A Comparative Study of Water Dispersible Polyaniline Nanocomposites Prepared by Laccase-Catalyzed and Chemical Methods

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ABSTRACT: A comparative study of chemical and enzymatic methods of aniline polymerization was carried out. Fungal laccase from *Trametes hirsuta* was used in the synthesis of polyaniline nanoparticles made with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS). Template polymerization of aniline was carried out in aqueous buffer. It was shown that the laccase had high long-term and operating stabilities under acidic condition favorable for synthesis of conducting polyaniline. UV-vis, FTIR spectroscopy, and cyclic voltammetry analysis are used for the characterization of the polyelectrolyte complexes of polyaniline and PAMPS. The incorporation of the polymeric acid in polyaniline has been demonstrated by atomic force microscopy. The size and morphology of the nanoparticles of the polyaniline–PAMPS complexes depended on the method of the synthesis. A comparison of some physical and chemical properties of water dispersible conducting polyaniline–PAMPS was performed under production by enzymatic and chemical methods. It was found a difference in structures and some physicochemical properties of polyaniline colloids prepared by chemical and laccase-catalyzed methods. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1544–1550, 2010

Key words: conducting polyaniline; enzymatic and chemical polymerization; laccase; poly(2-acrylamido-2-methyl-1-propanesulfonic acid)

INTRODUCTION

Conducting polymers have been extensively studied for their promising application in light-emitting diodes, electrochromic devices, chemo- and bio-sensors, electromagnetic shielding, etc.[1–6] Polyaniline (PANI) is one of the most important among conducting polymers due to its environmental stability, simple synthesis and possibility to adjust its physicochemical properties by changes in the oxidation state and in the degree of protonation. Consisting of two main structure units, the benzenoid diamine and quinonoid diimine, the generalized formula of polyanline is depicted in Scheme 1, whose average oxidation state is described by the parameter y, and x – depends on the length of polymeric chain. There are three main oxidation forms of polyaniline: leucoemeraldine ($y = 1$), emeraldine ($y = 0.5$), and pernigraniline ($y = 0$).[4,7] The conductive form of polyaniline is the protonated emeraldine (emeraldine salt).

The common method used for the synthesis of PANI is chemical oxidation of monomer. The reaction is carried out under strongly acidic conditions (usually in 1*M* HCl) at about 0°C using a large amount of strong oxidizing agent such as ammonium persulfate.[8] The chain growth occurs in the solid state and yields to insoluble and infusible precipitate of polyaniline. In general, the possible way to increase the solubility of polyaniline is its synthesis in colloidal form.[9–11] Usually stable colloidal dispersions of polyaniline are prepared via template polymerization. Surfactants,[12–14] electroneutral

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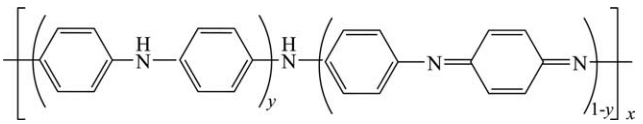

Scheme 1

polymers,[15] and polyanions[16–19] are used as templates to stabilize the polyaniline particles during aniline polymerization. As a result, a stable water dispersion of polyaniline can be obtained.

In comparison with chemical polymerization of aniline where a large amount of ammonium sulfate are released as by products, the use of enzymes as a catalyst in the synthesis of PANI is very attractive because the reaction can be performed under environmentally friendly conditions with the potential for producing in high yield industrial polymer without contaminant by products of oxidant degradation.[20,21] The template-guide synthesis of PANI complexes catalyzed by horseradish peroxidase,[17,22] palm tree peroxidase,[23,24] and template-free enzymatic synthesis of conducting polyaniline using soybean peroxidase[21] were reported previously. Hydrogen peroxide is the oxidant in the peroxidase-catalyzed reactions of aniline polymerization. It should be noted that peroxidases are very sensitive to hydrogen peroxide concentration and at concentration above 1 m*M* loss their initial activity, which requires stepwise addition of diluted hydrogen peroxide to the reaction medium. Some peroxidases (e.g. horseradish peroxidase) show low stability at pH below 4, due to theirs dissociation on heme and apoenzyme.[25] Recently, we developed a new enzymatic approach to synthesize water soluble and chiral conducting polyaniline using laccase as a catalyst for the aniline polymerization.[26,27] A novel method for the synthesis of water soluble polyaniline with the immobilized laccase was also developed.[28] The use of laccase as catalyst for the aniline polymerization has attracted great interest as alternative route in comparison with peroxidase-based synthesis. Laccase (benzenediol: oxygen oxidoreductase, EC 1.10.3.2), blue multicopper oxidase, contains four copper ions and catalyzes a four-electron reduction of oxygen to water with concomitant oxidation of various inorganic and organic compounds, including aniline.[29,30] Air oxygen is mild oxidant for this laccase-catalyzed reaction of aniline polymerization. It is environmental friendly and does not require a stepwise addition of diluted hydrogen peroxide to a reaction medium in contrary to peroxidase-catalyzed reaction.

