Pure", ammonium persulfate "Chemically Pure"; aniline "Pure for analysis", acetic acid glacial "Chemically Pure", hydrochloric acid "Chemically Pure", sulfuric acid "Chemically Pure", nitric acid "Chemically Pure".

Carbon nanotubes "Taunit-M" were used (manufactured by NanoTechCenter Ltd., Tambov) with average outer diameter of 8…15 nm and lengths up to several micrometers. Nanotubes were purified from minerals (rests of catalyst) by treatment with concentrated hydrochloric acid and thoroughly washed with water.

PANI/CNTs nanocomposites were prepared by oxidation of aniline with ammonium persulfate or potassium permanganate in acidic medium in presence of purified carbon nanotubes "Taunit-M".

Oxidative polymerization of aniline under action of ammonium persulfate was carried out at cooling of the reaction mixture to 0 °C. When potassium permanganate was used as oxidizing agent the reaction was performed at 20 °C. Carbon nanotubes were dispersed in water with using ultrasound installation "IL-10". The resulting suspension was placed in a round bottom flask fitted with a Teflon mechanical stirrer. Reagent solutions were fed into the reaction mixture using a syringe dispenser "DSHV-01". Temperature control was performed with using cryothermostat or water bath. After addition of oxidant reaction mixture was stirred more 0.5 h in the case of permanganate or 1 h in the case of persulfate and allowed to stand overnight, after which the insoluble product was filtered on polypropylene filter, washed with water until colorless filtrate and then with acetone. Washing with acetone was necessary to remove admixture of oligomeric products from the product. The resulting material was dried at 80 °C to constant weight. In the experiments the concentration of acid in the reaction mixture, the ratio of oxidant to aniline, the rate of addition of oxidant, the amount of carbon nanotubes added to the system were varied. In some experiments, carbon nanotubes were pre-oxidized with potassium permanganate in acidic medium for attachment of surface carboxyl groups.

Mass content of PANI in samples of PANI/CNT nanocomposites obtained was calculated as the difference between the dry mass of the composite and mass of starting carbon nanotubes.

To determine the mass content of manganese dioxide in the PANI composites the specimens were burned in a muffle furnace at 700 °C in air. Under these conditions, manganese oxide goes into the oxide of the composition of Mn_3O_4. Using the data obtained the content of MnO_2H_2O in the initial samples was calculated.

To determine the electrical resistivity the samples were placed into a glass tube with internal section of 0.060 cm^2, and squeezed between two metal plungers with diameter of 2.7 mm at a pressure of 10 MPa. Electrical resistance of samples was measured with M838 multimeter and then recalculated to the specific resistivity, Ω·cm, by the formula

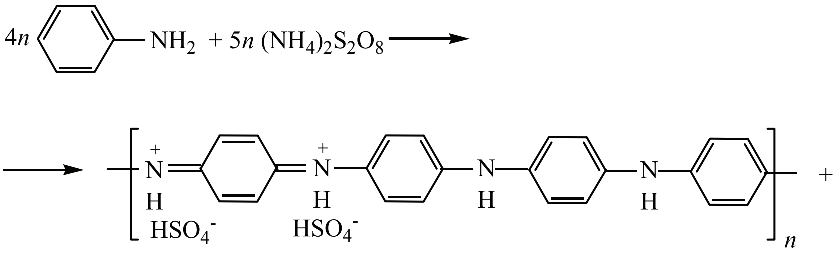
$$\rho = \frac{R_{\text{measured}} S}{h},$$

were R_{measured} – the measured electric resistance of material, Ω; S – internal section of glass tube (0.060 cm^2); h – height of the column of material under pressure, cm. As a rule, the height of the column of material was 0.3…0.4 cm.

The morphology of the composites based on carbon nanotubes modified with polyaniline was studied by electron microscopy using two-beam scanning electron microscopic complex Neon 40, Carl Zeiss.

