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Influence of Si nanocrystals on polyaniline conductivity

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The electrical properties of a complex of polyaniline with poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PANI-PAMPSA) and composites based on it with the addition of silicon nanocrystals (nc-Si) ranging in size from 30 nm to 100 nm are studied in this article. It was found that the dc conductivity of PANI-PAMSA decreases with the introduction of nc-Si. Investigations of alternating current showed that the frequency dependence of the conductivity of the polymer and composites based on it obeys the Jonscher law, which indicates a significant role of the hopping mechanism of conductivity. A mechanism of PANI-PAMPSA conductivity reducing by incorporation of silicon nanocrystals is proposed. The mechanism is associated with energy distribution of localized states in the band gap of the polymer changing and is independent of the nc-Si synthesis method.

Keywords: polyaniline, silicon nanoparticles, conductivity, nanocomposites.

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1. Introduction

From year to year more attention is paid to the development of alternative energy that can substitute traditional energy sources [1]. Solar power engineering is one of the most important direction in this field. Therefore, an active search for new materials for solar cells is performed currently [2] and, among other things, composite materials based on polymers with inorganic nanoparticles are of special interest [3]. Solar modules based on such hybrid structures are very promising because of their low cost due to the use of polymers [4] and the application of the roll-to-roll technology, the mechanical flexibility (the possibility to use flexible substrate), the possibility to change their functionality by varying polymer composition and structure, adding different inorganic nanoparticles [5].

Polyaniline (PANI) is one of the most extensively investigated conducting polymers [6]. Its popularity is due to the relative simplicity of synthesis and the environmental stability [7]. PANI complexes synthesized by oxidizing polymerization of aniline in the presence of polysulfonic acids are water-dispersion complexes having thin film conductivity in a range of $10^{-3}-10^{-1}$ S/cm [8,9]. In particular, the complex of PANI with poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPSA) forms a water dispersion with the stability of optic and electrical properties of thin films manifested for 2 years and longer [10]. In PANI-PAMPSA films, the mobility of holes, which are the main charge carriers, is about $1\,\mathrm{cm^2V^{-1}s^{-1}}$ [11]. Transparent PANI-PAMPSA films in solar cell arrays are used first of all to transfer charge carriers [12].

To modify properties of the PANI-PAMPSA polymer, in particular, to extend the spectral band of absorbed light, silicon nanoparticles are used [13]. However, the process of charge transfer in this type of composites is poorly investigated so far. Therefore, in this study PANI-PAMPSA/nc-Si composites with silicon nanocrystals were synthesized and the effect of silicon nanoparticles on the charge transfer process in composites was investigated. Parameters of the charge carrier transfer are determined by methods of conductivity investigation in direct and alternating current modes.

2. Methods of sample synthesis and investigation

The PANI polymer used in this study was synthesized in the presence of PAMPSA in accordance with the procedure described in a number of papers [1,2]. The relationship of aniline and PAMPSA concentrations was 1 : 1.5 N of sulfonic acid groups and the relationship of aniline and ammonium persulfate concentrations in the initial reaction medium was 0.01 M. Upon completion of the p[olymerization, the aqueous solution of PANI-PAMPSA complex was purified from residues of monomer, oxidizer and other low-molecular products by means of dialysis (ZelluTrans cellulose membrane, MWCO 8000−10000). Previously, it has been shown that the synthesized dispersion of PANI-PAMPSA (hereinafter referred to as PANI for the sake of brevity) continues to be stable in respect to phase separation and keeps its conductivity for several years [14].

The nc-Si powders investigated in this study were synthesized by two methods: electrochemical etching (ECE) and femtosecond pulsed laser ablation (FPLA). To synthesize nc-Si by the ECE method, boron-doped

