ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 5, pp. 1146–1151. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © K.A. Milakin, I.A. Yaremenko, A.V. Smirnova, O.A. Pyshkina, V.G. Sergeyev, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 5, pp. 852–858.

Effect of Multiwall Carbon Nanotubes Surface on Polymerization of Aniline and Properties of Its Products

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Received March 5, 2015

Abstract—The effect of surface of multiwall carbon nanotubes on the course of oxidative polymerization of aniline has been studied. In the presence of amorphous carbon fragments at the nanotubes surface, the polymerization at the monomer : nanotubes mass ratio of 10 : 1 yields the composite based on polyaniline and carbon nanotubes. At the same components ratio, carbon nanotubes purified of amorphous carbon inhibit polymerization of aniline, and the process results in oxidation of the nanotubes surface; however, at the lower purified nanotubes content the polymerization proceeds to give the polyaniline/nanotubes composite. Purification of the nanotubes of amorphous carbon significantly enhances electrochemical stability of their composites with polyaniline.

Keywords: multiwall carbon nanotubes, polyaniline, polymerization, free radical acceptor, surface structure, electrochemical properties

DOI: 10.1134/S1070363215050242

Polyaniline (PANI) is an organic conductive polymer recognized for the preparation simplicity, excellent stability under environmental conditions [1], and a wide range of possible applications including antistatic, corrosion-inhibiting, and conductive coatings [2], electrochromic devices [3, 4], lithium batteries [5], and sensors [6–8]. Multiwall carbon nanotubes (MWCNT) are known for outstanding electronic [9] and mechanical [10] properties and serve as promising components of advanced materials. The combination of electrochemical properties of PANI and high surface area of MWCNT allows for production of high-capacity electrochemical capacitors. Interestingly, electrical conductivity of the PANI/MWCNT composite may be higher than that of the initial components [11]. Furthermore, the presence of MWCNT in the polymerization mixture is known to affect the aniline polymerization course (the induction period is decreased) as well as the product properties (polyaniline is formed in the more oxidized state) [11]. To the best of our knowledge, the influence of the MWCNT surface nature on aniline polymerization and the properties of the formed polyaniline has not been reported in the literature so far. In order to fill in the gap, herein we present and discuss the relevant experimental data.

Transition metal salts [for instance, these of Fe(III) and Ce(IV)] act as mediators of oxidative polymerization of aniline [12, 13] and may change the formed polymer physico-chemical properties [12]; therefore, the MWCNT used in this work were purified of the residual metal catalyst via treatment with hydrochloric acid (cf. Experimental section and [14]). Figure 1 presents TGA data for pristine MWCNT and the nanotubes purified with hydrochloric acid (hereafter designated as $MWCNT_{HCl}$).

Thermal oxidative decomposition of the pristine MWCNT over 250–550°C was accompanied with mass loss of 15% (Fig. 1, curve *1*), likely corresponding to decomposition of fragments of amorphous carbon initially present at the MWCNT surface. The second stage of mass loss was observed at 550–650°C (the mass loss of 75%) and was assigned to decomposition of carbon nanotubes [15]. The high-temperature residue at 650°C was of 10% of the starting mass; the specimen mass somewhat increased upon further heating, likely due to oxidation of the metal catalyst. The mass loss at 250–550°C was not observed upon heating of the nanotubes purified with HCl (Fig. 1, curve *2*). Hence, treatment of MWCNT

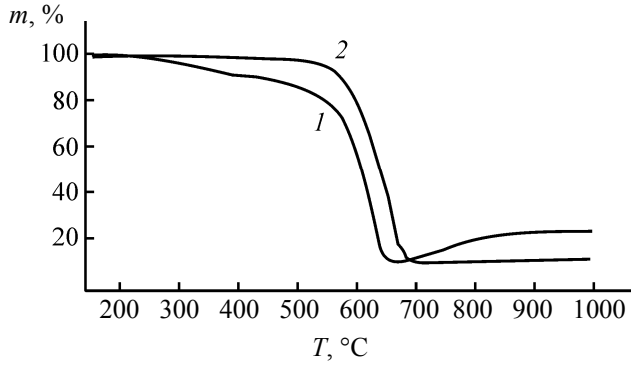


Fig. 1. TGA curves of (*1*) pristine multiwall carbon nanotubes and (*2*) $MWCNT_{HCl}$ in air.

with HCl allowed for complete removal of amorphous carbon admixture from the material. The mass loss corresponding to thermal oxidation of the so purified nanotubes was observed at 600–680°C, at higher temperature as compared to the pristine MWCNT. That was due to partial removal of metal catalyst residue (which presence is known to deteriorate the nanotubes stability against thermal oxidation [15]) from the material.