Results and discussion

The method with using ammonium persulfate as an oxidizing agent is most common for the synthesis of polyaniline and composite materials based on it [33, 34]. Usually the process is carried out at temperature of 0…+5 °C, with gradual addition of ammonium persulfate solution into acidic solution containing aniline and auxiliary substances (surfactants, CNTs, templates, etc.). The oxidative polymerization of aniline is characterized by continuous decrease of pH of the medium, as protons are released during the reaction. The total process of oxidation of aniline to emeraldine salt with ammonium persulfate can be described by the following equation [33, 34]:



$$+\ 3n\,H_2SO_4\ +\ 5n\,(NH_4)_2SO_4 \qquad (1)$$

The peculiarity of ammonium persulfate is high redox potential, making it to be an efficient oxidizes of aniline. However, the rate of oxidation-reduction reactions involving ammonium persulfate in the absence of catalysts (transition metal compounds) is relatively small. Ammonium persulfate is gradually hydrolyzed in aqueous solution, and the rate of hydrolysis depends on the temperature and pH of the solution. Cooling the reaction mixture allows to reduce the degree of hydrolysis of ammonium persulfate. The oxidation of aniline by ammonium persulfate in acidic media proceeds relatively slowly. The reaction has an induction period.

Permanganate, as well as persulfate, has a high redox potential:

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O,\ E^o = 1.507\ V;$$

$$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O,\ E^o = 1.692\ V;$$

$$S_2O_8^{2-} + 2e^- = 2SO_4^{2-},\ E^o = 2.010\ V.$$

However, potassium permanganate reacts in the redox reactions faster than ammonium persulfate. In this regard, there is a problem with the possibility of over-oxidation of organic substances due to local excess of permanganate when it is added to the reaction mixture. For example, aniline in the presence of excess of oxidant (manganese dioxide) in sulfuric acid is oxidized to *p*-benzoquinone [35, p. 418]. To minimize the effects of local over-oxidation, a solution of potassium permanganate was added to the reaction mixture through a thin (1 mm) teflon tube with vigorous stirring (400 rpm).

Redox potential and direction of redox reactions involving potassium permanganate is also dependent on acidity of the medium. In neutral and weakly alkaline and weakly acidic solutions, the reduction of permanganate proceeds primarily with formation of manganese dioxide

$$KMnO_4 + 3[H] \rightarrow MnO_2 + KOH + H_2O. \qquad (2)$$

As our experiments have shown, deposition of manganese dioxide from aqueous solution in a weakly acidic medium hydrated manganese dioxide with composition close to the monohydrate, MnO_2H_2O, is formed.

However, in strongly acidic medium reduction of permanganate proceeds to divalent manganese

$$2KMnO_4 + 10[H] + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O. \qquad (3)$$

Thus, during the permanganate oxidation of aniline in medium with sufficient concentration of acid deposition of manganese dioxide can be avoided or decreased to minimum. According to equation (3), in the process of reduction of potassium permanganate in acidic medium concentration of acid decreases. In order to maintain constant acidity during the synthesis of polyaniline solution of acid was added into the reaction mixture from a separate syringe. Concentration and feed rate of acid was calculated so that the acid concentration in the reaction mixture remained constant. While carrying out the reaction in weakly acidic medium it was taken higher ratio of permanganate to aniline, considering that the reaction could proceed by the scheme (2), where the oxidative equivalent of permanganate is larger.

Usually green form of polyaniline, protonated emeraldine, forms as a result of oxidative polymerization of aniline in acidic medium with the amount of oxidant, which is close to the theoretical or taken in a small excess [33]. Theoretically, for the formation of an ideal chain of "green" form of polyaniline it is necessary to subtract 2.5 hydrogen atoms from each molecule of aniline

$$4nC_6H_5 - NH_2 - 10n[H] \rightarrow [- C_6H_4 - N = C_6H_4 = N - C_6H_4 - NH - C_6H_4 - NH -]_n \qquad (4)$$

or

$$4nC_6H_5 - NH_2 + 5n[O] \rightarrow [- C_6H_4 - N = C_6H_4 = N - C_6H_4 - NH\text{-}C_6H_4 - NH -]_n, + 5nH_2O \quad (5)$$

(molecules of sulfuric acid, protonating the polyaniline, are omitted for convenience of calculation).