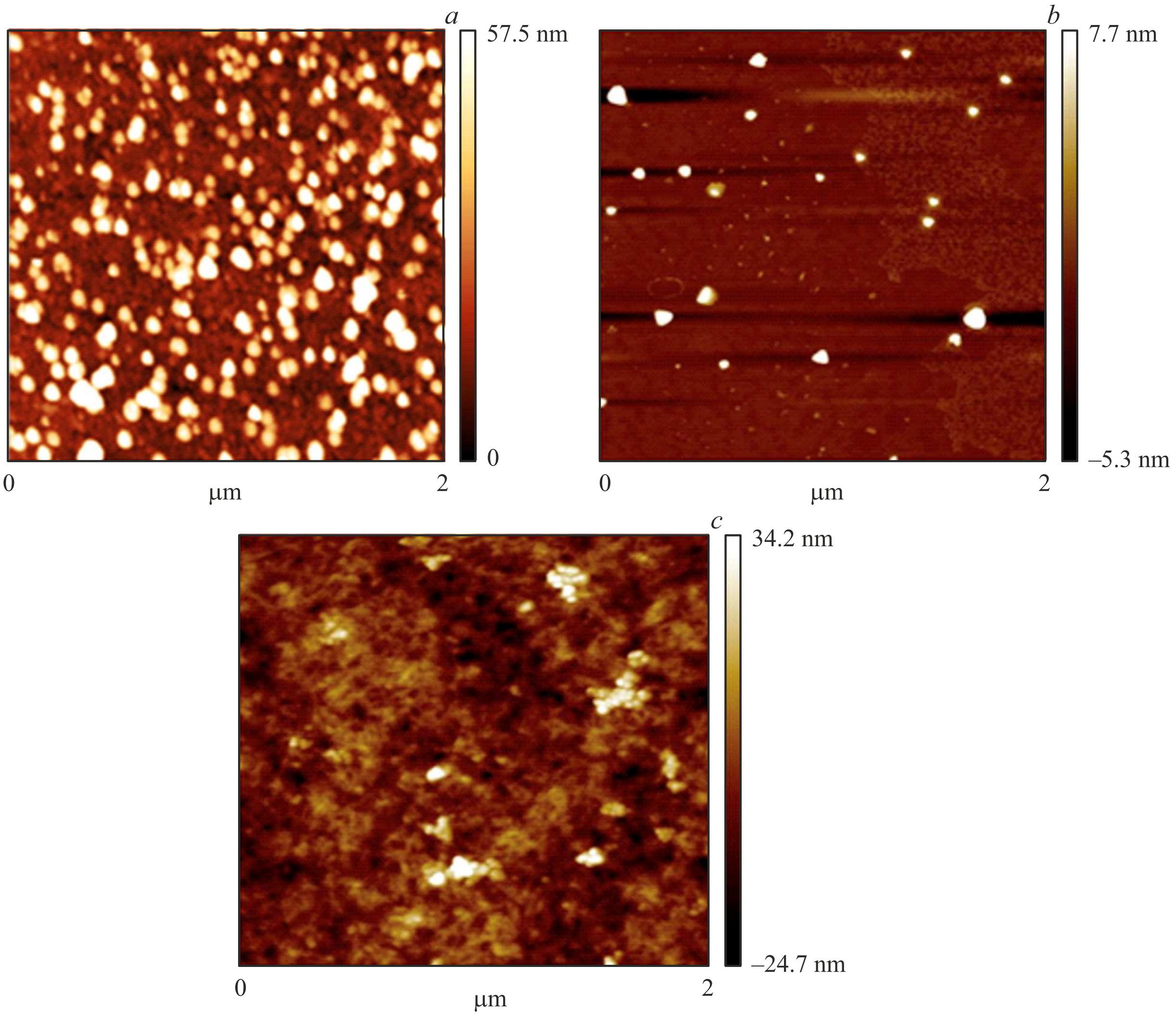

Figure 1. Atomic-force microscopy images: *a* — nc-Si powder synthesized by FPLA method, *b* — nc-Si powder synthesized by ECE method, *c* — PANI/nc-Si composite.

silicon plates with a specific electrical resistance of $0.01-0.02\,\Omega\cdot\text{cm}$ were etched in 50% alcohol solution of fluoride acid (HF) at a current density of $90\,\text{mA/cm}^2$. After the etching, the solution of nanoparticles was dried and nanoparticles were placed into ethanol. To synthesize nc-Si by the FPLA method, single crystal silicon substrates were exposed to laser ablation in ethanol. The laser pulse length was 125–180 fs, the laser wavelength was 1250 nm, the power density of the pulse was $1\,\text{mJ/cm}^2$, the frequency of pulses was 10 Hz.

Once synthesized, the nc-Si dispersion in ethanol was exposed to ultrasound for 2 h followed by centrifugation (at 6000 rpm, for 1.5 h) to separate aggregates of particles. The PANI/nc-Si nanocomposites were prepared by mixing nc-Si dispersions in ethanol and PANI with the appropriate concentration (to obtain nc-Si weight concentrations of 10, 30 and 50 wt%) under exposure to ultrasound for 10 min followed by pouring onto glass substrates.

Experimental samples were polymer or composite film of PANI applied on glass substrates with different weight concentrations of nc-Si (PANI/nc-Si): 0, 10, 30 and 50 wt%. The film thickness was about $1\,\mu$m. Aluminum contacts with a distance of 0.5 mm between them were deposited on the film surface in a planar configuration.

To determine sizes of the synthesized nanocrystals, images of the nc-Si powder were recorded using NanoscopeV atomic-force microscope (by Veeco Instruments). Current-voltage curves were measured by Keithley 6487 picoammeter in vacuum and in the air. The impedance spectroscopy of samples was performed by HP 4192A impedance analyzer in vacuum at room temperature. The alternating signal amplitude of the impedance spectroscopy was 50 mV and frequencies were in the range of 5 Hz–10 MHz.

3. Experimental results and discussion

Fig. 1 shows images recorded by an atomic-force microscope for the nc-Si powder synthesized by the FPLA method (Fig. 1, *a*), for the nc-Si powder synthesized by the

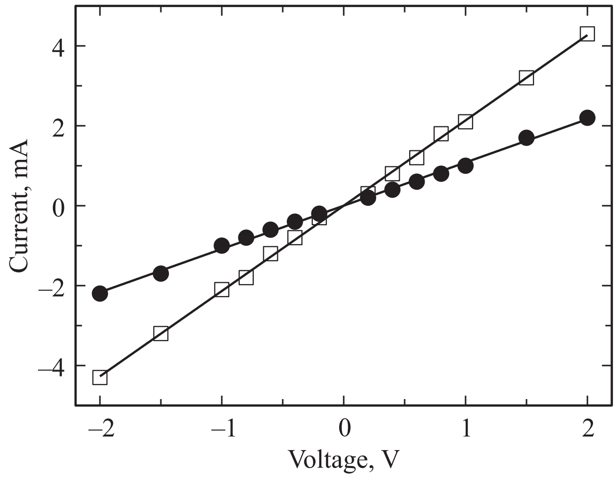

Figure 2. IU-curves of the PANI/nc-Si composite with 10% concentration of nc-Si synthesized by the ECE method in the air (squares) and in vacuum (circles). The lines show linear approximations of IU-curves.

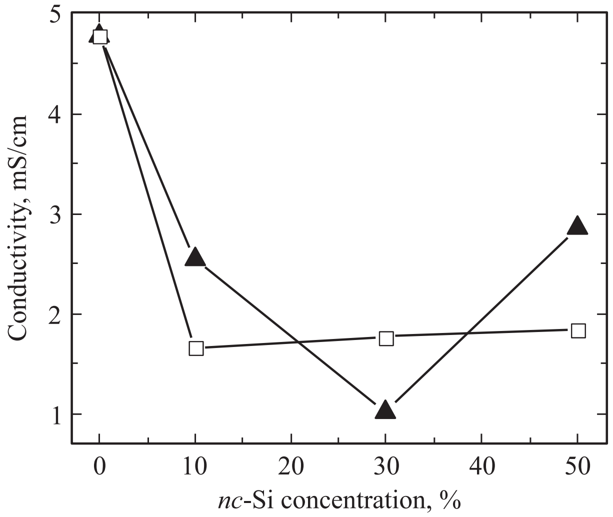

Figure 3. Specific conductivity of the PANI/nc-Si composite as a function of nc-Si concentration for materials synthesized by the ECE method (circles) and by the FPLA method (squares).

