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Three-Component Composite Systems Based on Multi-Walled Carbon Nanotubes, Polyacrylic Acid, and Silver Nanoparticles

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Abstract—Three-component systems containing multi-walled carbon nanotubes and silver nanoparticles dispersed in aqueous solutions of polyacrylic acid (*M* 2000 and 250000) have been studied by electronic absorption spectroscopy and transmission electron microscopy. The studied dispersions were stable during at least several months. Size of silver nanoparticles prepared in the absence and in the presence of the carbon nanotubes has been compared; the effect of polyacrylic acid molecular mass on silver nanoparticles size has been addressed as well.

Keywords: multi-walled carbon nanotubes, MWCNT, polyacrylic acid, silver nanoparticles, stable aqueous dispersion

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Nanostructured composite materials have recently attracted the emerging research interest; such materials are promising for various practical applications due to unique combination of properties. In this regard, materials combining mechanical stiffness and electrical conductivity of carbon nanotubes with properties of metal nanoparticles are of special importance. Such composites have already found applications in heterogeneous catalysis [1, 2], sensors development [3], electronics [4], and medicine [5].

Generally, dispersions of pristine carbon nanotubes are unstable towards sedimentation and aggregation, and thus they cannot be used in practice for preparation and stabilization of metal nanoparticles. In order to form a composite material based on carbon nanotubes, surface of the latter should be somehow activated. To do so, various chemical methods are often applied, including oxidation with strong inorganic acids [6]. This method suffers from some serious drawbacks: oxidation is usually accompanied with appearance of numerous structural defects at the modified nanotubes (hence, their electronic structure is disordered as well) and with shortening of the nanotubes due to partial degradation. Recently, a new approach has been suggested to prepare composites based on carbon nanotubes and metal nanoparticles using polyelectrolytes [7]. Indeed, macromolecules are capable of efficient solubilization of carbon nanotubes via cooperative action of weak dispersive forces; the high density of functional groups at the nanotubes surface is thus ensured [1, 7]. To generalize, macromolecules modify the nanotubes surface and further act as nanosized reactors facilitating synthesis and assembly of metal nanoparticles.

Earlier, we have demonstrated [8] that multi-walled carbon nanotubes (MWCNT) can be dispersed in solutions of polyacrylic acid (PAA) of different molecular mass to form dispersions stable towards sedimentation and aggregation over at least several months. Carboxylic groups are known to form complexes with silver ions and stabilize the appeared silver clusters and nanoparticles [9, 10]. In view of the above, it was of definite interest to prepare silver nanoparticles in dispersions of MWCNT stabilized with PAA and investigate the structure of the so formed three-component systems.

Dispersion of MWCNT in solutions of polyacrylic acids yielded stable aqueous suspensions; their electronic absorption spectra are shown in Fig. 1. Spectra of the PAA–MWCNT dispersions contained an absorption band with maximum at 260 nm, typical of individual carbon nanotubes and caused by plasmon

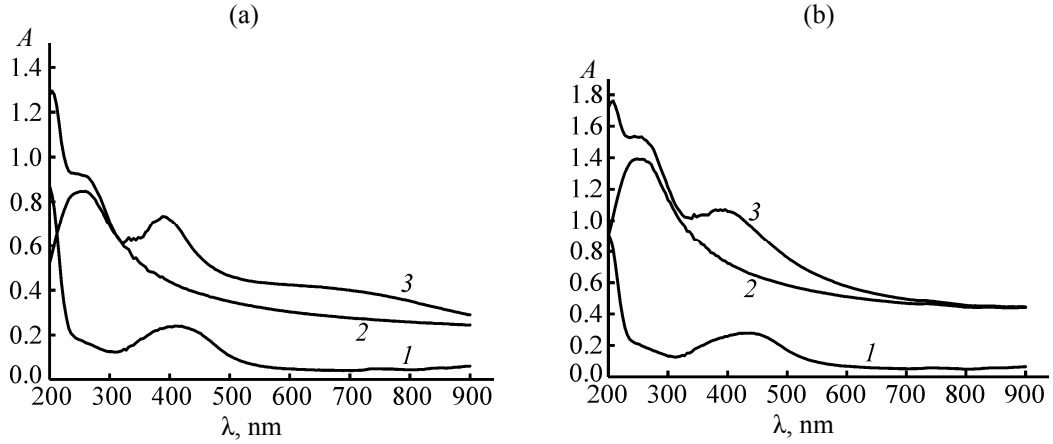

Fig. 1. Electronic absorption spectra of aqueous dispersions containing (a) PAA_{2000} and (b) PAA_{250000}. The dispersions composition: (*1*) PAA_x–Ag, (*2*) PAA_x–MWCNT, and (*3*) PAA_x–MWCNT–Ag.

resonance of free π-electrons of the nanotubes [12]. On top of that, strong scattering at 400 to 900 nm was observed in the spectra [11] (Fig. 1, curve *2*). Reduction of silver ions in the presence of the polyacid-modified MWCNT resulted in yellow coloration of the dispersions. Simultaneously a new band appeared in their electronic absorption spectra, its maximum being at 390 nm (Fig. 1a, curve *3*), caused by the irradiation-induced excitation of vibrations of free electrons in the surface layer of the nanoparticles (so called "surface plasmon absorption" [13]). Besides that band, the spectrum contained another broad band with maximum at 650 nm, seemingly assigned to formation of threaded agglomerates of the nanoparticles [14]. For the sake of comparison, electronic absorption spectrum of silver nanoparticles prepared in a solution of PAA_{2000} in the absence of MWCNT is shown in the same plot (Fig. 1, curve *1*). The latter spectrum contained a band of surface plasmon absorption of silver nanoparticles with maximum at about 405 nm. Hence, the presence of MWCNT in the system containing silver salt and PAA_{2000} had practically no effect on the spectral properties of the silver nanoparticles formed via reduction of its ions.

Electronic absorption spectrum of a tertiary dispersion MWCNT–PAA_{250000}–Ag shown in Fig. 1b (curve *3*) contained the bands with maxima of 260 nm and 430 nm, but the absorption band with maximum at 650 nm was absent in the spectrum. Therefore, in contrast to the case of PAA_{2000} (Fig. 1a), the presence of MWCNT in the system containing silver ions and PAA_{250000} resulted in the red shift of absorption band of silver nanoparticles surface plasmon. Since the position of the absorption maximum of that band was usually dependent of the nanoparticles size and shape [13], the natural step further was to estimate the actual nanoparticles size taking advantage of transmission electron microscopy (TEM) technique.

Figure 2 displays TEM images of MWCNT dispersions prepared in the presence of polyacrylic acids of varied molecular mass. In the both cases of PAA_{2000} and PAA_{250000}, isolated (non-aggregated) nanotubes were observed in the dispersion, the nanotubes surface was coated with uniform layer of adsorbed polyacid, about 5–15 nm thick.

Figure 3 shows images of silver nanoparticles prepared in solutions of PAA of different molecular mass in the absence of MWCNT. Independently of the polyacid molecular mass, the image indicated the presence of many small and a few large spherical nanoparticles and/or their aggregates. In the case of PAA_{250000}, nanoparticles of 2–10 nm were majorly formed, whereas in the case of PAA_{2000} the formed nanoparticles were somewhat smaller (1–5 nm). The latter observation explained the shift of the surface plasmon band of silver nanoparticles stabilized with polyacrylic acid of different molecular mass (Fig. 1, curve *1*). Similar effect of polyacrylic acid molecular mass of the size of formed silver nanoparticles was observed in [15].

Figure 4 shows TEM images of the MWCNT–PAA–Ag composites. In the presence of MWCNT modified with PAA_{2000}, silver nanoparticles were located close to each other, forming threads near the nanotube surface (Fig. 4a) and hence causing the

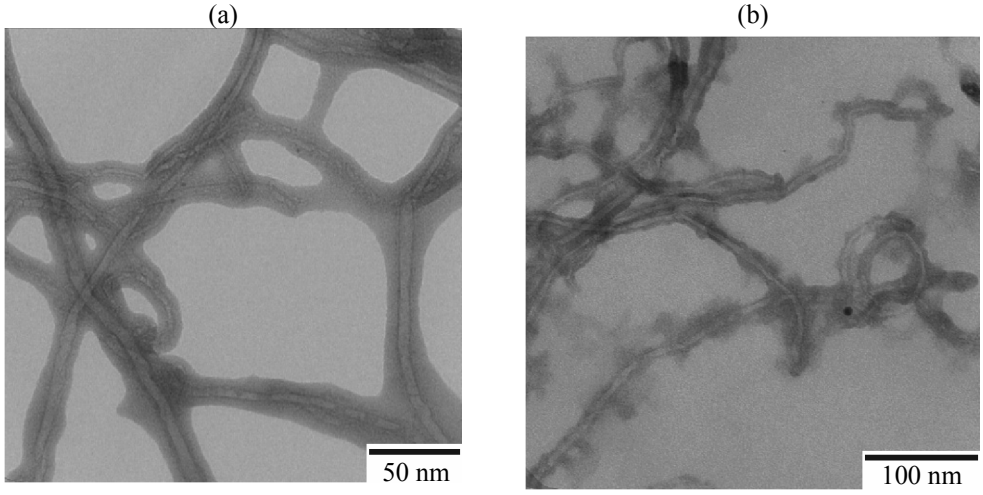

Fig. 2. TEM images of the (a) PAA_{2000}–MWCNT and (b) PAA_{250000}–MWCNT composites.

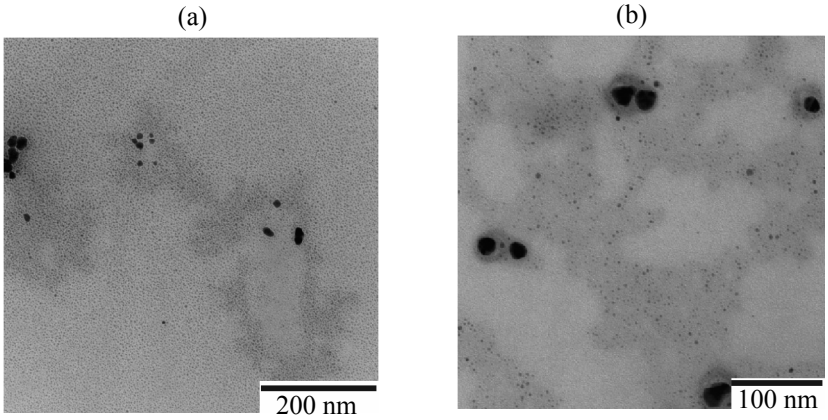

Fig. 3. TEM images of silver nanoparticles obtained in the presence of (a) PAA_{2000} and (b) PAA_{250000}.

appearance of broad absorption band at 650 nm (Fig. 1a, curve *3*). Such threaded aggregates of silver nanoparticles were not observed when PAA_{250000} was used instead of PAA_{2000}, other conditions being the same. Noteworthily, the both MWCNT–PAA–Ag dispersions described here were stable within several months.

Reduction of silver ions in the presence of PAA_{2000}–MWCNT mixture gave nanoparticles of the same size as in the presence of polyacid alone (1–5 nm). However, in the case of similar systems containing PAA_{250000}, about twice smaller silver particles were formed in the presence of MWCNT as compared with stabilization with the polyacid alone. The observed effect of MWCNT of the silver nanoparticles size triggered by molecular mass of PAA could be rationalized taking into account different flexibility of PAA_{2000} and PAA_{250000}. It is known that polyelectrolyte flexibility determines its conformation in solution and at a surface. A polyanion flexibility can be estimated comparing the mean-square distance between the chain ends h_0 and the macromolecule contour length L. Generally, $h_0 = \sigma \cdot h_f$, with h_f being the mean-square distance between the ends of freely-joint chain and a σ being a parameter reflecting the steric repulsion effect (independent of the chain length). For polyacrylic acid: $h_f = 363\sqrt{M/10^4}$ [nm] (M being the polyacid molecular mass) and σ 2.6 [16]. Contour length of a macromolecule is $L = Pl\sqrt{2}[1 - \cos(\pi - \theta)]$, with P, degree of polymerization; l the main chain C–C bond length; and $(\pi - \theta)$, supplement to the bond angle. For polyacrylic acid: $l = 0.154$ nm and $\cos(\pi - \theta) = 1/3$.

The calculation showed the mean-square distance between the ends of PAA_{2000} chain was of 4.2 nm, only

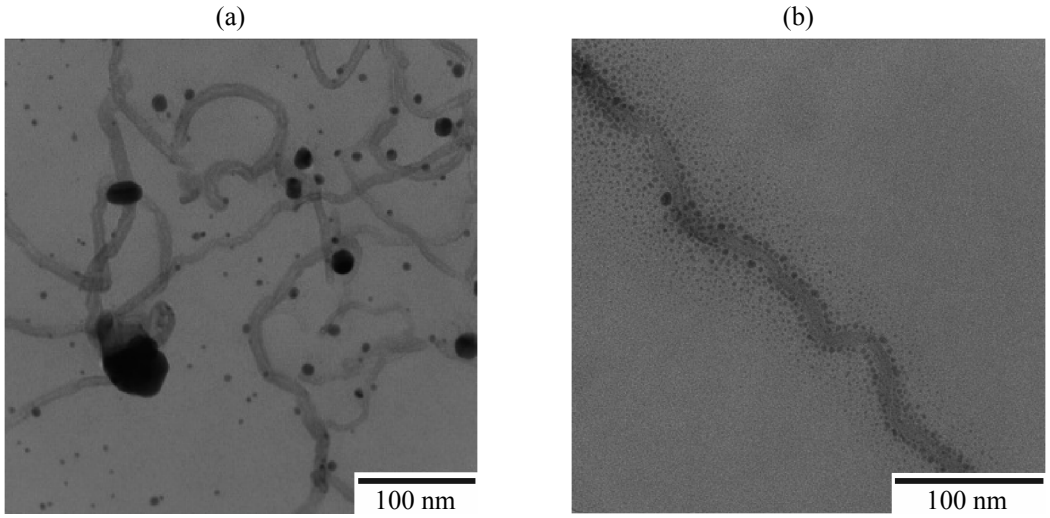

Fig. 4. TEM images of the (a) PAA_{2000}–MWCNT–Ag and (b) PAA_{250000}–MWCNT–Ag composites.

slightly less than the corresponding contour length (7 nm). Therefore, the PAA_{2000} macromolecules exist in the rod-like conformation in a solution. Adsorption of such macromolecules at the surface of MWCNT should not noticeably change their conformation; that is a reason why silver nanoparticles size was the same when prepared in the presence of PAA_{2000} (solution synthesis) and in the presence of PAA_{2000}–MWCNT (synthesis at the nanotubes surface).

In the case of PAA_{250000}, the h_0 value (18 nm) was much less than L (667 nm). Hence, $PAA_{2500000}$ existed in the form of statistical coil in a solution. It is known that adsorption of such coils at a surface makes them more flat and elongated [17]. The three-dimensional coils of PAA_{250000} are capable of coordination with many silver ions in the solution; in the course of silver reduction the neighboring clusters aggregated to form the 2–10 nm particles. At the same time, the somewhat flattened MWCNT-adsorbed PAA_{250000} macromolecules coordinated less of silver ions, and therefore their reduction resulted in smaller nanoparticles of 1–5 nm size.

To conclude, we prepared stable three-component aqueous dispersions based on multi-walled carbon nanotubes, polyacrylic acid, and silver nanoparticles. The metal nanoparticles were prepared in situ via silver ions reduction with sodium borohydride in the presence of two-component MWCNT–PAA dispersions. It was demonstrated that the silver particles size was affected by polyacrylic acid conformation that was in turn depended on the polyacid molecular mass.

EXPERIMENTAL

The following materials were used: multi-walled carbon nanotubes (MWCNT) NC 7000 (Nanocyl, Belgium), up to 2 μm long and 8–20 nm thick prepared via CVD method; polyacrylic acid (M_w 2000, "chemical pure" grade; M_w 250000, 35 wt % aqueous solution, Aldrich); $AgNO_3$ ("chemical pure" grade) and $NaBH_4$ (99%, Aldrich). All the materials were used as received.

Electronic absorption spectra were recorded using a Helios α spectrophotometer (Thermo Fisher Scientific, USA) in a quartz cell (optical path length of 1 cm). Dispersions morphology was studied with a Leo 912 AB Omega transmission electron microscope (Zeiss, Germany). The samples were prepared by placing a droplet of the aqueous dispersion at a copper grid with formvar support and drying in air.

Dispersions of the polyacid-stabilized MWCNT were prepared as follows. 0.01 g of the nanotubes was placed in an aqueous 0.1 wt % solution of PAA, and the mixture was sonicated during 1 min (a MOD. MEF 314 ultrasound generator, MELFIZ-ultrazvuk, Russia). Then required amount of MWCNT was introduced in 0.01 g portions, addition of each portion was followed by 10 min sonication. Finally, the prepared dispersion was centrifuged (10 min at ω 14100 rpm), and the MWCNT concentration was determined measuring the sample absorbance at λ 500 nm ε 42.2 mL mg^{-1} cm^{-1}) [11].

Sols of silver nanoparticles were prepared via reduction of $AgNO_3$ with freshly prepared $NaBH_4$ at constant molar ratio $[NaBH_4]/[AgNO_3] = 2$. PAA concentration in the dispersion in the course of reduction was of 0.1 wt % and the starting $AgNO_3$ concentration was of 0.007 mol/L.

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