TEM images revealed that pristine MWCNT sample contained individual carbon nanotubes as well as those surrounded with amorphous carbon fragments (Fig. 2a), whereas the $MWCNT_{HCl}$ one consisted exclusively of individual nanotubes (Fig. 2b).

Electrochemical properties of pristine MWCNT and $MWCNT_{HCl}$ were also different. As seen from cyclic voltammetry results (Fig. 3), voltammograms of the pristine MWCNT (curve *1*) was close to the rectangular shape, due to charging of the electrical double layer [16]. Weak oxidation peaks at ≈0.15 V and ≈0.3 V could be likely assigned to redox transitions of oxygen-containing groups present at the amorphous carbon part of the sample [14]. Those peaks were not observed in the voltammogram of the $MWCNT_{HCl}$ sample, the registered current corresponded exclusively to capacitance of the electrical double layer (curve *2*). Decrease of the specific capacitance of $MWCNT_{HCl}$ (2.5 F/g) as compared to that of pristine MWCNT (4.2 F/g) evidenced about the nanotubes surface change due to removal of the amorphous carbon fragments [17]. Hence, TGA, TEM, and cyclic voltammetry results demonstrated that treatment of pristine MWCNT with hydrochloric acid purified the nanotubes of amorphous carbon and the metal catalyst residue.

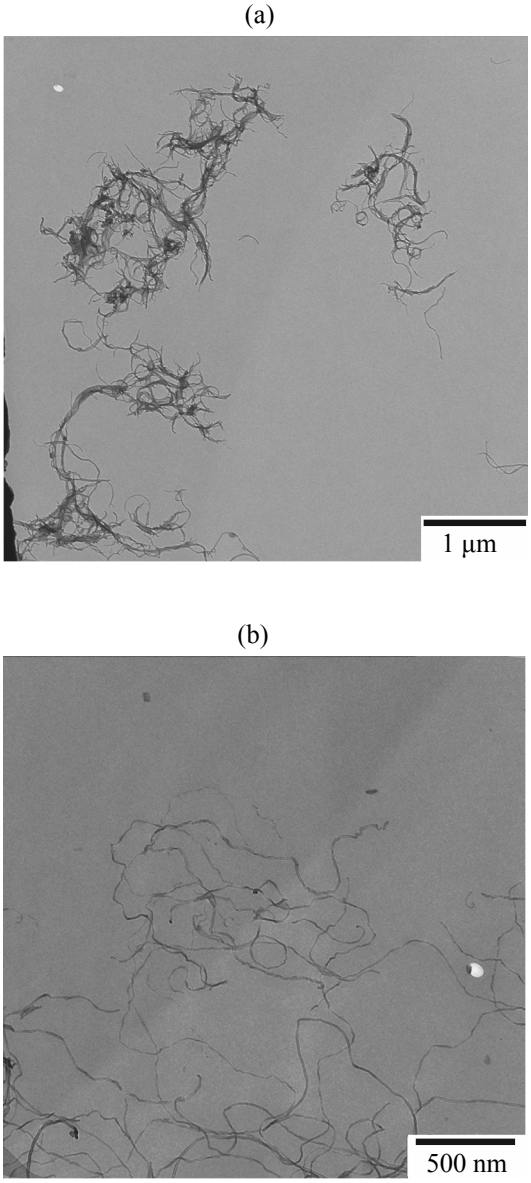


Fig. 2. TEM images of (a) pristine multiwall carbon nanotubes and (b) $MWCNT_{HCl}$.