This article describes a comparison of template synthesis of PANI in the presence of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) using ammonium persulfate and a "green" method of aniline polymerization with high redox potential fungal laccase from basidiomycete *T. hirsuta*. The detailed synthesis and characterization of a stable water soluble polyaniline obtained by both methods is presented.

EXPERIMENTAL

Material and instrumentation

Aniline (Labtech, Russia) was distilled under a reduced pressure before using. Na_2HPO_4, citric acid, PAMPS (MW ca. 1.000.000) were purchased from (Aldrich, Germany). Fungal laccase from *Trametes hirsuta* was purified to homogeneity as described previously.[31] The specific activity of the enzyme was ca. 80 units/mg of protein. All the solutions were prepared using water purified with Milli Q system (Millipore, USA).

The absorption spectra of PANI complexes were recorded on Hitachi 557 spectrophotometer (Japan). In every experiment distilled water was used as a control. PANI/PAMPS complexes were dedoped by treatment with 0.1*M* NaOH solution for 24 h, dried and washed with H_2O to remove NaOH and by products. ATR FTIR spectra of dedoped PANI/PAMPS complexes were recorded using Nicolet IR 200 (USA) spectrometer equipped with a single reflection ATR accessory "performer". Dry powder of dedoped PANI/PAMPS complexes were placed on a ZnSe crystal and 64 scans per spectrum at 8 cm^{-1} resolution were collected. The atomic force microscopy (AFM) images were obtained by scanning probe microscope, Solver P-47 (NT-MDT, Russia) using sample adsorption onto highly oriented pyrolytic grafite and semicontact mode in air.

Conductivity measurements were performed by two-point DC method at room temperature. Polyaniline films on insulating alumina substrates with gold contacts were used for experiments. Film thickness was about 5–10 μm measured by step-profilometry (Talystep, UK). Ohmic behavior of gold contacts to polyaniline films was tested by linearity of voltage-current characteristics. In all cases conductivity σ was registered at a fixed voltage of 1 V.

Laccase activity

The activity of laccase was measured spectrophotometrically, using 10 m*M* catechol as the chromogenic substrate ($\lambda = 410$ nm, $\varepsilon = 740\ M^{-1}cm^{-1}$) at 24°C in 0.1 *M* Na-citrate-phosphate buffer, pH 4.5. One unit of activity is defined as the amount of laccase oxidizing 1 μm of substrate per min. Specific activity is expressed as units of activity per mg of protein. The operating stability of laccase was determined by measuring enzyme activity in time during the

reaction of aniline polymerization resulting in the formation of PANI/PAMPS complex. For these experiments a 200 μL sample of the reaction mixture was taken and added to 2.5 mL 10 m*M* catechol in 0.1 *M* Na-citrate-phosphate buffer, pH 4.5.

