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In-situ prepared polyaniline–silver composites: Single- and two-step strategies

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ABSTRACT

Conducting polymer–metal composites, such as polyaniline–silver, can efficiently be prepared by two ways: (1) by the oxidation of aniline with silver ions or (2) by the reduction of silver ions with polyaniline. Both approaches yield the composites with limited conductivity. In order to increase the content of silver, and thus increase the conductivity, two strategies are proposed: (1) an increase of oxidant-to-aniline mole ratio in the oxidation of aniline with silver nitrate above stoichiometric value in a single step, and thus reduce excess silver ions to silver metal with produced polyaniline, or (2) in two steps, by preparing polyaniline–silver composite at first and then using polyaniline for the reduction of silver ions. The second approach yields the composites of higher conductivity of the order 100 S cm^{-1}. The role of aniline oligomers and interfacial barriers is discussed on the basis of UV–vis and FTIR spectra, and on morphology assessment. The changes in conductivity of composites after deprotonation and reprotonation of polyaniline part are also reported. Surprisingly, the conversion of conducting polyaniline salt to a non-conducting polyaniline base may be associated with an increase of composite conductivity.

1. Introduction

The materials having high conductivity are needed in various electrical and electronic applications. Conducting polymers rank among promising due to ease of preparation and favourable electrical and mechanical properties [1,2]. The conductivity of routinely prepared polymers usually does not exceed 10^0–10^1 S cm^{-1} [3]. The metals, such as silver having the conductivity of 10^5 S cm^{-1} [4], are thus difficult to be replaced with organic materials in this respect. On the other hand, the processing of metals often requires high temperatures exceeding their melting points or special deposition techniques and, in this respect, conducting polymers offer some benefits.

For various applications, the composite materials comprising high conductivity of metals and processing and mechanical properties of polymers might be of interest. In addition to good conductivity, such composite materials may display new features. For example, the conducting polymer can introduce an ionic component to the conduction. The temperature dependence of conductivity has a reverse character in conducting polymers and metals and their mutual compensation may provide material having conductivity virtually independent of temperature [5].

The strategies for the preparation of such composites have recently been reviewed [6,7] and are here illustrated on polyaniline (PANI) and silver. The simple mixing of components seems to be the simplest solution and, indeed, this approach has been tested [8,9]. The resulting conductivity, however, was not reported or the conductivity was poor because of low content of silver in composites afforded by this approach.

Polyaniline–silver composites can be prepared more efficiently by the reduction of silver salts to metal with PANI [10–19] (Fig. 1), a process known to electrochemists as electroless deposition of silver. Emeraldine form of PANI is oxidized to pernigraniline at the same time [20]. The simple stoichiometry reveals that the mass fraction of silver in the composite should be 29.1 wt.% silver [21]. A reduced leucoemeraldine form of PANI can be also used for the deposition of silver [15,16,18] with the final oxidation state of PANI depending on the acidity, concentration and type of silver anions used for the electroless deposition.

For a model system of conducting and non-conducting (or less conducting) spherical particles, the conductivity can be achieved in the composites exceeding the percolation limit at about 16–17 vol.% of conducting component [22]. There is a large difference between the density of organic materials in general, and polyaniline in particular, 1.2–1.4 g cm^{-3}, and metals, for example silver, 10.5 g cm^{-3}. Therefore, this corresponds to 61 wt.% of silver [6]. The way shown in Fig. 1 thus yields composites with silver content deeply below

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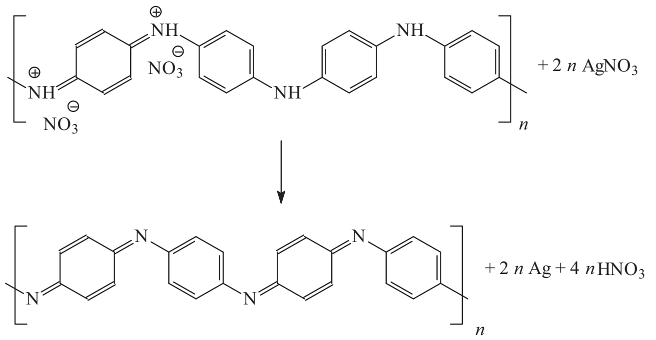

Fig. 1. Polyaniline in emeraldine form is able to reduce silver ions to metallic silver. Polyaniline is converted to pernigraniline form at the same time; nitric acid is a by-product [6].

the expected percolation threshold. For that reason, the conductivity of corresponding composites was usually close or below the conductivity of neat PANI [6], and only exceptionally conductivities of the order of 10^1 S cm^{-1} have been reported [21]. It should be noted, however, that above reasoning applies to spherical particles, and in with fibrilar or dendritic morphologies the situation might be more favourable.

Polyaniline–silver composites can alternatively be prepared directly by the oxidation of aniline with silver salts, such as silver nitrate (Fig. 2) [6,23,24]. Slow reaction, extending to months [5,19,20], is accelerated by addition of *p*-phenylenediamine [25] or ammonium peroxydisulfate [26], and thus be acceptable for routine synthesis.