According to these equations of redox reactions for conversion of aniline into the green form of polyaniline it is necessary to take amount of oxidant equivalent to 1.25 g-atom of oxygen per 1 mole of starting aniline, which is equivalent to 1.25 moles of ammonium persulfate or 0.5 moles of permanganate, if we consider the reaction of permanganate reduction to divalent manganese sulfate in acidic medium.

In [36] it was also found that the optimal yield and optimal electrical parameters of polyaniline obtained by oxidation of aniline with ammonium persulfate in hydrochloric acid medium, is achieved at molar ratio of 1.25 moles of ammonium persulfate per 1 mole of aniline, which coincides with the above theoretical calculation.

Thus, we can assume that potassium permanganate is used as an oxidizing agent its ratio to aniline should also be close to the theoretical (0.5 mole of permanganate per 1 mole of the starting aniline).

In Table there are shown synthesis conditions and parameters of the samples of polyaniline and its composites with carbon nanotubes and manganese dioxide obtained by oxidation of aniline with potassium permanganate and ammonium persulfate in acidic aqueous solutions under different conditions.

As it is shown in Table (samples No 1, 2), during the oxidation reaction of aniline with potassium permanganate in weakly acidic medium the samples contain significant amount of MnO_2 (as it was shown by the analysis of samples, during deposition from aqueous solution hydrated manganese dioxide is formed with a composition close to MnO_2H_2O). Nanocomposites PANI/manganese dioxide, PANI/manganese dioxide/ carbon nanotubes were synthesized in [37–41]. In these studies various methods for synthesis of these nanocomposites were proposed, namely, precipitation of manganese dioxide on a pre-synthesized polyaniline and polyaniline deposition on pre-synthesized nanoparticles of manganese dioxide. It was found that PANI and manganese dioxide in the nanocomposite have much greater capacity as electrode material in electric double layer capacitor (510 F/g) than the same components separately [41]. The samples obtained by us in weakly acidic medium, are nanocomposites PANI/manganese dioxide, which in this case are formed in one step. However, these samples have poor electrical conductivity. В литературе нет данных по электропроводности таких материалов. In literature there are no data on electrical conductivity of such materials. We can assume that in the polyaniline-manganese dioxide system donor-acceptor interaction occur between nitrogen atoms of PANI (electron pair donor) and tetravalent manganese ions (acceptor), resulting in violation of conjugation system along the polyaniline macromolecules, and thus, this is an obstacle for electron transfer. When performing the process in acidic medium with concentration of 0.1…2 M sulfuric acid (samples No 3–6) manganese dioxide in the resulting PANI is practically absent. Specific electric resistance of PANI samples obtained in these conditions varies from 42 to 570 Ω·cm, and, there is a minimum of resistivity at concentration of 0.5 M sulfuric acid (sample No 5). For reasons of optimum combination of electrical conductivity, product mass yield and acid consumption concentration of 0.1 M sulfuric acid was chosen for further experiments as optimal in this system.

When using ammonium persulfate as an oxidizing agent, an increase in polyaniline yield and its electrical conductivity was observed symbatically with acid concentration

Dependence of yield and properties of polyaniline and PANI/CNT composites on conditions of synthesis