Polymerization of aniline

A reaction solution containing both freshly-double distilled aniline (25 m*M*) and PAMPS (25 m*M*, based on the monomeric repeat unit) in 0.1 *M* Na-citrate-phosphate buffer (pH 3.5) was stirring for 1.5 h. In some experiments the concentrations of aniline and PAMPS in the reaction mixture varied from 10 m*M* to 75 m*M*. In the enzymatic syntheses polymerization was initiated by the addition of the laccase with final concentration of the enzyme in the reaction medium of 0.5 μ*M*. Air oxygen was used as oxidant in the reaction of polymerization. The chemical polymerization was initiated by slowly adding the 0.5 *M* solution $(NH_4)_2S_2O_8$ to the mixture of monomer and PAMPS (final concentration of $(NH_4)_2S_2O_8$ was 25 m*M*). The syntheses of PANI/PAMPS complexes were carried out in a humidity chamber at 20°C under the air saturated conditions at continuous stirring for 24 h to complete the reaction of polymerization. The obtained complexes were purified several times by dialysis against deionized water in order to remove excess of low molecular weight compounds. The final products were monitored using UV-vis spectroscopy.

Cyclic voltammetry

Electrochemical experiments were performed using a BAS CV-50W voltammetric analyzer (Bioanalytical System, USA) with a glass cell consisting of three electrodes. Cyclic voltammograms of the PANI/PAMPS complexes were recorded at pH 3.5 in 0.1 *M* Na-citrate-phosphate buffer. The solutions of PANI/PAMPS complexes were loaded in a one-compartment electrochemical cell consisted of an Ag/AgCl reference electrode (BAS, USA), a platinum wire counter electrode and a glassy carbon working electrode (BAS, USA). Measurements were carried out in the potential range from −200 mV to 700 mV and in reversible order from 700 mV to −200 mV. Cyclic voltammograms were recorded with a scan rate potential of 100 mV/s.

Atomic force microscopy investigations

Samples for AFM research were adsorbed onto highly oriented pyrolytic graphite for 10 min and washed by MilliQ water. AFM images were obtained in the semicontact mode using scanning probe microscope Solver P47 ("NT-MDT", Zelenograd, Moscow, Russia). High resolution noncontact "Golden" silicon cantilevers NSG11 series from NT-MDT Company with nominal spring constant 5.5 and 11.5 *N*/m, resonant frequency 150 and 255 kHz and tip radius 10 nm were used. The original images were recorded at a resolution of 512 × 512 and imaging was performed at room temperature in air. Typical scan rates were 1 Hz.

RESULTS AND DISCUSSION

Synthesis of water dispersible polyaniline complexes

It is necessary that an enzymatic reaction of the aniline polymerization should be carried out at acidic pH more below than pKa value of aniline (pKa = 4.63), to form the ionic complex with the high degree complexation between positively charged aniline and negatively charged PAMPS and to minimize the parasitic branching of PANI.

The most of biocatalysts are active and stable only at neutral pH values. Therefore, stability of laccase under the conditions of polyaniline synthesis (operating stability of laccase) is very important. In this work fungal laccase from basidiomycete *T. hirsuta* was used as the catalyst in the oxidative polymerization of aniline in the presence of PAMPS. At pH 3.0 and 3.5 laccase from *T. hirsuta* had also sufficient operating stability: the enzyme preserves 40% of the initial activity after 24 h of aniline enzymatic polymerization at 20°C, pH 3.5 (Fig. 1). As laccase was active and stable under acidic conditions, therefore chemical and laccase-catalyzed polymerization of aniline was carried out at pH 3.5.

In the case of enzymatic and chemical template polymerization of aniline at pH of 3.5 in aqueous buffed conditions, a dark green solution was formed indicating the emeraldine salt formation. The laccase-catalyzed reaction of oxidative polymerization of aniline monomer in PAMPS solution had small

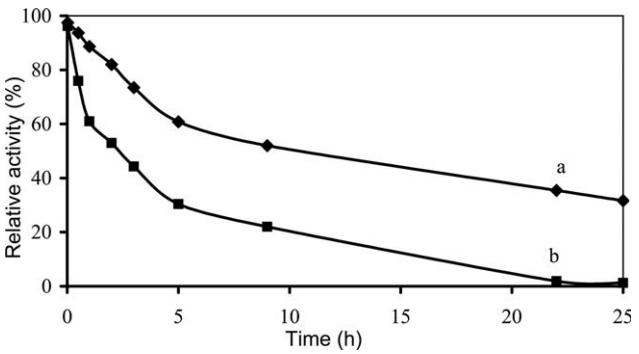

Figure 1 Operating stability of laccase during formation of PANI/PAMPS complex at pH 3.5 (a) and 3.0 (b). Conditions: 0.1 *M* Na-citrate-phosphate buffer, [aniline] = [PAMPS] = 25 m*M*, [laccase] = 0.5 μ*M*.