Raman spectroscopy is among the widespread methods to study carbon materials allowing estimation of relative defectiveness of MWCNT from the ratio of the I_G (≈1600 cm^{-1}, C–C stretching in graphene sheets) and I_D (≈1330 cm^{-1}, vibration of the defective fragments of the nanotubes [14]) band intensities. In the case of MWCNT, the D band is mostly contributed by defects of the graphene sheets rather than the amorphous carbon admixture [18]. Figure 4 displays Raman spectra of the pristine MWCNT and the $MWCNT_{HCl}$ samples at the excitation wavelength of 514 nm.

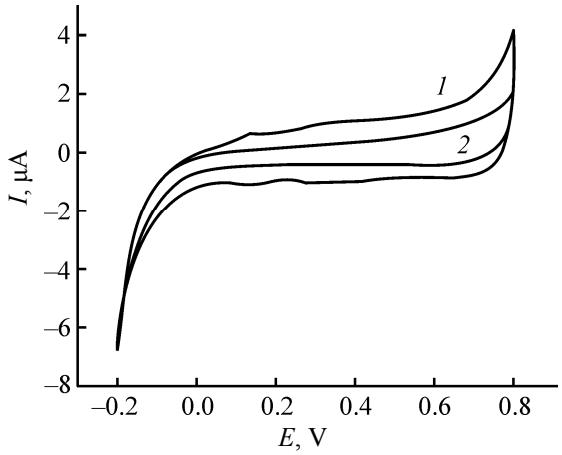


Fig. 3. Cyclic voltammograms of (*1*) pristine multiwall carbon nanotubes and (*2*) $MWCNT_{HCl}$.

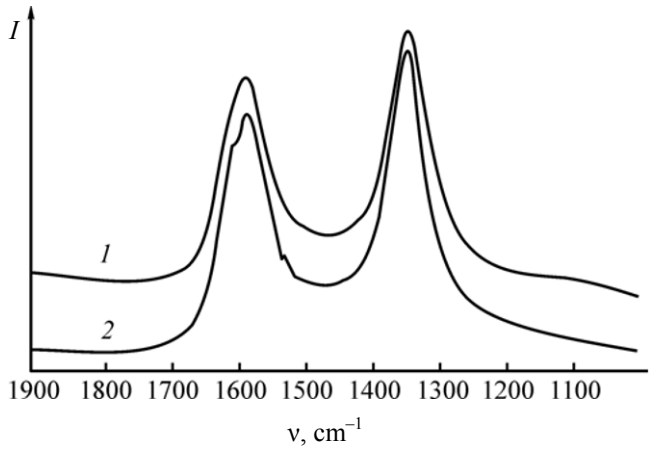


Fig. 4. Raman spectra of (*1*) pristine multiwall carbon nanotubes and (*2*) $MWCNT_{HCl}$.

The I_D/I_G ratio in spectra of $MWCNT_{HCl}$ (1.2) was lower than that of the pristine MWCNT (1.35). The presence of a strong D band in the Raman spectrum of the nanotubes treated with HCl evidenced about the presence of defects in their walls, becoming exposed to the reaction mixture after removal of the amorphous carbon fragments.

Oxidative polymerization of aniline with ammonium persulfate in the acidic medium (pH 0) was performed in the presence of the $MWCNT_{HCl}$ (the aniline : nanotubes mass ratio being of 10 : 1 or 30 : 1) or in the presence of the pristine MWCNT (10 : 1). Figure 5 shows IR spectra of the reaction products under those conditions.

