



Conductive composites of polyaniline–polyacid complex and graphene nanostacks



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ABSTRACT

Nanocomposites based on graphene and polyaniline–polyacid complexes with tunable electrical conductivity are elaborated. An influence of graphene oxidation degree on conductivity of the nanocomposites is investigated. The change of optical and electrical properties after graphene introduction into polyaniline–polyacid complexes is explained by the formation of graphene nanostacks of different size and their different distribution in the film bulk. The role of (i) internal interactions between graphene sheets revealed by high-resolution TEM and AFM and (ii) external interactions between graphene and polyaniline or polyacid of different hydrophobicity elucidated by UV–vis, FTIR-spectroscopies and pH-measurements is discussed. In case of uniform distributed graphene sheets having a low oxidation degree, the electrical conductivity of the nanocomposites based on polyaniline complexed with more hydrophilic polyacid increases up to 20 times in respect to initial polyaniline complex.

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1. Introduction

Successful preparation of graphene/polymer nanocomposites is one of the topical issues of the modern material science aiming to improve both the processability of graphene and the physical properties of the host polymers [1].

Graphene is nearly transparent, cost-effective and relatively easy to prepare (“easy of access”) material possessing high electron mobility and stability [2]. It has been established already that small graphene sheets can provide polymer nanocomposites with new functions and applications in various electronics-related systems [3]. In turn, a conductive polymer is a preferable component of the graphene/polymer nanocomposites, since it is known to possess sufficient conductivity [4–6]. Such a combination promotes synergistic effect of the advantages of the both components [7]. Due to known environmental stability, low cost of monomer and simplicity of the polymer synthesis, polyaniline (PANI) seems to be one of the most promising conductive polymers. Moreover, the compatibility of PANI and graphene resulting from interactions between them is expected [8]. The different types of PANI–

graphene nanocomposites and their potential applications are briefly reviewed in Refs. [6,9,10].

PANI–polyacid complex prepared by chemical oxidative polymerization of aniline in the presence of a polyacid seems to be particularly promising for nanocomposite creation. In addition to other advantages described thoroughly in refs. [11,12], the most attractive property of PANI–polyacid complex for practical application is its water-dispersancy. The introduction of graphene into PANI–polyacid complexes has been reported in several articles only [13–17]. Majority of these studies considers the introduction of graphene into the reaction medium before aniline polymerization (in situ chemical polymerization of aniline over graphene dispersion) [13–16].

In the preliminary studies [18,19] on one type of PANI–polyacid complex, we have already shown that the electrical conductivity of its thin films can be increased upon the introduction of a small amount of graphene.

In the present study, we report a detailed investigation of the preparation of nanocomposites based on graphene of different oxidation degree and different PANI–polyacid complexes. Polyacids with various hydrophilicity of the side chain were employed that allowed us to regulate the interactions between nanocomposite components. Moreover, the nanocomposite formulation was optimized by using graphene of the different

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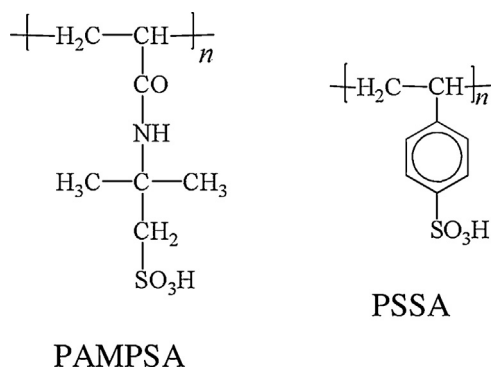


Chart 1. The monomer units of polyacids.

oxidation degree. Two different procedures for the preparation of PANI–polyacid/graphene nanocomposite were developed. Ultraviolet-visible and Fourier transform infrared-spectroscopies (UV-vis and FTIR-spectroscopies, respectively) as well as atomic-force microscopy (AFM) and high-resolution transmission electron microscopy (HR TEM) were used to elucidate the improvement of the electrical conductivity of the nanocomposite thin films. Such complex approach in the study of the graphene/conductive polymer nanocomposites was used for the first time.

2. Experimental

The aniline polymerization was carried out in the presence of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) or poly(4-styrenesulfonic acid) (PSSA) (Chart 1) with ammonium persulfate as an oxidizer. The details of the synthesis is described in [11].