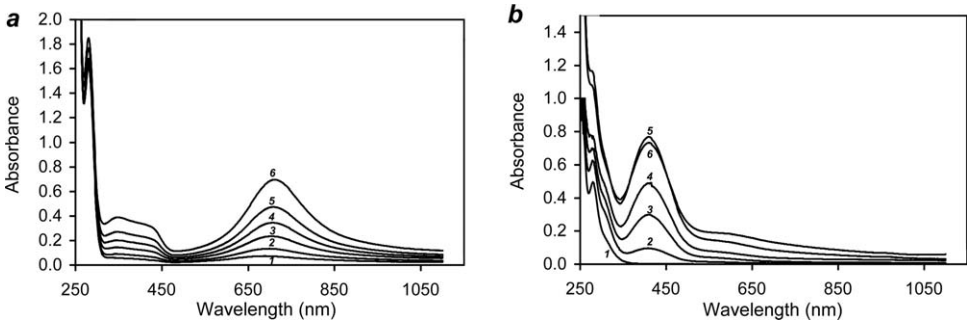

Figure 2 Evolution of UV-vis spectra of products of enzymatic (a) and chemical (b) PANI syntheses with reaction time: (1_a) - 5 min, (2_a) - 10 min, (3_a) - 20 min, (4_a) - 30 min, (5_a) - 40 min, (6_a)-60 min; (1_b) - 6 min, (2_b) - 22 min, (3_b) - 30 min, (4_b) - 37 min, (5_b) - 45 min, (6_b) - 62 min. The experimental conditions: 0.1 *M* Na-citrate-phosphate buffer; pH of reaction medium 3.5; [aniline] = [PAMPS] = 25 m*M*; [laccase] = 0.2 μ*M*; [ammonium persulfate] = 25 m*M*. The samples after chemical synthesis were diluted with buffer (1 : 4).

induction period (less than 5 min) [Fig. 2(a)] and depended on the laccase concentration. In polymerization of aniline by chemical oxidation with ammonium persulfate in the same experimental conditions, the induction period was about 1 h [Fig. 2(b)].

As a result of the both syntheses stable dispersions of the PANI/PAMPS complexes were formed. Theirs optical absorption spectra are presented in Figure 3. As seen in Figure, a strong polaron absorption bands at about 700–800 nm observed at pH 3.5 indicating the formation of conducting polyaniline salt. Usually the polaron band of polyaniline is observed at about 840 nm.[32] But in polyaniline complexes with a polyacid containing electron-withdrawing sulfonic groups the polaron bands shift to ca. 750–800 nm.[24] The red shift of polaron band and appearance of free carrier tail of PANI complex produced by chemical method in comparison with laccase-catalyzed synthesis suggested some changes of the polyaniline structure. The exact position of this localized polaron is sensitive to slight variations in the experimental procedure. It is known that Cu^{2+} complexes can catalyze the reaction of aniline polymerization. We have shown that heat-inactivated laccase cannot catalyze this reaction.

It is well known that polyaniline at pH 3.0 and higher is in emeraldine base form and such a state transfer results in the loss of its ability to conduct the current.[33] Contrary to polyaniline, its polyelectrolyte complex with PAMPS is in the protonated form up to pH 6.0–7.0. This conclusion was made on the basis of results obtained from titration of the polyelectrolyte complexes by NaOH or H_3PO_4 in the pH range 2.0–11.0 (Fig. 4). It can be observed from the figure that the absorption characteristics undergo a series of changes upon increasing the solution pH from 2.0 to 11.0. It was found that at pH higher than pH 5.0 the intensity of absorption bands typical for conducting polyaniline at 780 nm gradually decreased, shifted to much shorter wavelength, which is attributed to deprotonation of the polyaniline backbone. Finally at pH 9.9 the complex absorption at 550 nm arising from excitation transition of the quinoid rings in emeraldine base is observed. This process was reversible up to pH 9.0. The similar results were obtained for PANI/PAMPS complex

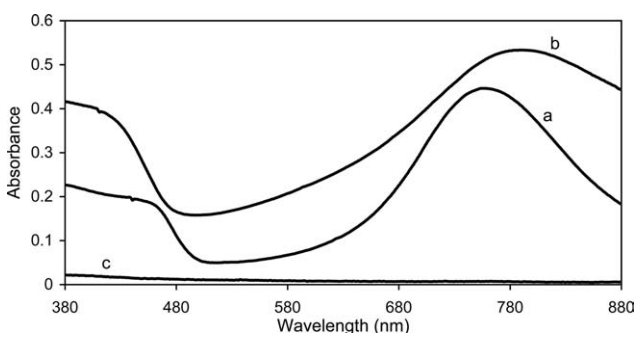

Figure 3 Optical absorption spectra of PANI/PAMPS complexes produced by enzymatic (a), chemical (b) aniline polymerization. No aniline polymerization is observed in the presence of heat-inactivated enzyme (c). Conditions: 0.1 *M* Na-citrate-phosphate buffer (pH 3.5); [aniline] = [PAMPS] = 25 m*M*, [laccase] = 0.5 μ*M*, [ammonium persulfate] = 25 m*M*. The samples were diluted with buffer (1 : 70).

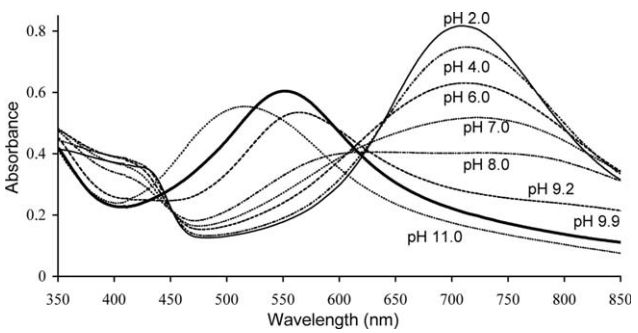

Figure 4 Optical absorption spectra of the enzymatically synthesized PANI/PAMPS complex at different pHs. Conditions: 0.1 *M* Na-citrate-phosphate buffer (pH 3.5); [aniline] = [PAMPS] = 25 m*M*, [laccase] = 0.5 μ*M*. The samples were diluted with buffer (1 : 50).

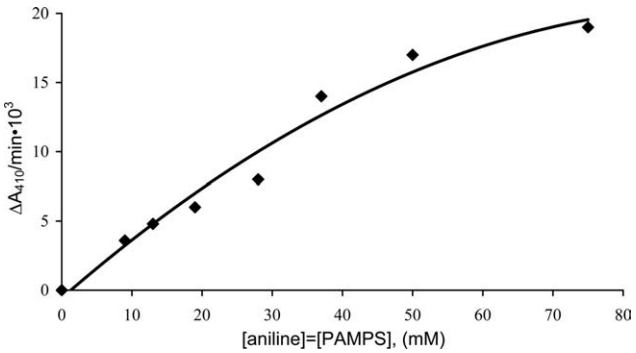

Figure 5 Influence of aniline concentrations on the initial rate of the enzymatic synthesis of polyaniline. Conditions: 0.1 *M* Na-citrate-phosphate buffer, pH 3.5; [aniline]: [PAMPS] = 1 : 1, [laccase] = 0.5 μ*M*.

prepared by chemical polymerization (data not shown). To evaluate the effect of the enzymatic polymerization rate, kinetics of enzymatic polymerization was studied varying of the monomer concentration in aniline/PAMPS complex from 10 to 75 m*M*. The rate of aniline polymerization increased linearly with increasing of monomer concentration up to 35 m*M*. However, at higher concentration of PAMPS the effect of decreasing of the reaction rate was observed due to increasing of viscosity of the reaction medium. The results are presented in Figure 5.

FTIR analysis of PANI/PAMPS complexes

Figure 6 shows the FTIR spectra of PAMPS (a) and PANI/PAMPS complexes synthesized by both chemical (b) and laccase-catalyzed (c) methods. The spectra chemically synthesized PANI/PAMPS complex is quite similar to that of enzymatically prepared. The spectra of PANI/PAMPS complexes exhibit the characteristic absorption bands arising from both components, i.e. PANI and PAMPS.

In the spectrum of PAMPS (a) SO_3 stretching (symmetric and asymmetric) at 1044 and 1227–1117 cm^{-1}, respectively, C=O stretch at near 1660 cm^{-1} are observed.[34] The sulfonic acid group is the active lateral group of PAMPS that should interact with the nitrogen atoms of PANI and give a sulfonate absorption band in the PANI/PAMPS composite material. FTIR absorption spectra of the both PANI/PAMPS nanocomposites show the vibration characteristics of both the PAMPS and PANI polymers. For example, the PANI/PAMPS nanocomposites feature a sulfonic acid group stretching band at region 1220–1110$cm^{-1,}$ C=O stretching at near 1660 $cm^{-1.}$ These bands are associated with PAMPS. Meanwhile, the characteristic band near 1600 cm^{-1} arises mainly from both C=N and C=C stretching of the quinonoid diimine unit, while the band near 1500 cm^{-1} is attributed to the C—C aromatic ring stretching of the benzenoid diamine unit. The intensity ratio of these two absorption peaks (quinone diimine/benzene diamine) is indicative of the extent of PANI oxidation. This ratio is about 0.8 for emeraldine base and decreases as the reduction of PANI backbone proceeds.[35] For example, this ratio is ca. 0.92 for PANI/PAMPS complex enzymaticaly synthesized and decrease to ca. 0.72 for chemically synthesized. A increase in the peak intensity at 1600 cm^{-1} indicates that the benzoid rings in PANI are oxidized to the quinoid rings during the enzymatic synthesis.

Electrochemical characterization of PANI/PAMPS complexes

The synthesized polyelectrolyte complexes of PANI and PAMPS were dialyzed several times against deionized water to eliminate any unreacted monomer, oligomers, and buffer components. Cyclic

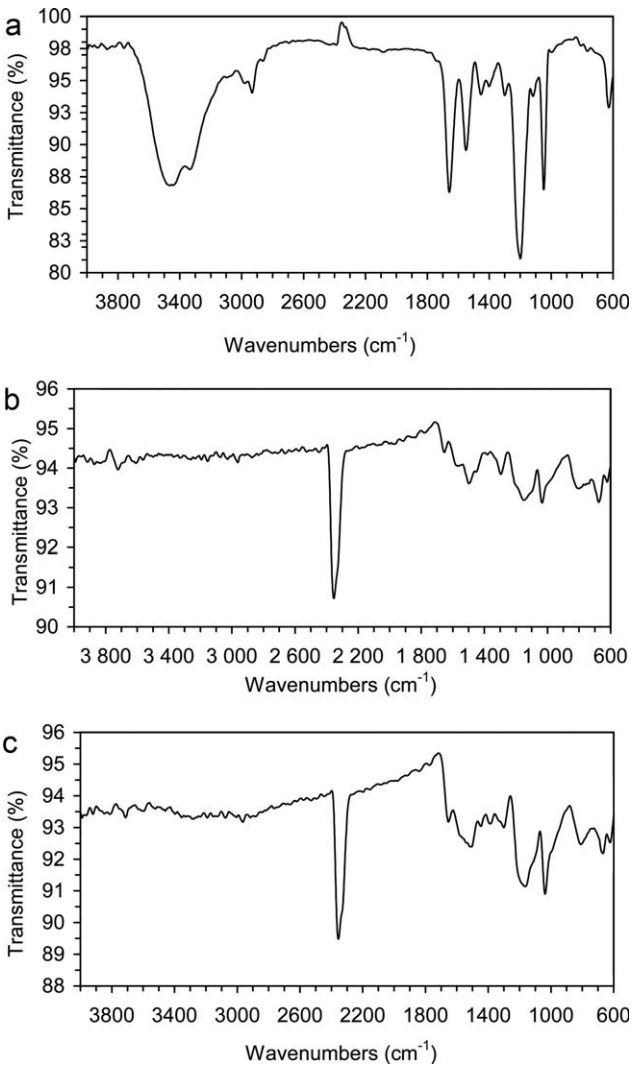

Figure 6 FTIR spectra of PAMPS (a) and dedoped PANI/PAMPS nanocomposites prepared by chemical (b) and enzymatic syntheses (c).

