



The oxidation of aniline with silver nitrate to polyaniline–silver composites

Natalia V. Blinova^a, Jaroslav Stejskal^{a,*}, Miroslava Trchová^a, Irina Sapurina^b, Gordana Ćirić-Marjanović^c

^a Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Square 2, 162 06 Prague 6, Czech Republic

^b Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg 199004, Russian Federation

^c Faculty of Physical Chemistry, University of Belgrade, 11158 Belgrade, Serbia

ARTICLE INFO

Article history:

Received 16 July 2008

Received in revised form

24 October 2008

Accepted 27 October 2008

Available online 5 November 2008

Keywords:

Polyaniline

Silver

Conducting polymer

ABSTRACT

Silver nitrate oxidizes aniline in the solutions of nitric acid to conducting nanofibrillar polyaniline. Nanofibres of 10–20 nm thickness are assembled to brushes. Nanotubes, having cavities of various diameters, and nanorods have also been present in the oxidation products, as well as other morphologies. Metallic silver is obtained as nanoparticles of ~50 nm size accompanying macroscopic silver flakes. The reaction in 0.4 M nitric acid is slow and takes several weeks to reach 10–15% yield. It is faster in 1 M nitric acid; a high yield, 89% of theory, has been found after two weeks oxidation of 0.8 M aniline. The emeraldine structure of polyaniline has been confirmed by FTIR and UV–vis spectra. The resulting polyaniline–silver composites contain 50–80 wt.% of silver, close to the theoretical expectation of 68.9 wt.% of silver. The highest conductivity was 2250 S cm⁻¹. The yield of a composite is lower when the reaction is carried out in dark, the effect of daylight being less pronounced at higher concentrations of reactants.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The composites of conducting polymers, such as polyaniline (PANI), with noble metals find applications in electrocatalysis [1–3], catalysis [4,5], design of fuel-cell electrodes [6–10], sensors [11], conducting printing inks [12,13], recovery of noble metals [14,15], etc. The oxidation of aniline with tetrachloroauric acid, resulting in the PANI–gold composite, has often been reported [16–20]. Also, the synthesis of PANI using hexachloroplatinate has been successful [21,22]. The oxidation of the substituted aniline with palladium acetate similarly yielded composites of palladium as nanoparticles dispersed in the polymer matrix [23]. Silver is the next noble metal which can be combined with PANI.

The composites of PANI and noble metals can generally be prepared in three ways: (1) by the synthesis of PANI in the presence of metal particles, (2) by using PANI as a reductant of noble-metal salts or acids, or (3) by the oxidation of aniline with noble-metal compounds. Silver has recently received considerable attention in this respect. The first method has only been used exceptionally for modifying silver nanoparticles with PANI [24,25] or substituted PANI [26]. Composites of silver and PANI have been prepared by the second technique, by the direct reduction of silver nitrate with PANI [14,27–29] or PANI derivatives [30]. The latter chemical process

may cause some reduction in the conductivity of the resulting materials due to the oxidation of emeraldine to pernigraniline. The use of colloidal PANI dispersions [31], instead of a PANI powder, gave rise to materials with unique morphologies [32,33]. The reduction of silver nitrate with PANI nanotubes has recently been used to discuss the loci of silver in the composites [34].

The third approach, the oxidation of aniline with silver nitrate to PANI–silver composites, has been demonstrated by de Barros et al. [12,13]. These authors have used a paper soaked with aniline dissolved in nitric acid and a pattern was printed on it with silver nitrate solution. A green image became visible after development with UV-light irradiation. Spectra typical of PANI have been recorded and the conductivity of the printed patterns was 0.02 S cm⁻¹. Polyaniline nanowires were obtained in a similar reaction carried out in solution, again subject to UV-light irradiation [35]. Also, other authors have used UV light for a similar purpose [36]. The electropolymerization of a mixture of aniline and silver nitrate in 1 M nitric acid produced fibrous composites [37]. Huang and Wen [38] and Neelgund et al. [39] have recently reported the preparation of PANI and poly(2,5-dimethoxyaniline) by the oxidation of corresponding monomer with silver nitrate in the presence of poly(styrenesulfonic acid). The general absence of the characteristic absorption maximum at long wavelengths in the visible spectra, however, suggests that these products were not an analogy of a conducting PANI but rather non-conducting aniline oligomers composed of mixed *ortho* and *para*-linked aniline constitutional units [40,41]. The oxidation of aniline with silver nitrate using

* Corresponding author. Tel.: +420 296809351; fax: +420 296809410.
E-mail address: stejskal@imc.cas.cz (J. Stejskal).

ultrasonic waves or γ -irradiation [42] probably also yielded such oligomers as main product.

The present study reports the oxidation of aniline with silver nitrate in an aqueous solution of nitric acid yielding PANI–silver composites. The study was stimulated by several reasons: (1) composite materials containing silver particles embedded in a matrix of conducting polymer may exhibit good electrical and thermal conductivities. Electronic components are the obvious application target [43]. (2) The only by-product of the oxidation is nitric acid, which can easily be evaporated. There is no need to separate copious amounts of inorganic salts, like ammonium sulfate, produced in the oxidations with ammonium peroxydisulfate (APS) [44]. (3) Silver makes a good model for the deposition of more expensive noble metals, such as gold, platinum, palladium, and rhodium that are used in catalytic and electro-catalytic applications. (4) The antimicrobial activity of silver is well known and a similar ability has recently been reported for PANI [45,46]. The combination of these two materials might have synergetic effects worthy of consideration [28]. (5) Moreover, PANI has been successfully tested for compatibility with animal tissues [47] and in experiments with cell cultures [48]. Applications of PANI–silver composites in neural tissue engineering, artificial muscles, and various monitoring devices can be anticipated [49,50] if suitable materials were available.