ECE method (Fig. 1, *b*) and for the PANI/nc-Si composite (Fig. 1, *c*). Silicon nanoparticles can be seen as white inclusions. The study of the nc-Si powder by atomic-force microscopy has shown that most of particles produced by the FPLA method have diameters of 30–100 nm and particles produced by the ECE method have diameters of 70–100 nm. At the same time, in both powders agglomerates of particles with diameters of 150–200 nm occur.

Fig. 2 shows current-voltage curves (IU-curves) of the PANI/nc-Si composite with 10% concentration of nc-Si synthesized by the ECE method in vacuum and in the air in the direct current mode. Similar curves were obtained for other samples as well. IU-curves demonstrate a linear behavior both in the air and in vacuum. In vacuum, a more than 2-times decrease in conductivity of the material is observed. This fact may be related to modification of the sample surface in the air. Molecules from the air, for example, water settle on the surface of the polymer and form a layer with increased conductivity. In vacuum, the same molecules are removed from the surface. This hypothesis is confirmed by the fact that conductivity of a sample increases up to the previous level when the sample is moved from vacuum to the air. All the results presented in the study were obtained in vacuum.

Fig. 3 shows specific conductivity of samples as a function of nc-Si concentration for samples synthesized by different methods. It follows from the results, that an addition of nc-Si considerably decreases conductivity of the material in the direct current mode. Previous studies have shown that the addition of nc-Si to P3HT polymer results in a change in the distribution of the density of localized states, over which the hopping mechanism of charge carriers is implemented [15]. This change takes place due to the change in degree of polymer crystallinity. It can be suggested that the addition of nc-Si to PANI results in its disordering, which is reflected in the increase in energy spread of localized states and, respectively, in the decrease in charge carrier mobility determined by thermally activated hops.

Fig. 4 shows frequency dependencies of conductivities for the samples. It can be seen, that at low frequencies pristine PANI has a considerably higher conductivity than that of samples with nc-Si, which corresponds to the results obtained in the direct current mode. However, at high frequencies conductivities of all samples are close to each other and are nearly independent from the concentration of nanoparticles. Frequency dependencies of conductivity have a similar behavior for all samples. The frequency dependence of conductivity for a sample can be split into two sections, which are distinguished by the dependence behavior. At low frequencies (5–400 Hz) the conductivity of samples follows the Jonscher's law [16]:

$$\sigma = \sigma_0 + A(2\pi f)^s, \tag{1}$$

where f is frequency of the alternating signal, σ_0 is conductivity in the direct current mode, A and s are constant values. At high frequencies of 300–10000 Hz a smooth transition to plateau is observed, which is kept up to a frequency of 4 MHz.

Values of σ_0, A and s parameters for PANI/nc-Si composites with different concentrations of nc-Si

Concentration nc-Si	Method of synthesis nc-Si	σ_0, mS/cm	A, 10^5 S/cm	s
0	–	4.9 ± 0.4	2.6 ± 0.4	0.83 ± 0.03
10	ECE	1.8 ± 0.2	3.6 ± 0.5	0.90 ± 0.03
30	ECE	2.1 ± 0.2	3.9 ± 0.5	0.46 ± 0.03
50	ECE	1.9 ± 0.2	2.7 ± 0.5	0.79 ± 0.03
10	FPLA	2.6 ± 0.2	3.4 ± 0.1	0.79 ± 0.06
30	FPLA	0.3 ± 0.2	3.3 ± 0.9	0.80 ± 0.06
50	FPLA	1.0 ± 0.2	1.6 ± 0.2	0.81 ± 0.03

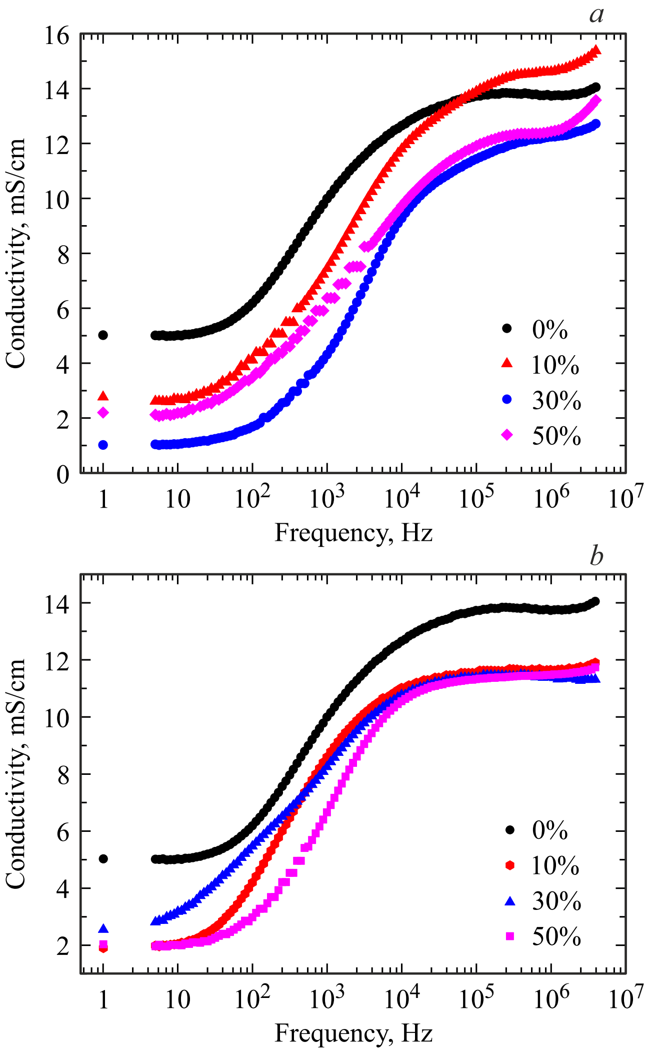

Figure 4. Frequency dependencies of conductivity for PANI/nc-Si samples with different concentrations of nc-Si synthesized by the ECE method (*a*); by the FPLA method (*b*).

The Table shows approximations of experimental frequency dependencies of conductivity by the Jonscher's law. The method to produce nanoparticles has no significant effect on parameters of the approximation. It can be seen, that the addition of silicon nanoparticles to the polymer does not result in a significant change in parameters of A. The power exponent of s for all samples is within the range of 0.46–0.9. Such power exponent is typical for the hopping mechanism of conductivity [17].

At high frequencies (above 400 Hz) the charge carrier only has time for one hop to the state of the nearest neighbor within a half-cycle of the external field. In this case the energy spread of localized states over which hops are performed has no longer a prominent role, which leads to nearly the same conductivity of samples with different contents of nc-Si.

Due to the fact that the surface composition of nanoparticles synthesized by two different methods (ECE and FPLA) may be considerably different, the observed effects are independent from the composition of the surface and are only determined by the concentration of nanoparticles.

4. Conclusion

In the study, composites of the PANI-PAMPSA polymer and Si nanocrystals with a size from 30 nm to 100 nm and with a concentration of up to 50% of composite weight were synthesized. The nanocrystals were produced by two different methods, i.e. FPLA and ECE, to eliminate the effect of the surface composition on the properties of nanocomposites. The conductivity of nanocomposites in the air is lower than that in vacuum, which is due to the modification of sample surface in the air and adsorption of air molecules on the surface. It is shown, that the addition of nc-Si to the PANI polymer results in a significant decrease in its conductivity in the direct current mode. In the alternating current mode at low frequencies pure PANI has a considerably higher conductivity than that of samples with nc-Si, which corresponds to the results obtained in the direct current mode. However, at high frequencies conductivities of all samples are close to each other and are nearly independent from the concentration of nanoparticles.

It is found that in the frequency range up to 400 Hz, conductivity of the PANI polymer and PANI/nc-Si composites is described by the Jonscher's law. The power exponent obtained via approximation of the alternating current conductivity by the Jonscher's law is in the range of 0.45–0.9, which corresponds to the hopping mechanism of charge carrier transfer. An explanation is suggested that the decrease in conductivity of PANI with addition of silicon nanocrystals may be related to the disordering of the PANI structure and the increase in energy spread of localized states in the band gap of the polymer. The increase in energy spread of localized states decreases mobility of the electrons that are responsible for the thermally stimulated hopping conductivity over the band gap of the polymer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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