Aniline was preliminary distilled; ammonium persulfate was used without additional purification. PAMPSA (Mw ~ 2,000,000, 15 wt.% in H₂O, Aldrich) and PSSA (Mw ~ 75,000, 30 wt.% in H₂O, Aldrich) were used as purchased.

The molar ratio of aniline to oxidizer was 1:1 mol/mol, the ratio of aniline to a sulfonic group of polyacid was always kept at 1:2 mol/g-eq. sulfonic groups. Aniline concentration in all cases was equal to 0.003 M.

pH-measurement was made by an OP-208/1 pH-meter (Radelkis), the accuracy of the measurement was ±0.05.

For nanocomposite preparation the hydrophobic unoxidized graphene, G, and hydrophilic partially oxidized graphene, poG, were used. Graphenes of both types were obtained by mechanochemical procedure as described in Ref. [20] and Ref. [21], respectively. The detailed material characterization was made before [20,21].

The graphene content in nanocomposite was varied from 0.1 to 30 wt.% based on PANI–polyacid complex.

Two procedures were applied for PANI–graphene nanocomposite preparation. The procedure I included graphene dispersion addition into the polymerization medium before PANI synthesis; procedure II consisted of the mixing obtained PANI–polyacid and graphene dispersions (Scheme 1). PoG was used in form of aqueous dispersion, G was dispersed in ethanol. Totally, 8 types of PANI–polyacid/graphene nanocomposites were obtained using two methods of nanocomposite preparation.

After polymerization the obtained PANI–polyacid or PANI–polyacid/graphene dispersions were dialyzed against water (cellulose membrane ZelluTrans (Roth), MWCO 8000–10000).

The electron spectra recording during PANI–polyacid complex synthesis without or with graphene and the final spectra of the nanocomposites were registered by a diode scanning spectrophotometer “AvaSpec 2048”.

The thin nanocomposite films were obtained by drop-casting on pre-prepared glass support with following drying on air.

The thickness of the films, *t*, was determined by KLA-Tencor D-100 Profiler. The measured value was in the range of 50–60 nm.

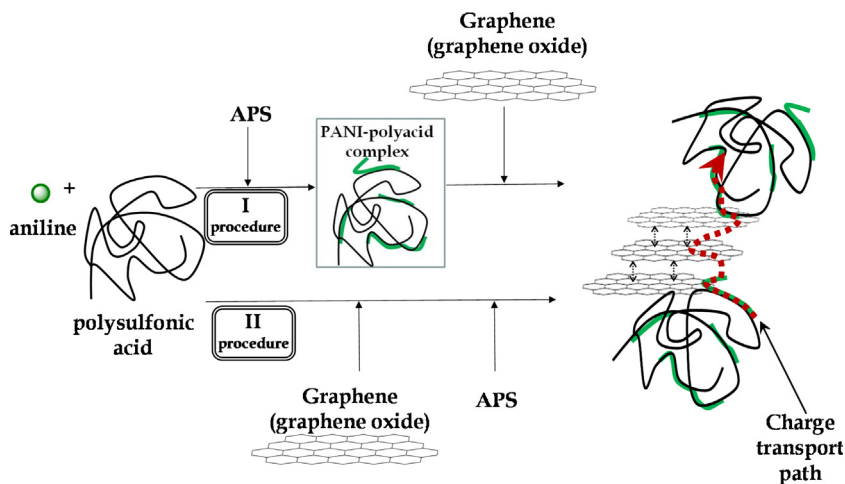
The DC-conductivity was measured by four-probe technique as described earlier [18,19]. Measurements of the electrical conductivity of the nanocomposites were carried out on different samples several times. The conductivity measurement error did not exceed 5%.

The films of graphene–polyacid mixtures on silicon substrates for FTIR-studies were dried at a room temperature. FTIR-spectra were registered on an EQUINOX 55 FTIR spectrometer (Bruker) using the OPUS/IR program.

The surface morphology of the nanocomposite films (AFM) was recorded using an Enviroscope scanning probe microscope (Bruker).

HR TEM images of G and poG stacks in the nanocomposites with PANI–polyacid complexes were obtained using a C_s-corrected JEM2100 F transmission electron microscope operating at 200 kV.

All the experiments were reproduced twice at least with reliable results obtained.



Scheme 1. Schematic presentation of applied procedures for PANI–polyacid/graphene nanocomposite preparation.

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