Sample	[*A*], M	Ox/aniline, mole	*t*, h	% MnO_2	% PANI	PANI yield, %	ρ, Ω·cm
1) MnO_2/PANI	0.1 M acetic	1 MnO_4^-	5.62	31.4	68.6	78.4	$>10^9$
2) MnO_2/PANI	0.005	0.813 MnO_4^-	4.49	53.4	46.6	48.3	$>10^9$
3) PANI	0.1	0.5 MnO_4^-	3.75	<0.1	100	38.4	220
4) PANI	0.25	0.5 MnO_4^-	3.75	<0.1	100	25.4	480
5) PANI	0.5	0.5 MnO_4^-	3.75	<0.1	100	24	42
6) PANI	2	0.5 MnO_4^-	3.75	<0.1	100	4.1	570
7) PANI	0.5	1.25 $S_2O_8^{2-}$	2	–	100	34	250
8) PANI	1	1.25 $S_2O_8^{2-}$	2	–	100	37	35
9) PANI	2	1.25 $S_2O_8^{2-}$	2	–	100	75	27
10) PANI/CNT*	0.1	0.5 MnO_4^-	3.75	<0.1	67.7	50.4	5.4
11) PANI/CNT*	0.1	0.5 MnO_4^-	7.49	<0.1	73.7	67.7	8.4
12) PANI/CNT	0.1	0.5 MnO_4^-	7.49	<0.1	65.6	45.9	1.9
13) PANI/CNT	0.1	0.7 MnO_4^-	7.49	<0.1	72.6	63.9	3.0
14) PANI/CNT	0.1	0.5 MnO_4^-	7.49	<0.1	35.3	78.6	0.5
15) PANI/CNT	1	1.25 $S_2O_8^{2-}$	2	–	80.7	84	9.4
16) PANI/CNT	2	2 $S_2O_8^{2-}$	2	–	49	89	0.6
17) PANI/CNT	2	2.5 $S_2O_8^{2-}$	2	–	40	71	0.4
18) PANI/CNT*	1	1.25 $S_2O_8^{2-}$	2	–	53	92	2.3

[*A*] – concentration of acid in the reaction system, mole/L (sulfuric acid with potassium permanganate or hydrochloric acid with ammonium persulfate, for sample 1 – acetic acid).

Ox/aniline – molar ratio of oxidant (potassium permanganate or ammonium persulfate) to starting aniline.

t – duration of addition of oxidant.

% MnO_2 – mass content of manganese dioxide monohydrate in a sample (polyaniline – the rest).

% PANI – mass content of PANI in a sample (manganese dioxide monohydrate or CNTs – the rest).

PANI yield – in % from mass of starting aniline.

ρ – Specific electrical resistivity of a sample.

*The starting CNTs were additionally oxidized with potassium permanganate.

(samples No 7–9). Interestingly, when oxidation of aniline by ammonium persulfate was performed at approximately the same concentration of hydrogen ions (sample No 8, 1M HCl) as for the “permanganate” sample No 5 (0.5M H_2SO_4) electrical resistivity of the resulting polyaniline salt was 35 Ω·cm, which is close to 42 Ω·cm for sample No 5. The same analogy can be traced by comparing the sample No 4, obtained by oxidation of aniline with potassium permanganate in 0.25 M sulfuric acid solution, with the sample No 7, obtained by oxidation of aniline by ammonium persulfate in 0.5 M hydrochloric acid solution, when the resistivity of the samples are respectively 480 and 250 Ω·cm – of the same order of magnitude. Thus, the degree of protonation of polyaniline, which which is of the utmost impact on its conductive properties, is only slightly dependent on the nature of the oxidant, but is determined, above all, by the concentration of acid in the reaction solution. The increase in resistivity of the material obtained by oxidative polymerization of aniline in presence of $KMnO_4$ in 2M sulfuric acid (sample No 6), possibly appears due to the partial transition of emeraldine form of polyaniline into less conductive pernigraniline form.

According to the work of Stejskal et al. [33, 34], in the process of aniline oxidation by ammonium persulfate increasing of the duration of induction period of the reaction of oxidative polymerization with increasing acidity of the medium was observed, in which nucleates were formed, which are growth centers for polyaniline chains with high molecular weight. As a result, content of oligomers in the product decreased.