IR spectrum of the product of oxidative polymerization of aniline in the presence of $MWCNT_{HCl}$ (aniline : $MWCNT_{HCl}$ = 10 : 1) (Fig. 5, curve *1*) contained no characteristic absorption bands of PANI (around 1600, 1500, and 1300 cm^{-1}) but exhibited strong bands at 1390 cm^{-1} and at 1100 cm^{-1} (broad). Similar absorption bands assigned to COH deformation [19] and C–O stretching [20] have been observed in IR spectrum of MWCNT treated with ammonium persulfate [21, 22]. Hence, under the mentioned conditions aniline almost was not polymerized; instead, $MWCNT_{HCl}$ were oxidized with ammonium persulfate to introduce oxygen-containing groups at the nanotubes surface. As seen from Fig. 5 (curve *2*), when the aniline : nanotubes ratio was changed to 30 : 1, IR spectrum of the reaction mixture contained characteristic absorption bands of PANI: 1570 cm^{-1} (C=C stretching in quinonediimine fragments), 1490 cm^{-1} (C–C stretching in phenylenediamine fragments), and 1300 cm^{-1} (C–N deformation vibrations [23]) as well as 1250 and 1130 cm^{-1} ($C–N^{+}$* stretching in the polaron structures [24]). The spectrum of product of oxidative polymerization of aniline in the presence of the pristine MWCNT (10 : 1) (Fig. 5, curve *3*) contained the characteristic absorption bands of PANI (1566, 1481, 1296, 1240, and 1130 cm^{-1}) as well. On top of that, the absorption band at 1403 cm^{-1} was observed, and the band at 1460 cm^{-1} was broadened; those changes pointed at formation of side products along with PANI. In summary, IR spectroscopy of the reaction products evidenced that at the aniline : $MWCNT_{HCl}$ ratio of 10 : 1 aniline was not polymerized, but PANI was formed in the similar system at the aniline : $MWCNT_{HCl}$ ratio of 30 : 1 or in the aniline/pristine MWCNT (10 : 1) system. Major absorption bands of the prepared PANI samples were shifted towards higher wavenumbers as compared with those of PANI synthesized in the absence of any carbon nanotubes. Hence, the interaction between PANI and pristine MWCNT (or $MWCNT_{HCl}$) could be pointed out.

Polymerization of aniline follows the scheme shown below; each stage of the monomer addition includes oxidation of the terminal amino group of the growing chain with the initiator or its decomposition product (for instance, sulfate anion-radical) [25]. The chain propagates while the oxidizer was present in the reaction mixture [26], therefore the monomer-to-oxidizer is a crucial parameter determining the possibility of aniline polymerization to yield high-molecular weight PANI (Scheme 1).

Carbon nanotubes have been recognized as efficient free radicals trap [27–30]; they could hence intercept

the active anion-radicals present in the system, thus inhibiting the polymerization. It was the anion-radicals trapping with the defects at the nanotubes surface that decreased the effective oxidizer concentration and inhibited PANI chains propagation in the presence of $MWCNT_{HCl}$ (aniline : $MWCNT_{HCl}$ ratio of 10 : 1). The observed difference in the behavior of the pristine MWCNT and the $MWCNT_{HCl}$ was due to the exposition of the nanotubes defects (acceptors of free radicals) to the reaction mixture after removal of amorphous carbon during the acidic treatment.

Electrochemical properties of the products of aniline polymerization in the presence of the pristine MWCNT (10 : 1) and $MWCNT_{HCl}$ (30 : 1) were further studied by means of cyclic voltammetry (Fig. 6). In the both cases, the voltammograms (2nd cycles) contained the anodic peaks at ≈0.1 V and ≈0.55 V, typical of the redox transitions of PANI (leucoemeraldine → emeraldine and emeraldine → pernigraniline, respectively).

The voltammograms shown in Fig. 6 demonstrated that cycling behavior of the studied composite materials was significantly different. In particular, cyclic voltammogram of the composite prepared via polymerization in the presence of pristine MWCNT exhibited the steadily weakening of peaks assigned to PANI redox transitions with the cycle number growing from 2 to 10; the overall current decreased to reach the constant value (the equilibrium specific redox capacitance of 42 F/g). In the case of the composite prepared in the presence of $MWCNT_{HCl}$, the voltammogram shape and intensity were practically constant up to 10th cycle, the equilibrium redox capacitance of the material being of about 45 F/g. The different electrochemical behavior of PANI composites prepared in the presence of the pristine MWCNT and $MWCNT_{HCl}$ was attributed to the structural properties of the nanotubes surface; in particular, with the nature of interaction of PANI with conjugated aromatic system of $MWCNT_{HCl}$ (π-stacking) and with the pristine MWCNT (hydrogen bonding with oxygen-containing groups at the amorphous carbon fragments).