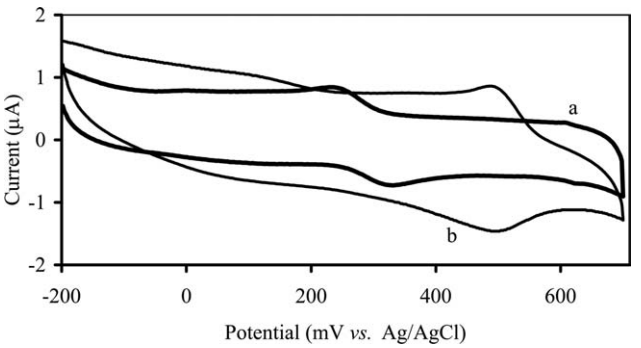

Figure 7 Cyclic voltammograms of PANI/PAMPS complexes formed by enzymatic (a) and chemical (b) syntheses. Conditions: scan rate – 100 mV/s. The samples were diluted with 0.1 *M* Na-citrate-phosphate buffer, pH 3.5 (1 : 10).

voltammograms of PANI/PAMPS complexes synthesized by enzymatic and chemical methods are presented in Figure 7. Both polyelectrolyte complexes of PANI in aqueous buffer solutions were electrochemically active and exhibited on the cyclic voltammograms one well expressed quasi reversible redox couples with middle point potentials 491 mV for chemical prepared PANI/PAMPS complex and 282mV for enzymatic method, respectively. However, the electrochemical properties of both complexes had very important differences. The positions of the anodic and cathodic current peaks recorded at pH3.5 for chemical synthesized PANI/PAMPS samples shifted to positive potential range in comparison with those prepared by laccase-catalyzed method. Apparently, it is connected with the oxidation states of polyaniline backbone formed upon aniline polymerization using chemical and enzymatic method. FTIR spectroscopy provides evidence that the PANI backbones were more oxidized during the laccase-catalyzed synthesis compared with those synthesized by chemical method. It is worthy mention that second redox couples at more negative potential range of both PANI complexes were broad and not well expressed. If the oxidation potential is higher than 800 mV, polyaniline will be converted to pernigraniline.

Atomic force microscopy

AFM investigations of both PANI/PAMPS samples prepared by chemical and laccase-based methods indicate important differences of the prepared particles morphology. Figure 8 shows the AFM images of such PANI/PAMPS samples deposited on a surface of highly oriented pyrolytic graphite by adsorption from the water.

The main motive for the laccase produced PANI/PAMPS samples images is worm-shaped particles with the height about 2 nm and length about 100 nm