Introduction of carbon nanotubes increases the electrical conductivity of polyaniline and composites based on it. These nanocomposites were synthesized by the addition of carbon nanotubes into the starting reaction mixture. Deposition of polyaniline was carried out under conditions corresponding to the synthesis of the polyaniline sample No 3 in the Table, that is, the medium of 0.1M sulfuric acid, amount of permanganate 0.5 mole/mole of the starting aniline. In experiment No 13 amount of permanganate was increased to 0.7 mole/mole of the starting aniline. In experiments No 10, 11, before the introduction of the original nanotubes into the reaction mixture they were oxidized with acidified potassium permanganate solution (0.830 g of potassium permanganate 1 g of CNTs).

As is shown in Table, the introduction of carbon nanotubes leads to significant decrease of electrical resistivity of the samples, from 220 Ω·cm for polyaniline synthesized without CNTs under comparable conditions, up to 0.5…5.4 Ω·cm for the nanocomposites polyaniline/CNT, due to better electrical conductivity of CNTs compared to polyaniline. Increasing of time of addition of potassium permanganate (compare samples No 10 and 11), at the same other conditions, leads to increase of the mass content of PANI in the PANI sample and yield of PANI from aniline. It can be assumed that the polymerization of aniline oligomers formed initially is slow, and their overoxidation by too rapid addition of oxidant in this system leads to decrease of the PANI yield.

Additional oxidation of the CNTs before introduction into the reaction mixture is likely to promote better adhesion of polyaniline to nanotubes, which led to the increase of PANI yield from 45.9 to 67.7 % (samples No 11 and 12). It can be assumed that the oxidized surface of carbon nanotubes containing carboxyl groups works as a template on which (first) adsorption of aniline molecules occurs, followed by their oxidative polymerization. По видимому наличие темплата приводит к увеличению выхода полианилина из анилина и его олигомеров. Apparently the presence of template increases the yield of polyaniline from aniline and its oligomers. In experiment No 13 amount of permanganate was raised relative to the starting aniline. As result, nanocomposite was obtained, which, as well as samples with pre-oxidized carbon nanotubes, was characterized by higher content of PANI.

In Fig. 2 there is shown electrical resistivity of nanocomposites PANI/ CNT vs. mass content of CNTs in the composite. As can be seen, regardless of the oxidant used the data fit in a single curve, if non-oxidized CNTs were used for synthesis. However, preliminary oxidation of carbon nanotubes with permanganate increases electrical resistance of the PANI/CNTs samples, and these data are in Fig. 2 above the plot. It should be noted that similar effect occurs when CNTs are introduced into various electrically non-electroconductive polar polymers. Oxidation of the CNTs surface, promoting better compatibility of CNTs with polymer, leads to increase of electrical resistance at the same mass content of CNTs in the sample. It can be assumed that the oxidized surface of carbon nanotubes behaves as a template for aniline and its oligomers, which favors formation of more dense and uniform polymer coating on the surface of CNTs. As a result, electrical contacts between individual nanotubes are interrupted, which leads to increasing of electrical resistance. It is also possible that the oxidized nanotubes are less aggregated in the matrix of the polar polymer or in the reaction medium while deposition of PANI, which interrupts contacts between nanotubes and increases the electrical resistance of the nanocomposite.

Typical electronic images (scanning electron microscope) of the original CNT Taunit-M, polyaniline and nanocomposites PANI/CNT are shown in Fig. 3–5.

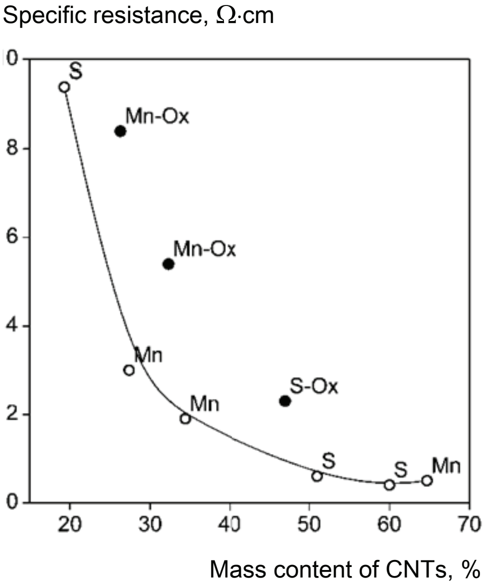


Fig. 2. Dependence of the specific electrical resistivity of nanocomposites polyaniline/ carbon nanotube on mass content of carbon nanotubes:
Mn – the samples obtained with use of potassium permanganate; S – the samples obtained with use of ammonium persulfate; Ox – initial CNTs were pre-oxidized

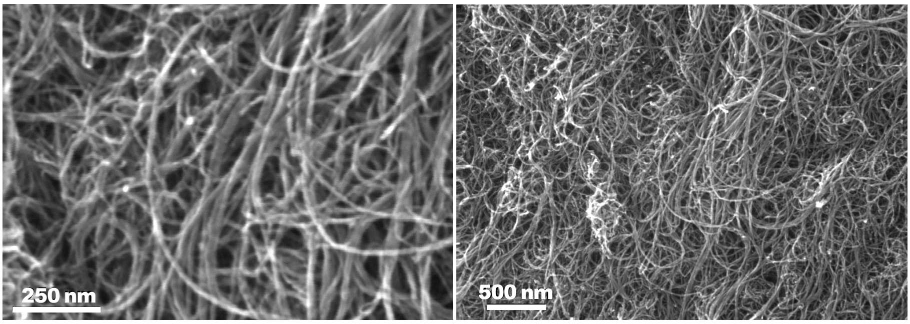


Fig. 3. Carbon nanotubes Taunite-M (SEM)

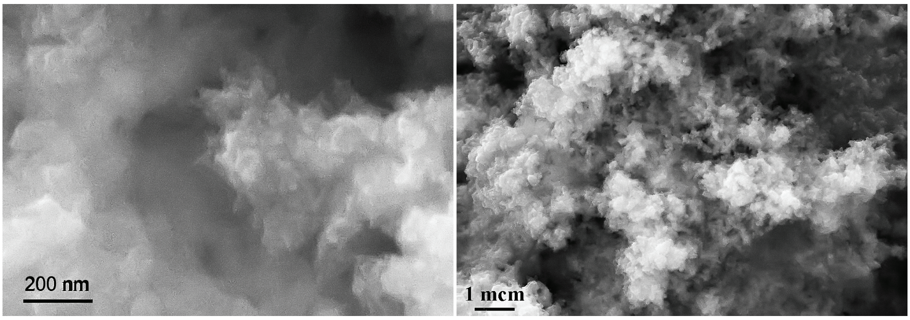
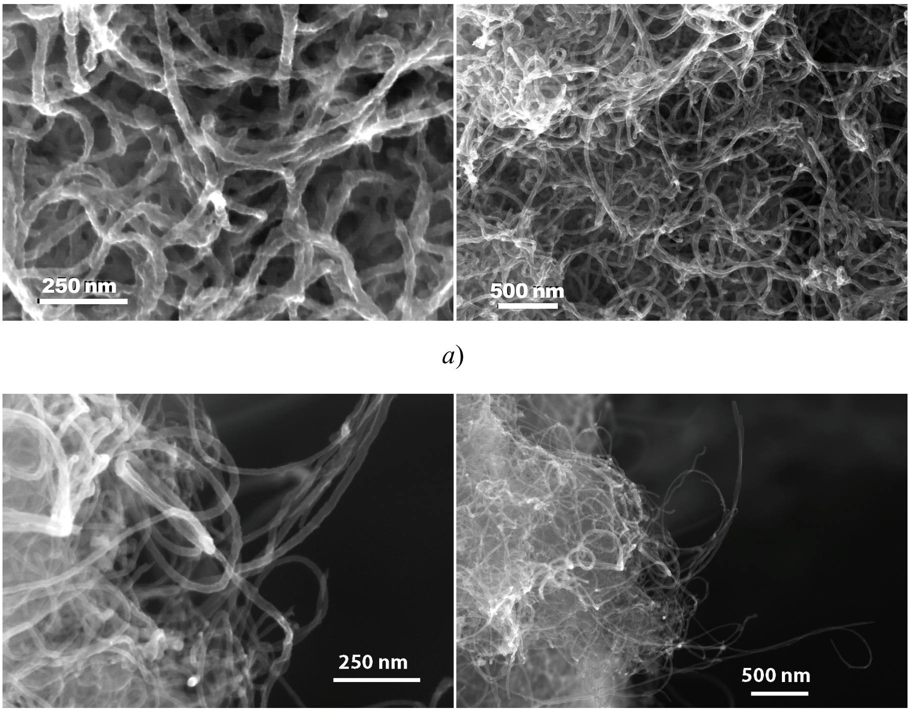