2. Experimental

2.1. Synthesis

Aniline (Fluka, Switzerland) was dissolved in 0.4 or 1 M nitric acid, as was silver nitrate (Fluka, Switzerland). The solutions were mixed to start the oxidation at room temperature, $\sim 20^\circ\text{C}$. The concentration of aniline was 0.1–0.8 M, the silver nitrate-to-aniline molar ratio was 2.5 (Fig. 1). The reaction is slow, characterized by an induction period extending for weeks. The unstirred mixtures were left to stand in a laboratory, and occasionally briefly shaken. The access of daylight was not generally prevented, some mixtures were kept in dark for comparison. Green solids produced in the oxidation were collected on a filter after 6 weeks in 0.4 M nitric acid or after 2 weeks in 1 M nitric acid, rinsed with corresponding nitric acid, and dried at room temperature over silica gel. Parts of the samples were deprotonated in excess of 1 M ammonium hydroxide to convert PANI nitrate in composites with silver to corresponding PANI bases, and dried as above.

2.2. Characterization

JEOL JSM 6400 and JEOL JEM 2000FX microscopes have been used to assess the morphology. TGA was performed in air flow ($50\text{ cm}^3\text{ min}^{-1}$) at a heating rate of $10^\circ\text{C min}^{-1}$ with a Perkin Elmer TGA 7 Thermogravimetric Analyzer to determine the content of silver as a residue. Infrared spectra in the range $400\text{--}4000\text{ cm}^{-1}$ were recorded, at 64 scans per spectrum at 2 cm^{-1} resolution, using a fully

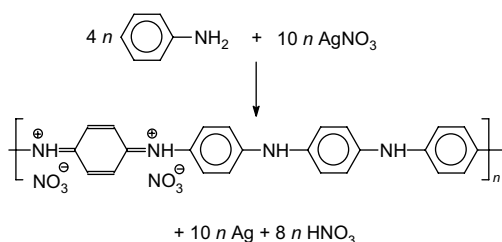


Fig. 1. Aniline is oxidized with silver nitrate to polyaniline (emeraldine) nitrate.

computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. The conductivity was measured by a four-point van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press using a current source SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card. For non-conducting samples, a two-point method using a Keithley 6517 electrometer was applied. Before such measurements, circular gold electrodes were deposited on both sides of the pellets. The density of a composite was evaluated using a Sartorius R160P balance by weighing the pellets in air and immersed in decane. UV–vis spectra of deprotonated samples dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK).

3. Results and discussion

3.1. Polymerization

The oxidation of aniline with silver nitrate (Fig. 1) is slow. An induction period, extending up to several weeks, where no obvious reaction takes place to the naked eye, is followed by a faster polymerization and dark green precipitate is then produced within a few days. This is probably the reason why only processes accelerated with the UV irradiation have been reported in the literature so far [13,35].

The oxidation of 1 g of aniline with the stoichiometric amount of silver nitrate (Fig. 1), 4.56 g, yields theoretically 1.31 g of PANI nitrate and 2.90 g of silver, *i.e.* 4.21 g of composite containing 68.9 wt.% Ag. The yield of reaction in 0.4 M nitric acid was low, but much higher in 1 M nitric acid (Table 1). The composition of composites was generally close to expectation (Table 1).

Weight-average molecular weight of the sample prepared by the oxidation of 0.2 M aniline in 0.4 M nitric acid was determined by gel-permeation chromatography in *N*-methylpyrrolidone as $M_w = 41,400$. Broad distribution of molecular weights, characterized by weight-to-number molecular weight ratio $M_w/M_n = 7.7$, suggests the presence of both oligomers and polymers in the sample.

One has to realize that a part of nitric acid is neutralized by aniline. The increase in aniline concentration enhances the rate of polymerization and the yield (Table 1) but, at the same time, reduces the acidity of the medium, which acts against the polymerization of aniline. At 0.4 M aniline in 0.4 M nitric acid, all nitric acid is neutralized and the yield of reaction decreases (Table 1), at higher aniline concentration, the reaction did not therefore take place. This is the reason for higher yields obtained in 1 M nitric acid.

The standard reduction potential of the reaction $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ is $E^0 = +0.80\text{ V}$. This is a much lower value than $+2.01\text{ V}$ for

Table 1
The oxidation of aniline with silver nitrate in solutions of nitric acid.

Concentration of aniline ^a , mol L ⁻¹	Light condition	Yield, % theory	Composition, wt.% Ag	Conductivity, S cm ⁻¹	Density, g cm ⁻³
0.4 M HNO ₃					
0.1	Daylight	8.3	81.0	149	3.81
0.2 ^b	Daylight	15.8	70.7	709	3.54
0.4	Daylight	11.1	50.7	384	2.73
1 M HNO ₃					
0.4	Daylight	29.1	51.8	2250	3.68
0.4	In dark	23.2	71.2	2150	3.83
0.8 ^c	Daylight	89.0	69.2	18.5	3.76
0.8 ^c	In dark	87.6	69.6	49.0	3.13

^a Mole ratio of silver nitrate to aniline = 2.5.

^b The morphology is shown in Figs. 2–4.

^c The morphology is shown in Fig. 8.

the reduction of the currently used peroxydisulfate, $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$, yet slightly higher than the value +0.77 V for the reduction of iron(III) salts, $Fe^{3+} + e^- \rightarrow Fe^{2+}$. The successful oxidation of aniline with iron(III) salts has been reported in the literature [51,52]. It is thus not surprising that silver ions have similar oxidation ability.