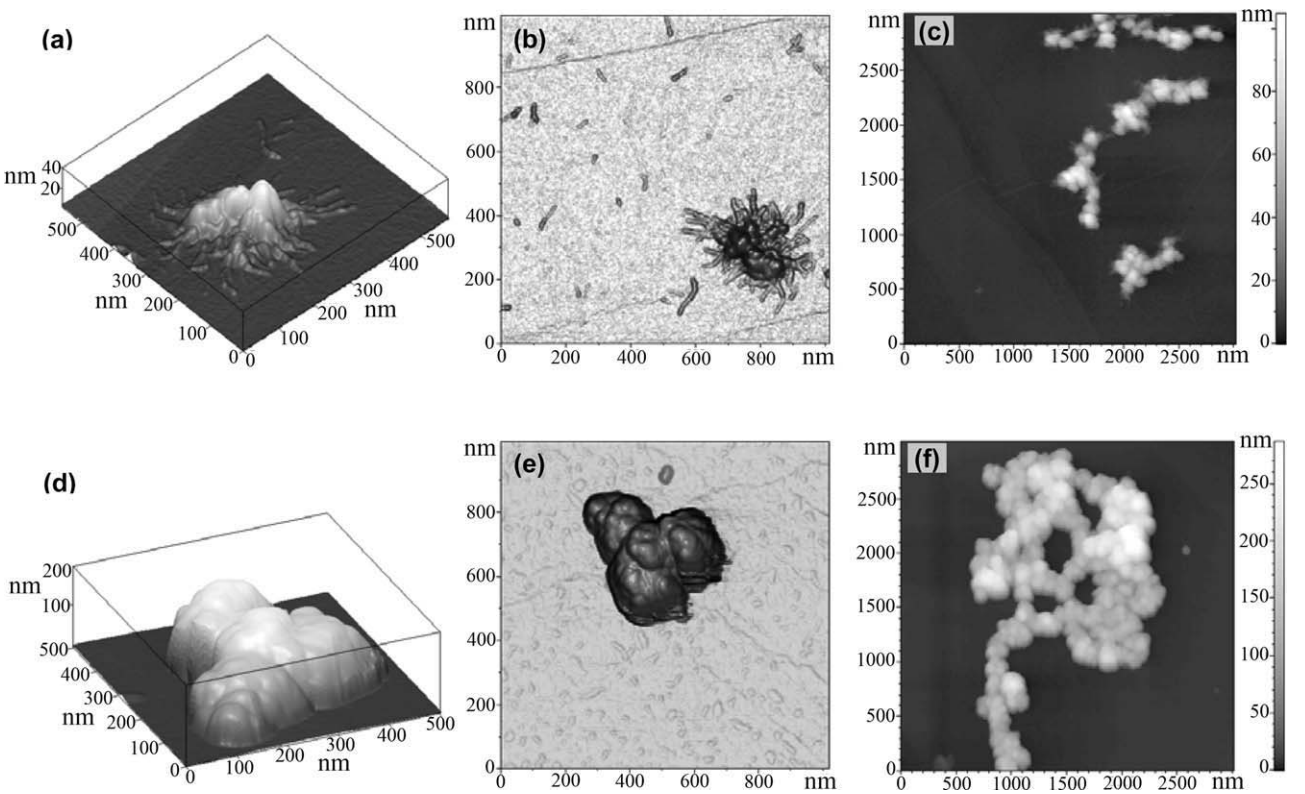

Figure 8 AFM images of PANI/PAMPS complexes produced by enzymatic (a, b, c) and chemical (d, e, f) methods. The images are presented as three-dimensional gray scale (a, d), two-dimensional gray scale (c, f) and representations two-dimensional gray scale (b, e) and lighting mode (with the reflecting from virtual lighting source).

[Fig. 8(a,b)]. The worm-shaped objects tend to form the star-shaped aggregates [Fig. 8(a,b,c)] with the height about 50–80 nm and diameter about 100–200 nm.

The chemical template produced PANI/PAMPS samples formed small [Fig. 8(d,e)] and large aggregates [Fig. 8(f)] containing globular particles with the height about 120–180 nm and diameter about 200–300 nm.

Conductivity

The conductivity values of the PANI/PAMPS complexes measured by two-point probe method were in the ranges of 2–3 mS/cm and 1–2 mS/cm for polyaniline prepared by chemical and enzymatic methods, respectively. It is similar to those measured previously for water soluble polyaniline produced by other methods.[22] Decreasing of buffer concentration in reaction medium to 0.05 *M* resulted in increasing the conductivity of enzymatically synthesized PANI/PAMPS complex up to 10 mS/cm. The higher conductivity of PANI complex in lower molar buffer solution could be due to a more homogenous protonation of the imine nitrogen and more ordered chain conformation of the polymer.

CONCLUSIONS

The physical and chemical characteristics of the material prepared by the "green" synthesis of conducting polyaniline nanocomposite using fungal high redox potential laccase differ from those of chemically synthesized preparation. PANI nanoparticles obtained by the two methods are morphologically distinctive. In addition, the mechanism of enzymatic aniline polymerization is of a radically different kind from that of the chemical synthesis. The latter proceeds with a significant induction period, which is not observed in the laccase-catalyzed reaction. Thus, as laccase belongs to industrial enzyme (http://www.novozymes.com), aniline polymerization by the "green" method is very promising for industrial application.

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