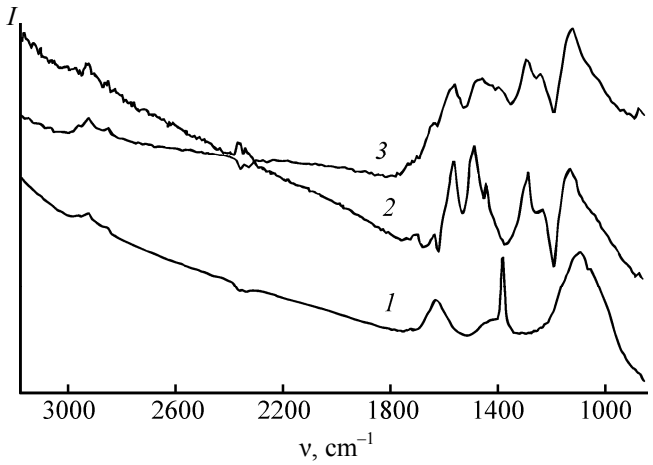


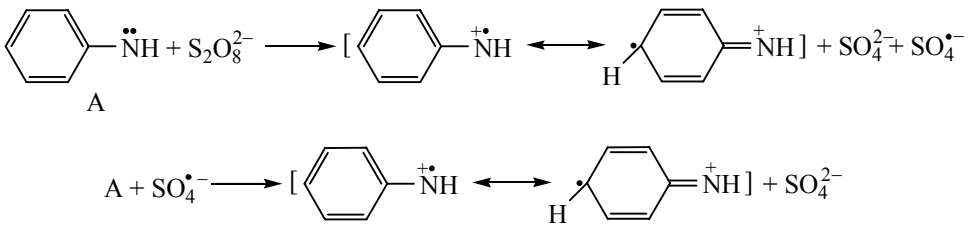
Fig. 5. IR spectra of products of oxidative polymerization of aniline in the presence of $MWCNT_{HCl}$ [aniline : $MWCNT_{HCl}$ = 10 : 1 (*1*) and 30 : 1 (*2*)] and (*3*) in the presence of pristine multiwall carbon nanotubes [aniline : nanotubes = 10 : 1].

To conclude, we demonstrated the effect of the surface nature of multiwall carbon nanotubes (in particular, the presence of amorphous carbon fragments) on oxidative polymerization of aromatic amines taking aniline as an example. The presence of $MWCNT_{HCl}$ acting as free radicals trap prevented the oxidative polymerization; however, at the lower nanotubes loading PANI was formed as emeraldine salt. Similarly, in the presence of the pristine MWCNT with the radical traps shielded with amorphous carbon the emeraldine form of PANI was formed. Purification of the nanotubes of amorphous carbon allowed significant enhancement of electrochemical stability of the prepared composite PANI materials.

EXPERIMENTAL

Aniline hydrochloride (MP Biomedicals, USA) and ammonium persulfate (ICN Biomedicals, USA) were used as received. Hydrochloric acid (1 mol/L) solution

Scheme 1.