3.2. Morphology

The morphology of PANI depends on the conditions used for the preparation [40,41]. The dominant morphology of the present oxidation products prepared in 0.4 M nitric acid is represented by the arrays of thin PANI nanofibres that constitute elongated brushes (Figs. 2 and 3). Similar nanofibers of ca 10–20 nm diameter have been reported to be a part of the “micromats” [53] produced when the polymerization took place in dilute solutions of aniline or when microspheres were generated by the oxidation of aniline initiated in an alkaline medium [54]. Analogous nanofibrillar morphology was also obtained when PANI was prepared on the surface of mesoporous carbon [55], when vanadic acid was used as an oxidant of aniline [56], in the presence of triblock copolymer [57], and after addition of inorganic salts [58]. It is a characteristic feature that thin nanofibres constitute a higher well-organized morphology, brushes in the present case, or spheres [58,59]. Obviously, there is a hierarchy of organization of conducting polymers at various dimensional levels, just as proteins exhibit primary,

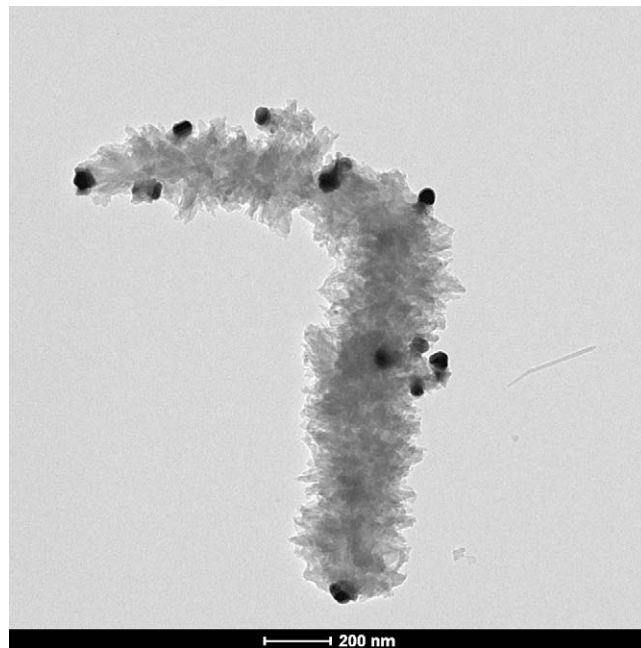


Fig. 3. Transmission electron micrograph of polyaniline–silver composite shown in Fig. 2.

secondary, and tertiary structures. The thickness of many other nanowires produced e.g. in interfacial [60,61], electrochemical [62], or other polymerizations [63] is larger, 30–300 nm. Such nanowires do not undergo organization to produce a secondary structure but, on the contrary, they can be composed of thin nanofibres [56].

Silver is produced as nanoparticles, relatively uniform in size ~50 nm (Fig. 3). They are shown to be separated in Fig. 3, but they often produce clusters. Macroscopic silver flakes are visible in the samples to the naked eye. The proportion between the nanoparticles and macroscopic objects is difficult to assess. Polyaniline nanotubes are also present in the samples as a minority component. The inner cavity of the nanotubes may exceed 100 nm in diameter (Fig. 4a), or it may be a hardly discernible thread-like opening, <20 nm (Fig. 4b). The walls of the nanotubes have about the same thickness, ~70 nm, in all cases. Simultaneous formation of PANI nanotubes and gold particles has also been reported, when aniline was oxidized with tetrachloroauric acid [64]. Nanorods without any cavity are also present (Fig. 4c) but the apparently hollow space may simply be below the limits of microscopic resolution. We assume that the origin of the nanotubes and nanorods is the same, guided by the stacking of phenazine-like constitutional units in aniline oligomers [65]. The dimeric oxidation product of 1,2-phenylenediamine, *i.e.* 2,3-diaminophenazine, has recently been shown to self-assemble to microfibrils [66,67] or nanobelts [68] in aqueous media. The stacking of phenazine-based molecules was proposed to be due to the interplay of π – π interactions, and hydrogen bonding, assisted by the phase separation caused by hydrophobic effects [66].

3.3. Composition

The silver content in the composites can conveniently be determined as a residue in thermogravimetric analysis (TGA; Fig. 5, Table 1). The TGA curves provide additional information about the composition of the oxidation products. The first decrease in mass below 100 °C is associated with sample humidity; a step starting at 145 °C is connected with the sample deprotonation and the loss of nitric acid. The complete destruction of organic material takes place

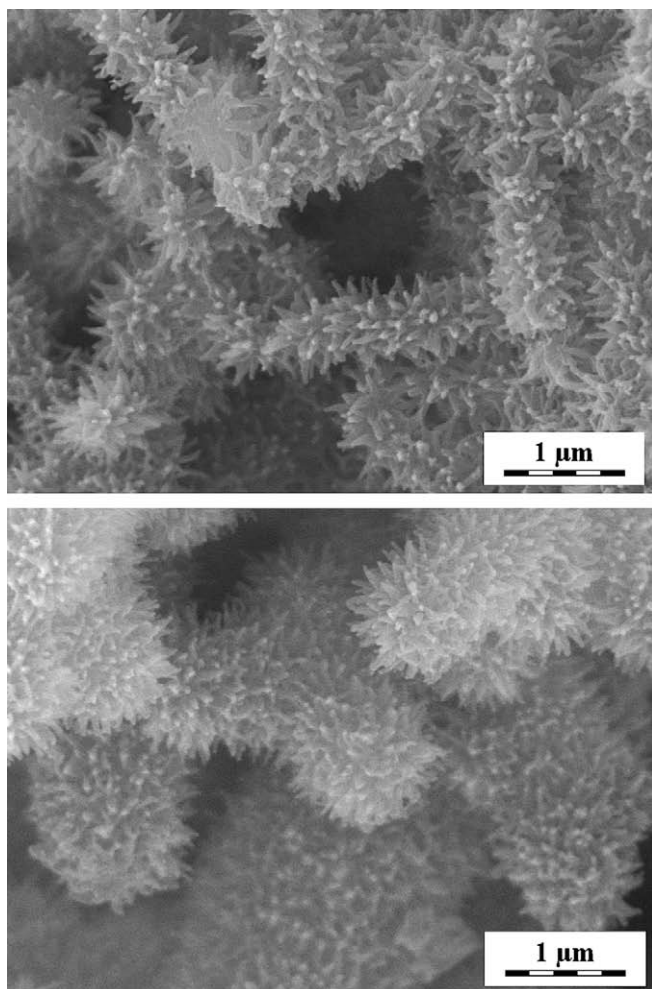


Fig. 2. Scanning electron micrograph of polyaniline–silver composite (0.2 M aniline was oxidized with 0.5 silver nitrate in 0.4 M nitric acid).

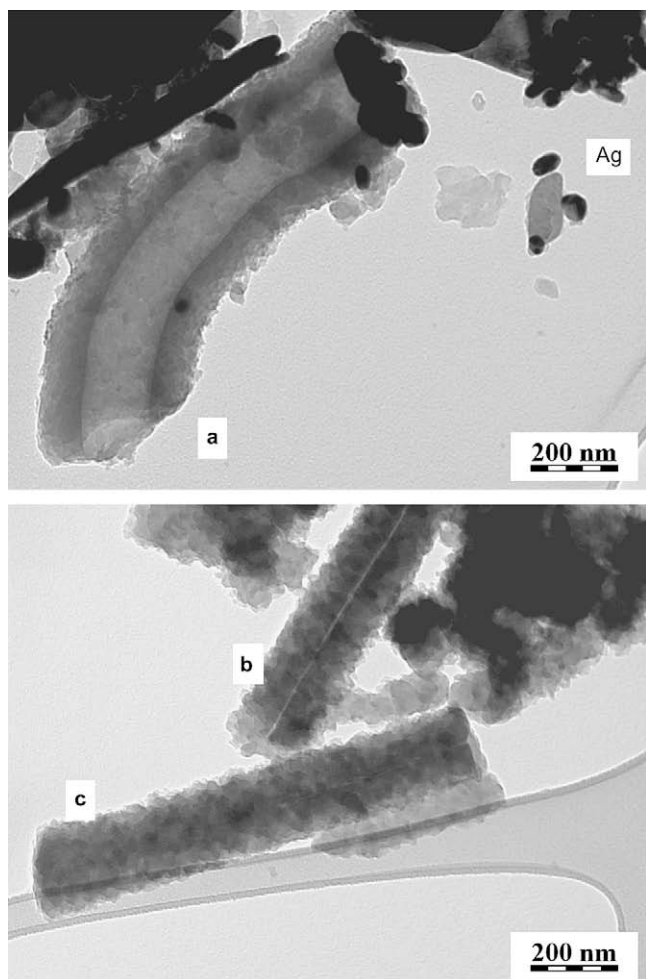


Fig. 4. Transmission electron micrographs of polyaniline-silver composite. The nanotubes are occasionally observed. Their cavity can be (a) well developed, (b) hardly discernible, or (c) absent. Silver nanoparticles (Ag) are located outside the nanotubes.

before 600 °C is reached. The presence of two components differing in decomposition temperature is observed in the sample prepared at 0.4 M aniline concentration (Fig. 5). The presence of two components in the oxidation products, a non-conducting oligomer

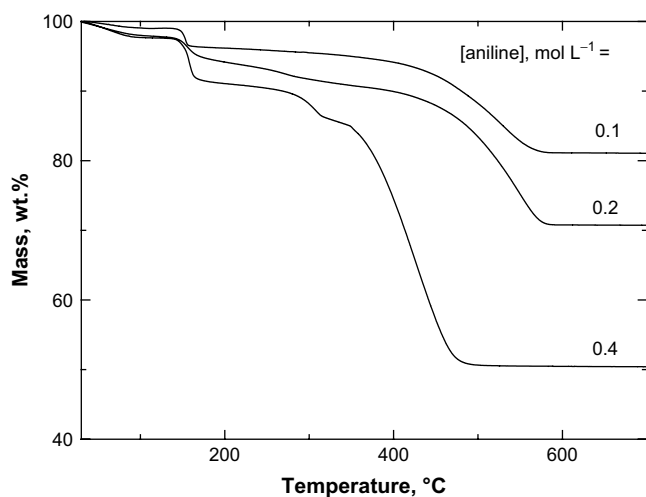


Fig. 5. The decrease in mass of PANI-Ag composites observed in the thermogravimetric analysis. The samples were prepared at aniline concentrations (a) 0.1, (b) 0.2, and (c) 0.4 mol L⁻¹ and [AgNO₃]/[aniline] = 2.5 in 0.4 M nitric acid.

and a conducting polymer, has been observed when aniline was oxidized with peroxydisulfate at low acidity [40,69] or in water [70].

The presence of silver is also well identified by the density values (Table 1). The correlation between the densities and silver content determined by TGA is not perfect due to the inhomogeneity of composites that contain macroscopic silver flakes. Density determined on ~300 mg pellets thus better reflects the average content of silver in the composites than TGA, which uses samples of milligram mass.

3.4. Molecular structure

Visible spectra of PANI bases obtained from samples prepared by the oxidation of aniline with silver nitrate and in a classical manner with APS are the same within experimental error (Fig. 6). The absorption maxima located at ca 330 and 630 nm are the characteristics of PANI bases [71].