Fig. 4. Polyaniline synthesized by oxidative polymerization of aniline under the action of potassium permanganate (SEM)



a)

b)

Fig. 5. Nanocomposite based on carbon nanotubes Taunit-M modified with polyaniline
(SEM, sample No 12 (*a*) and 14 (*b*) in Table)

As can be seen from the figures, deposition of PANI leads to significant increase in the observed diameter of the nanotubes compared to the initial CNTs Taunit-M. Virtually all PANI is in the form of coating on the surface of nanotubes, as extrinsic particles in the images are not observed. For the sample No 14, in which mass content of PANI is less compared to the sample No 12, observed diameter of the coated nanotubes is considerably less.

Conclusions

1. Oxidation of aniline with potassium permanganate in weakly acidic medium leads to formation of manganese dioxide-polyaniline nanocomposites, which are characterized by poor electrical conductivity.
2. Oxidation of aniline with potassium permanganate in medium of sulfuric acid with concentration of 0.1M and more gives conductive polyaniline, which does not contain impurities of manganese dioxide. Electrical conductivity of polyaniline obtained depends to a larger extent on the acid concentration in the reaction medium than on the nature of the oxidant.
3. Electrical conductivity of the nanocomposites polyaniline/CNT increases with increasing mass content of CNT and decreases if surface of CNTs. was preliminary oxidized.

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Влияние природы окислителя и условий синтеза на свойства нанокомпозитов полианилин/углеродные нанотрубки

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Ключевые слова и фразы: перманганат калия; персульфат аммония; полианилин; углеродные нанотрубки.

Аннотация: Получены нанокомпозиты на основе углеродных нанотрубок, модифицированных полианилином. Полианилин синтезирован методом окислительной полимеризации анилина под действием перманганата калия или персульфата аммония. Исследовано влияние природы окислителя и условий синтеза на электропроводность и морфологию полученных материалов.

Einwirkung der Natur des Oxydiermittels und der Bedingungen der Synthese auf die Eigenschaften von den Nanokompositen das Polyanilin/die Kohlenstoffnanoröhre

Zusammenfassung: Es sind die Nanokomposite aufgrund der Kohlenstoffnanoröhre, die vom Polyanilin modifiziert sind, erhalten. Das Polyanilin ist von der Methode der Oxidationspolyrisation des Anilins unter dem Einfluß des

Kaliumpermanganat oder des Ammoniumperoxodisulfates synthetisiert. Es ist die Einwirkung der Natur des Oxydiermittels und der Bedingungen der Synthese auf die Leitfähigkeit und die Morphologie der erhaltenen Materialien untersucht.

Influence de la nature de l'oxydant et des conditions de la synthèse sur les propriétés des nanocomposites polyaniline/nanotybes carboniques

Résumé: Sont obtenus les nanocomposites à la base des nanotybes carboniques modifiés par polyaniline. La polyaniline est synthésée par la méthode de la polymérisation oxydante du permanganate du potassium ou du persulfate de l'ammonium. Est étudiée l'influence de la nature de l'oxydant et des conditions de la synthèse sur la conductibilité électrique des matériaux obtenus.

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