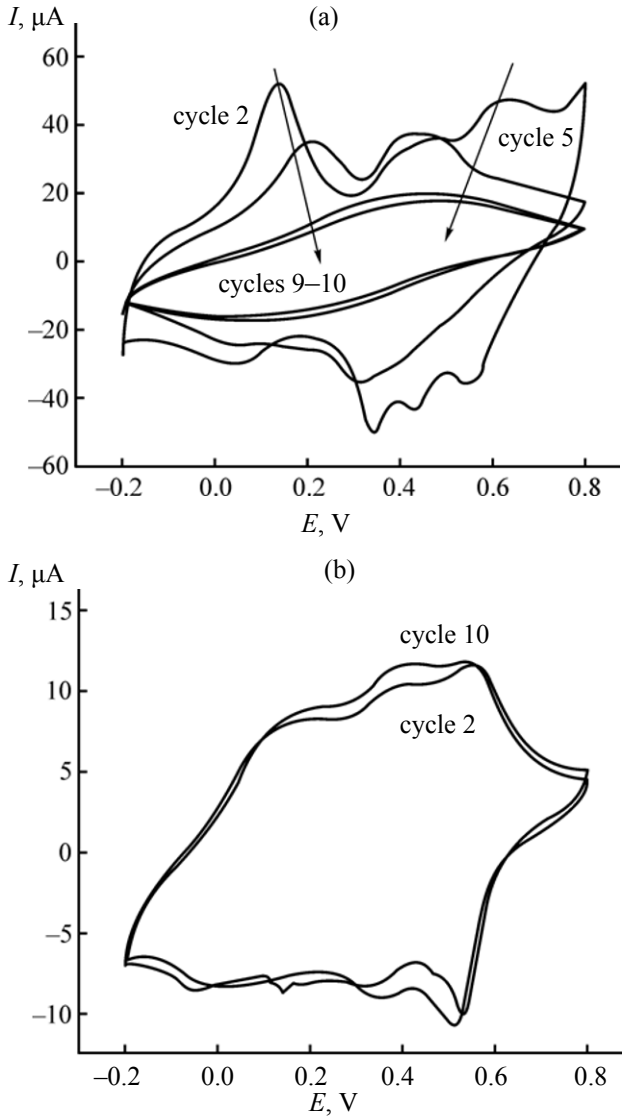


Fig. 6. Cyclic voltammograms of products of oxidative polymerization of aniline in the presence of pristine multiwall carbon nanotubes (10 : 1) (a) and $MWCNT_{HCl}$ (30 : 1) (b). Arrows point at the curve change with the cycle number.

was prepared from the standard titrimetric sample. Twice distilled water was used as solvent.

Multiwall carbon nanotubes produced via CVD (diameter of 8–20 nm and up to 2 μm long, Nanocyl NC-7000, Belgium) were either used as received or treated with hydrochloric acid (100 mg of the pristine MWCNT were stirred with 100 mL of conc. HCl during 24 h at 20°C). The purified nanotubes were filtered off using a nylon filter (pores diameter of 0.2 μm), washed with water till neutral reaction of the washings, and dried in air.

Aniline polymerization in the presence of pristine MWCNT (10 : 1). A dispersion of 10 mg of MWCNT in 90 mL of water was ultrasonicated (at MELFIZ-ultrazvuk ultrasound probe, Russia) during 10 min on an ice bath. Then, 10 mL of conc. HCl, 100 mg of aniline hydrochloride, and 2 mL of 0.39 M solution of ammonium persulfate in 1 M aqueous HCl were added to the nanotubes dispersion (the aniline to the oxidizer ratio was equimolar). The reaction mixture was stirred and incubated in air during 16 h. The reaction products were isolated via filtration through nylon filter (pores diameter of 0.2 μm), washed with 1 M aqueous HCl, and dried in air.

Polymerization of aniline in the presence of the $MWCNT_{HCl}$ (10 : 1 and 30 : 1) was performed similarly, using 10 or 3.3 mg of the purified nanotubes, respectively.

IR spectra of KBr pellets were recorded at 400–4000 cm^{-1} with the resolution of 4 cm^{-1} using a ThermoNicolet IR200 spectrometer. Raman spectra were recorded using a Renishaw inVia spectrometer (λ_{ex} = 514 nm) at 1000–2000 cm^{-1}.

TGA was performed with an STA 449 F3 Jupiter instrument (Netzsch) under linear heating from 25 to 1000°C at 10 K/min in air.

TEM studies were performed using a LEO912 AB OMEGA microscope (Carl Zeiss, Germany).

Electrochemical measurements were performed in 0.1 M. aqueous HCl using a three-electrode cell based on an EmStat potentiostat (PalmSens, the Netherlands) at the potential scan speed of 10 mV/s. The specimen dispersion was deposited at the working surface of a planar electrode (Rusens, Russia) consisting of the working electrode (graphite paste C10903P14, Gwent), the auxiliary electrode (graphite paste C2030519D4, Gwent), and the silver/silver chloride reference electrode. Specific capacitance of the material was calculated as follows [31]:

$$C = \{1/[2vm(E_2 - E_1)]\}\int_{E_2}^{E_1} i(E)dE,$$

with C, specific capacitance of the specimen; E_1 and E_2, limits of the potential range; v, potential scan rate; m, specimen mass (voltammogram area).

ACKNOWLEDGMENTS

Authors are grateful to Dr. A.K. Berkovich for TGA experiment and Dr. S.S. Abramchuk for TEM studies.

This work was financially supported by Russian Foundation for Basic Research (projects 14-03-31332_mol_a and 13-03-00605_a).

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