FTIR spectra also suggest that the molecular structures of products obtained with APS (Fig. 7a) and silver nitrate as oxidants (Fig. 7b and c) are very close. The spectra corresponding to oxidation products obtained with the latter oxidant, however, differ slightly in shape and include an additional peak at 1384 cm⁻¹ corresponding to nitrate counter-ions (Figs. 1 and 7d). This is confirmed by its disappearance after deprotonation to PANI bases (Fig. 8b and c). Other peaks observed in the spectra of protonated forms (Fig. 7b and c) at 1444 and about 3230 cm⁻¹ are retained in the spectra of the corresponding bases (Fig. 8b and c). The spectrum of PANI obtained with silver nitrate as an oxidant in 1 M nitric acid resembles the product of aniline oxidation using APS in solutions of weak acids, such as acetic acid [65,69] (Fig. 8d) or in water [70]. Such products are composed of non-conducting aniline oligomers containing phenazine-like units and conducting PANI [70]. It seems that, also with silver nitrate, the oxidation products have a two-component character, even though the oxidation of aniline has been carried out in solutions of a strong acid, and not in mildly acidic media. This conclusion has already been made on the account of the TGA data.

Ring substitution of aniline or PANI with nitro groups has to be considered. When the polymerization of 0.2 M aniline with 0.25 M APS has been carried out in 1 M nitric acid, the resulting PANI has been obtained in good yield and had a conductivity of

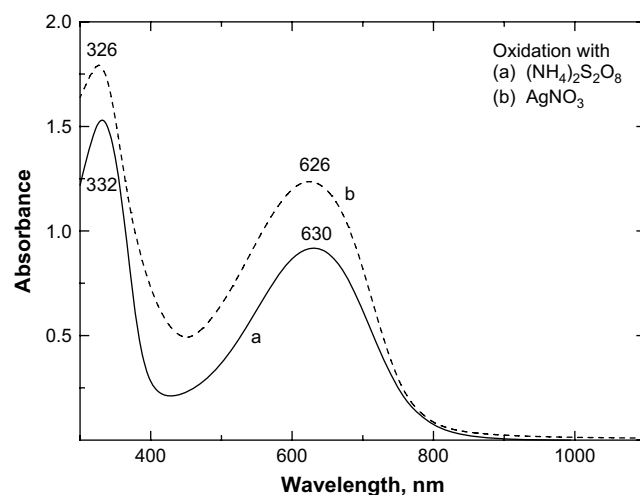


Fig. 6. UV-vis spectra of the products of 0.2 M aniline oxidation with (a) 0.5 M silver nitrate in 0.4 M nitric acid and (b) 0.25 M APS in 0.1 M sulfuric acid, after conversion to the bases and dissolution in *N*-methylpyrrolidone. The positions of the individual maxima are shown at the spectra.

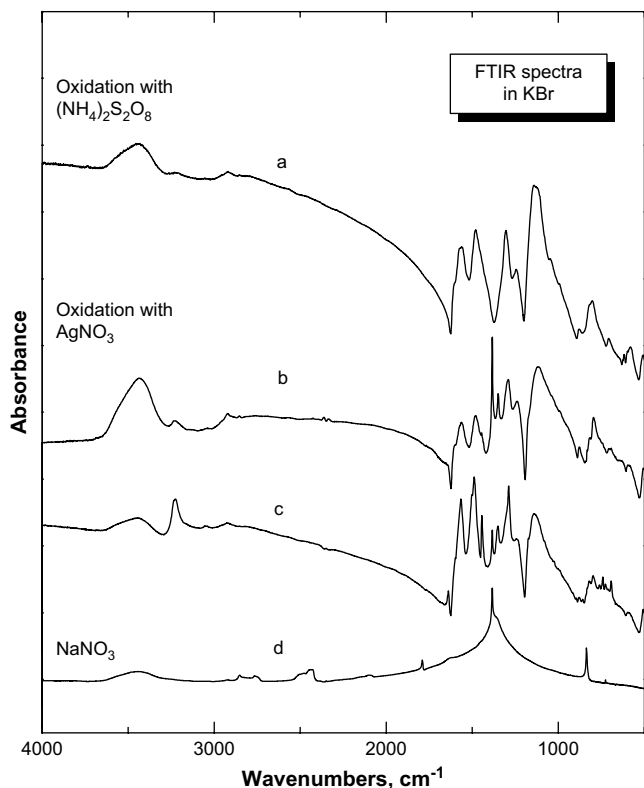


Fig. 7. FTIR spectra of PANI prepared by the oxidation of (a) 0.2 M aniline with 0.25 M APS in 0.1 M sulfuric acid (a “common” PANI sulfate), (b) 0.2 M aniline with 0.5 M silver nitrate in 0.4 M nitric acid, (c) 0.4 M aniline with 1.0 M silver nitrate in 0.4 M nitric acid, and (d) FTIR spectrum of sodium nitrate.

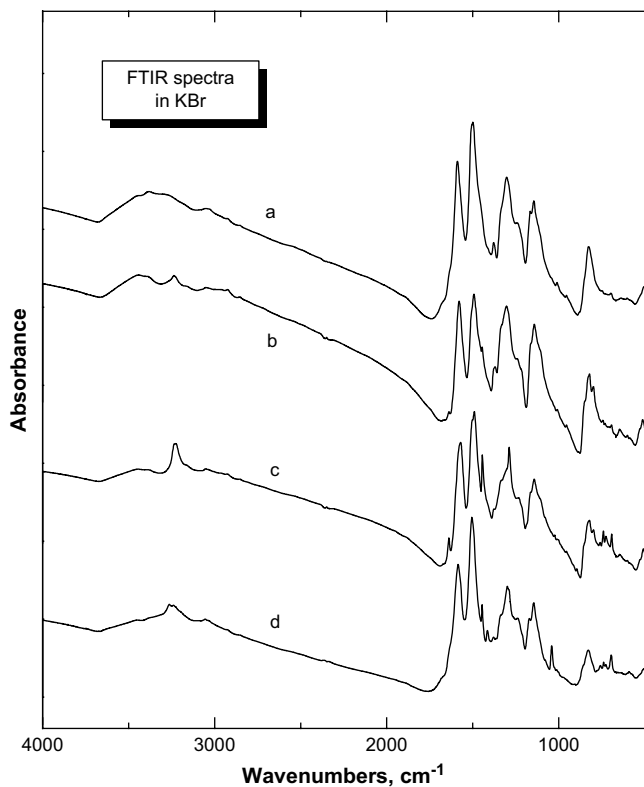


Fig. 8. FTIR spectra of PANI bases obtained after deprotonation of the products prepared by the oxidation of (a) 0.2 M aniline with 0.25 M APS in 0.1 M sulfuric acid (a “common” PANI base), (b) 0.2 M aniline with 0.5 M silver in 0.4 M nitric acid, (c) 0.4 M aniline with 1.0 M silver nitrate in 0.4 M nitric acid, and (d) 0.2 M aniline with 0.25 M APS in 0.4 M acetic acid.

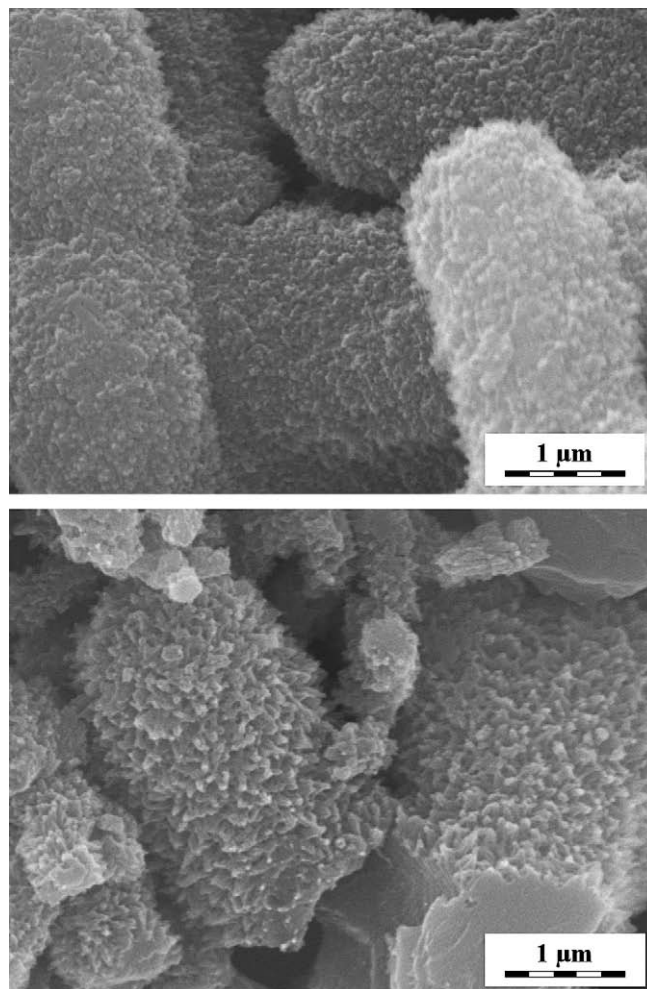


Fig. 9. Scanning electron micrograph of polyaniline-silver composite prepared at daylight (top) and in dark (bottom). 0.4 M aniline was oxidized with 1.0 M silver nitrate in 1 M nitric acid.

7.7 S cm^{-1} [72]. This suggests that the nitration, if any, has been limited because otherwise a reduction of conductivity would have been observed. The similar oxidation carried out at 5 M nitric acid, however, has led to a non-conducting product, and similarly the conductivity of a standard conducting PANI deteriorated after exposure to 5 M nitric acid. The absence of nitro groups in the PANI structure is also confirmed by FTIR spectra of PANI bases (Fig. 8).

3.5. Conductivity

The highest conductivity, 2250 S cm^{-1} , has been found with the composite having relatively low content of silver, 51.8 wt.% Ag (Table 1). The conductivity of the composites will depend on the morphology of both PANI and silver and the simple correlation of the conductivity with silver content is thus not possible.

Silver is the most conducting metal, its conductivity being $6.3 \times 10^5 \text{ S cm}^{-1}$ at 20 °C [73]. One would expect that the composites containing silver would automatically exhibit a high conductivity but this is not often the case. The content of noble metals seems to be relatively high when expressed on mass basis, e.g. $\sim 70 \text{ wt.}\%$ Ag (Table 1). When, however, the composition is recalculated to volume fractions, $\sim 22 \text{ vol.}\%$ Ag, the content of silver is just above the percolation limit predicted at 16–17 vol.% of the conducting component for mixtures of spherical conducting and

non-conducting particles [74]. A reduction in silver content may thus cause the loss of percolation associated with a consequent decrease in the conductivity. That is why the conductivity of composites containing gold or platinum, metals having still much higher density than silver and, consequently, much lower volume fraction in the composite, is generally low. The gold composites with PANI prepared by the oxidation of aniline with tetrachloroauric acid had a conductivity of $3.1 \times 10^{-2} \text{ S cm}^{-1}$ [16]. In another study, the PANI–platinum composite had a conductivity of only $3.2 \times 10^{-7} \text{ S cm}^{-1}$ [21].

3.6. The effect of daylight

The oxidation of aniline with silver nitrate was reported to be promoted by UV-irradiation [12,13]. For that reason, the oxidations in 1 M nitric acid have been carried out both in daylight and in dark (Table 1). The effect of daylight was not pronounced in the present experiments but the yield was indeed slightly reduced when the samples were kept in dark (Table 1). The PANI nanobrushes seem to be more compact when the polymerization was carried out in 1 M nitric acid (Fig. 9) compared with samples prepared in 0.4 M nitric acid (Fig. 2). The certain effect of daylight on the produced morphology is suspected also in this case.

4. Conclusions

- (1) Silver nitrate is able to oxidize aniline to polyaniline in the aqueous solutions of nitric acid. The oxidation products are composed of two conducting components, polyaniline and metallic silver. The theoretical composition calculated from stoichiometry is 70 wt.% of silver; 50–80 wt.% have been found in the experiment. The polymerization is slow and takes several weeks.
- (2) The oxidation proceeds more easily at higher concentration of aniline but only when nitric acid is present in molar excess with respect to aniline. At 0.4 M concentration of aniline, it is therefore more efficient in 1 M nitric acid than in 0.4 M nitric acid. Still two weeks are needed for successful polymerization.
- (3) The polyaniline has a standard molecular structure corresponding to the emeraldine form, as evidenced by UV–vis spectra. FTIR spectra confirm this finding. Both FTIR spectra and TGA suggest the presence of an oligomeric component in the samples.
- (4) The dominant morphology is represented by arrays of polyaniline nanofibres of $\sim 20 \text{ nm}$ diameter organized into brushes of submicrometre diameter. Polyaniline nanotubes have also been observed in the products. Silver is generated as nanoparticles of $\sim 50 \text{ nm}$ size but also as macroscopic silver flakes.
- (5) The conductivity of the polyaniline–silver composites was of the order $10^1\text{--}10^3 \text{ S cm}^{-1}$, the highest value being 2250 S cm^{-1} . There was marginal difference in the yield and morphology when the oxidation of aniline took place in daylight or when kept in dark.

Acknowledgments

The authors thank the Czech Grant Agency (202/06/0419 and 203/08/0686), the Ministry of Education, Youth, and Sports of the Czech Republic (ME 847), and the Ministry of Science and Environmental Protection of Serbia (Contract No. 142047) for financial support. Thanks are also due to J. Kovářová from the Institute of Macromolecular Chemistry, and to J. Prokeš, from the Charles University in Prague, for the characterization of samples.

References

- [1] Yang Q, Wang Y, Nakano H, Kuwabata S. *Polym Adv Technol* 2005;16:759.
- [2] Sapurina IYu, Kompan ME, Zabrodskii AG, Stejskal J, Trchová M. *Russ J Electrochem* 2007;43:528.
- [3] Mourato A, Correia JP, Siegenthaler H, Abrantes LM. *Electrochim Acta* 2007;53:664.
- [4] Drelinkiewicz A, Waksmundzka-Góra A, Sobczak JW, Stejskal J. *Appl Catal A Gen* 2007;333:219.
- [5] Amaya T, Saio D, Hirao T. *Tetrahedron Lett* 2007;48:2729.
- [6] Shi J, Guo D-J, Wang Z, Li H-L. *J Solid State Electrochem* 2005;9:634.
- [7] Wu G, Li L, Li J-H, Xu B-Q. *Carbon* 2005;43:2579.
- [8] Lee K-P, Gopalan AI, Santhosh P, Lee SH, Nho YC. *Compos Sci Technol* 2007;67:811.
- [9] Liu F-J, Huang L-M, Wen T-C, Yin K-C, Hung J-S, Gopalan A. *Polym Compos* 2007;28:650.
- [10] Huang L-M, Tang W-R, Wen T-C. *J Power Sources* 2007;164:519.
- [11] Wang A, Ye X, He P, Fang Y. *Electroanalysis* 2007;19:1603.
- [12] de Barros RA, de Azevedo WM, de Aguiar FM. *Mater Charact* 2003;50:131.
- [13] de Barros RA, Martins CR, de Azevedo WM. *Synth Met* 2005;155:35.
- [14] Dimeska R, Murray PS, Ralph SF, Wallace GG. *Polymer* 2006;47:4520.
- [15] Dimeska R, Little S, Ralph SR, Gordon G. *Fibers Polym* 2007;8:463.
- [16] Shiigi H, Yamamoto Y, Yoshi N, Nakao H, Nagaoka T. *Chem Commun* 2006:4288.
- [17] Peng Z, Guo L, Zhang Z, Tesche B, Wilke T, Ogermann D, et al. *Langmuir* 2006;22:10915.
- [18] Mallick K, Witcomb MJ, Scurrill MS. *Gold Bull* 2006;39:166.
- [19] Wang Z, Yuan J, Han D, Niu L, Ivaska A. *Nanotechnology* 2007;18:115610.
- [20] Guo Z, Zhang Y, Huang L, Wang M, Wang J, Sun J, et al. *J Colloid Interface Sci* 2007;309:518.
- [21] Kinyanjui JM, Harris-Burr R, Wagner JG, Wijeratne NR, Hatchett DW. *Macromolecules* 2004;37:8745.
- [22] Kinyanjui JM, Wijeratne NR, Hanks J, Hatchett DW. *Electrochim Acta* 2006;51:2825.
- [23] Mallick K, Witcomb MJ, Scurrill MS. *Eur Phys J E* 2006;19:149.
- [24] Oliveira MM, Castro EG, Canestraro CD, Zanchet D, Ugarte D, Roman LS, et al. *J Phys Chem B* 2006;110:17063.
- [25] Kang YO, Choi SH, Gopalan A, Lee KP, Kang HD, Song YS. *J Non-Cryst Solids* 2006;352:463.
- [26] Reddy KR, Lee K-P, Lee Y, Gopalan AI. *Mater Lett* 2008;62:1815.
- [27] Wang H-L, Li W, Jia QX, Akhadov E. *Chem Mater* 2007;19:520.
- [28] Kelly FM, Johnston JH, Borrmann T, Richardson MJ. *Eur J Inorg Chem* 2007;2007:5571.
- [29] Stejskal J, Trchová M, Kovářová J, Prokeš J, Omastová M. *Chem Pap* 2008;62:181.
- [30] Dawn A, Nandi AK. *J Phys Chem B* 2006;110:18291.
- [31] Stejskal J. *J Polym Mater* 2001;18:225.
- [32] Li W, Jia QX, Wang H-L. *Polymer* 2006;47:23.
- [33] Jing S, Xing S, Yu L, Wu Y, Zhao C. *Mater Lett* 2007;61:2794.
- [34] Stejskal J, Trchová M, Brožová L, Prokeš J. *Chem Pap*, in press. doi: 10.2478/s11696-008-0084-1.
- [35] Li J, Tang H, Zhang A, Shen X, Zhu L. *Macromol Rapid Commun* 2007;28:740.
- [36] Khanna PK, Singh N, Charan S, Viswanath AK. *Mater Chem Phys* 2005;92:214.
- [37] Zhou HH, Ning XH, Li SL, Chen JH, Kuang YF. *Thin Solid Films* 2006;510:164.
- [38] Huang L-M, Wen TC. *Mater Sci Eng A* 2007;445:7.
- [39] Neelgund GM, Hrehorova E, Joyce M, Bliznyuk V. *Polym Int* 2008;57:1083.
- [40] Stejskal J, Sapurina I, Trchová M, Konyushenko EN. *Macromolecules* 2008;41:3530.
- [41] Sapurina I, Stejskal J. *Polym Int* 2008;57:1295.
- [42] de Azevedo WM, de Barros RA, da Silva Jr EF. *J Mater Sci* 2008;43:1400.
- [43] Wu Y, Li Y, Ong BS. *J Am Chem Soc* 2007;129:1862.
- [44] Stejskal J, Gilbert RG. *Pure Appl Chem* 2002;74:857.
- [45] Bhat NV, Seshadri DT, Nate MM, Gore AV. *J Appl Polym Sci* 2006;102:4690.
- [46] Shi N, Guo X, Jing J, Gong J, Sun C, Yang KJ. *Mater Sci Technol* 2006;22:289.
- [47] Kamallesh S, Tan P, Wang J, Lee T, Kang E-T, Wang C-H. *J Biomed Mater Res* 2000;52:467.
- [48] Li M-Y, Bidez P, Guterman-Tretter E, Guo Y, MacDiarmid AG, Lelkes PI, et al. *Chin J Polym Sci* 2007;25:331.
- [49] Park KH, Jo EA, Na K. *Biotechnol Bioprocess Eng* 2007;12:463.
- [50] Guimard NK, Gomez N, Schmidt CE. *Prog Polym Sci* 2007;32:876.
- [51] Davied S, Nicolau YF, Melis F, Revillon A. *Synth Met* 1995;69:125.
- [52] Zhang LJ, Wan MX, Wei Y. *Macromol Rapid Commun* 2006;27:366.
- [53] Zhou C, Han J, Song G, Guo R. *Macromolecules* 2007;40:7075.
- [54] Jin E, Wang X, Liu N, Zhang W. *Mater Lett* 2007;61:4959.
- [55] Wang Y-G, Li H-Q, Xia Y-Y. *Adv Mater* 2006;18:2619.
- [56] Li G, Jiang L, Peng H. *Macromolecules* 2007;40:7890.
- [57] Han J, Song G, Guo R. *Adv Mater* 2007;19:2993.
- [58] Zhang Z, Deng J, Yu L, Wan M. *Synth Met* 2008;158:712.
- [59] Wan M. *Adv Mater* 2008;20:2926.
- [60] Huang J, Kaner RB. *Chem Commun* 2006:367.
- [61] Yan XB, Han ZJ, Yang Y, Tay BK. *Sens Actuators B* 2007;123:107.
- [62] Guo Y, Zhou Y. *Eur Polym J* 2007;43:2292.
- [63] Zhao W, Ma L, Lu K. *J Polym Res* 2007;14:1.
- [64] Wang ZJ, Yuan JH, Han DX, Zhang YJ, Shen YF, Kuehner D, et al. *Cryst Growth Des* 2008;8:1827.

- [65] Stejskal J, Sapurina I, Trchová M, Konyushenko EN, Holler P. *Polymer* 2006;47:8253.
- [66] Sun X, Hagner M. *Langmuir* 2007;23:10441.
- [67] Wang L, Guo S, Dong S. *Mater Lett* 2008;62:3240.
- [68] He D, Wu Y, Xu B-Q. *Eur Polym J* 2007;43:3703.
- [69] Konyushenko EN, Stejskal J, Šeděnková I, Trchová M, Sapurina I, Cieslar M, et al. *Polym Int* 2006;55:31.
- [70] Trchová M, Šeděnková I, Konyushenko EN, Stejskal J, Holler P, Čirić-Marjanović G. *J Phys Chem B* 2006;110:9461.
- [71] Stejskal J, Kratochvíl P, Radhakrishnan N. *Synth Met* 1993;61:225.
- [72] Stejskal J, Hlavatá D, Holler P, Trchová M, Prokeš J, Sapurina I. *Polym Int* 2004;53:94.
- [73] Lide DR, Frederikse HPR, editors. *CRC handbook of chemistry and physics*. 76th ed. Boca Raton: CRC Press; 1995. p. 12–46.
- [74] Scher H, Zallen R. *J Phys Chem* 1970;53:3759.