Such prepared composites are predicted to contain 68.9 wt.% silver on the basis of stoichiometry [6,23] (Fig. 2). Although this seems to be a high content expressed on mass basis, corresponding volume fractions are low, ≈20 vol.%, yet close to the conventional percolation threshold. The concrete value depends on the type of acid, degree of protonation, and the content of aniline oligomers. For that reason, the conductivity sensitively reflects the metal particle size and its distribution. The conductivity reported in the literature varied in a wide range, 10^{-1} to 10^4 S cm^{-1}, and was difficult to predict or control [6]. It has been proposed that the morphology of both components is decisive, rather than merely the silver content.

The obvious way to increase the conductivity would be still to increase the content of silver safely above the percolation threshold. This can be, in principle, done by the combination of above two synthetic protocols. There are two strategies. In a single step, this would be done by increasing the stoichiometric ratio of silver nitrate and aniline from 2.5 (Fig. 2) to 3.5. The excess silver nitrate is then expected to convert the produced PANI to pernigraniline form (Fig. 1). Additional portion of silver would be generated, thus increasing the silver content in the composite.

The experiment can also be designed in two subsequent steps. After the preparation of a PANI–silver composite (Fig. 2), the resulting product can be exposed to silver nitrate solution and used for the deposition of additional silver according (Fig. 1). In the present contribution, both synthetic strategies are compared.

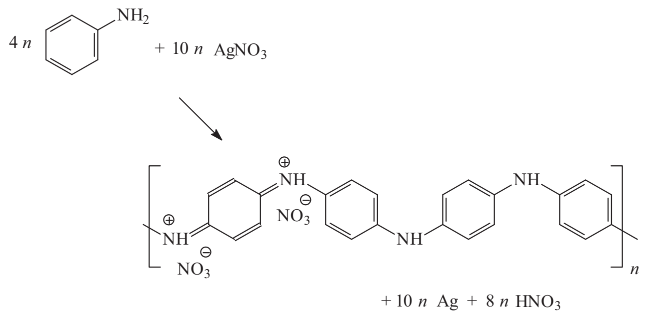

Fig. 2. Aniline is oxidized with silver nitrate to a polyaniline–silver composite [6,19]. Also here, nitric acid is a by-product. Various aniline oligomers are produced simultaneously.

2. Experimental

2.1. Single-step preparation

Aniline (Fluka, Switzerland) and silver nitrate (Lach-Ner, Czech Republic) were separately dissolved of 1 M aqueous solutions of methanesulfonic acid and mixed. The concentration of aniline was kept 0.2 M, and the silver nitrate-to-aniline mole ratio was varied between 0.5 and 3.5. In a typical experiment, when this ratio was equal to 2.5, 1.86 g of aniline was dissolved in 50 mL of 1 M methanesulfonic acid, 8.5 g of silver nitrate also in 50 mL of 1 M methanesulfonic acid, and both solutions were mixed. The reaction was accelerated by 1 mol% of *p*-phenylenediamine (Sigma–Aldrich) relative to aniline, which was introduced to aniline solution prior to the addition of silver nitrate solution. At other silver nitrate-to-aniline mole ratios, the amount of silver nitrate was adjusted correspondingly. Reaction mixtures were left to stand at room temperature for 24 h. The solids were isolated by filtration on paper filter, rinsed with acid solution, acetone, dried in air at room temperature, and then over silica gel. Polyaniline in part of composites was converted to a base form by immersion in excess of 1 M ammonium hydroxide and dried as above. The ammonium hydroxide solution, containing the ammonium salts of acids originally constituting salts with PANI, was evaporated and the collected solids are referred to as “filtrates”. A part of composite was reprotonated in 1 M methanesulfonic acid. This acid was selected because it does not form insoluble salts with silver cations and does not cause chemical changes in PANI.

2.2. Two-step synthesis

In the second approach, the selected samples prepared as described above were immersed in excess of 0.2 M silver nitrate solution and the suspension was left for one day and occasionally briefly stirred. The solids were then isolated and dried. In a part of composite, PANI was converted to base form and reprotonated with methanesulfonic acid as above.

2.3. Characterization

Silver content in the composites was determined as a residue in analytical determination of ash. Room temperature conductivity of composites was measured on pellets compressed at 540 MPa [2] by a four-point van der Pauw method using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter, and a Keithley 705 Scanner equipped with a Keithley 7052 Matrix Card. For low-conducting samples, <10^{-3} S cm^{-1}, a two-point method using a Keithley 6517 electrometer after deposition of gold electrodes on both sides of pellets was employed. Density was evaluated by weighing the pellets with a Mettler Toledo XS205 DualRange balance in air and immersed in decane at 20 °C.

Transmission electron microscope (TEM) JEOL JEM 2000 FX was used to assess the morphology. Optical images were obtained with a Research grade Leica DM LM microscope with objective magnification 10×. Fourier-transform infrared (FTIR) spectra of the powders dispersed in potassium bromide pellets have been registered with a Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC