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Conductive polymer preparation under extreme or non-classical conditions

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Abstract Polyaniline (PANI) emeraldine salt form and PANI/silver composites have been synthesized by sonochemical and ionizing radiation methods. These composite materials were obtained through sonication and γ irradiation of an aqueous solution of aniline and silver nitrate, in room temperature, respectively. The mechanisms suggested to explain the formation of these products are based on the fact that both methods produce hydroxyl radical $^{\bullet}$OH and hydrogen radical $^{\bullet}$H, where hydroxyl radical $^{\bullet}$OH acts as an oxidizing agent in the polymerization process of aniline monomer; and hydrogen radical $^{\bullet}$H, as a reducing agent for silver ions. Spectroscopic, X-ray, and SEM measures show that PANI and silver nano particles of 40 nm average diameter are produced with ultrasonic methods, whereas silver nano particles of 60 nm average, and fibrillar, highly network morphology for PANI with 60 nm fibrillar diameter average are obtained using γ radiation).

Introduction

In the past 15, 20 years, literature has witnessed a significant increase in the number of articles using what may be called non-traditional or non-classical experimental approaches. In other studies, ambient or close to ambient conditions have been extended, by orders of magnitude, providing advantages for synthesis, reaction mechanism insight and, in some cases, novel chemistry, which is not accessible under ambient conditions. These special conditions may be called extreme.

Among several methods and types of chemistry that may be included within the categories of extreme or non-classical conditions, some areas have become more evident in literature, such as microwave chemistry, sonochemistry techniques, supercritical fluid methods, plasma applications, and ionization radiation [1].

From the experimental techniques developed to prepare polymeric materials mentioned above, the use of ultrasound radiation [2–4] turned out to be a very attractive and alternative tool for many researchers. The main advantages of ultrasound waves in the polymerization process are the absence of external chemical initiators and the possibility of bulk polymerization. Propagation of ultrasound waves through a fluid causes the formation of cavitations bubbles [5]. Collapse of these bubbles, described as an adiabatic implosion in the hot-spot theory, is the origin of extreme local conditions: high temperature (5,000 K) and high pressure (1,000 atm)[5]. Cooling rates obtained after collapse are greater than 10^{10} K s^{-1} [6–7], which leads these experimental conditions to be classified as *extreme or non-classical conditions*.

This technique has been used in the polymerization of methylmethacrylate [8], a metal polymer composite material [9, 10]. A more recently application has been performed in the conducting polymer and conducting polymer metal composite preparation. However in the majority of reports, ultrasound has been used as a co-adjuvant in the polymerization process, as in the preparation of conducting polymer colloids [11] microemulsion polymerization assisted by ultrasonic waves [12] and

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conductive polyaniline (PANI)/nanocrystalline titanium oxide [13]. In all cases, a conventional oxidant, such as ammonium persulfate was used, together with ultrasound radiation, in the polymerization process.

In relation to high energy ionizing radiation, another extreme reaction medium, such as electromagnetic radiation (X-rays and γ-rays), and particles (α-particles, β-particles or electrons, protons, and neutrons), we have noticed that few articles on conducting polymer have been published, and the majority of them is concerned with the effects of radiation in conducting polymer properties [14–16], or the preparation of metal nanocomposite using gamma radiation [17]. Again we have noticed that conventional oxidants are used together with gamma radiation to start polymer preparation.

Earlier studies in sonochemistry of conducting polymer solution [18] and ionization radiation effects on conducting polymer conductivity [19] developed in our group have shown that when PANI dissolved in DMSO interacts with ultrasound radiation, conducting polymer changes its oxidation states and is reduced, as a consequence of the radical produced by homolises of water molecule present in the solvent. On the other hand, when ionization radiation interacts with conducting polymer, polymer conductivity changes several orders of magnitude depending on the doped state of the polymer. In this case adsorbed water molecule plays an important role in the interaction process. Once, in both examples above, radicals are produced as a consequence of radiation interaction with reaction medium, we have decided to investigate in this communication the possibility to use these radicals only as the oxidizing agents for monomer polymerization and the preparation of organic–inorganic nanocomposite.

Experiment

Aniline (Nuclear) was distilled twice under atmospheric pressure, stored in a in dark and at low temperature prior to synthesis. Ammonium hydroxide (Merck), ethanol (Merck), nitric acid (Merck), silver nitrate (Merck), DMSO (Merck), acetonitrile (Aldrich) and all the other reagents were used without further purification. All aqueous solutions were prepared using distilled and deionized water. Stock solution of desired concentration of aniline in nitric acid and silver nitrate in aqueous solution, was prepared and stored at low temperature, in a dark place, prior to use.

Aniline polymerization synthesis using ultrasound waves was carried out in test tube, where a solution of 0.5 M aniline in 1.0 M of nitric acid was added to a 0.5 M silver nitrate solution, and the mixture was treated with ultrasound waves for at least 1 h in air atmosphere at 25 °C, using a commercially ultrasonic bath, Branson model 2,210 (47 kHz, 35 W cm^{-2}), or with a home made ultrasonic equipment (475 kHz, 50 W cm^{-2}). At regular time intervals, an aliquot of the solution was taken for analysis. Afterwards, solution was centrifuged and the precipitated material was washed with water and acetonitrile, several times, until the remaining solution became clear.

For ionization radiation synthesis, solutions were irradiated inside a gamma cell Cobalt Irradiator, from Radionics Laboratory, Scotch Plains, New Jersey, USA (dose rate of 0,2114 Gy/min), in the dose range from 0 to 10 kGy. After irradiation, the precipitated material was washed with water and acetonitrile several times until the remaining solution became clear.

Spectroscopic characterization in UV-visible and infrared region was performed with Perkin Elmer spectrophotometer model Lambda 6 and with FTIR Bruker model IFS66 spectrophotometer, respectively, whereas scanning electron microscope (SEM) analysis and X-ray diffraction (XRD) patterns were performed using JEOL microscope model JSM 5,600 and Rigaku DMAX model 2,400 X-ray diffractometer with Cu target ($\lambda = 0.154178$ nm), respectively.

Results and discussion

The effect of the interaction of ultrasound wave with aniline plus nitrate solution can be seen in the absorption spectra as a function of reaction time. At the beginning, solution is colorless. As reaction time increases, solution turns into yellow and, finally, becomes green with subsequent precipitation of the polymer. Figure 1 shows the absorption bands of the solution as a function of irradiation time. As we can see, there is only one band at 410 nm after 1 h, and this absorption band increases with irradiation time. This band may be assigned to surface plasmon resonance absorption of the electrons in the conducting silver bands. The absorption band at 410 nm is a characteristic of colloidal metal particles, which are large enough ($R > 1$ nm) to exhibit bulk metallic properties [20]. These results indicate that the diameter of silver particles can be estimated to be between 20 and 40 nm, once the predicted value of extinction coefficient for small particles ($R = 1–10$ nm) has nearly the same plasma resonance wavelength and, it is difficult to assign unique values to colloidal particle size in this region [20].

As sonication times increases, two new bands appear: one at 420 nm and the other at 800 nm, which is attributed to polaron-π^*, and polaron-π transitions, respectively. These absorption bands are a characteristic of conducting polymer PANI, synthesized in conducting state [21, 22].

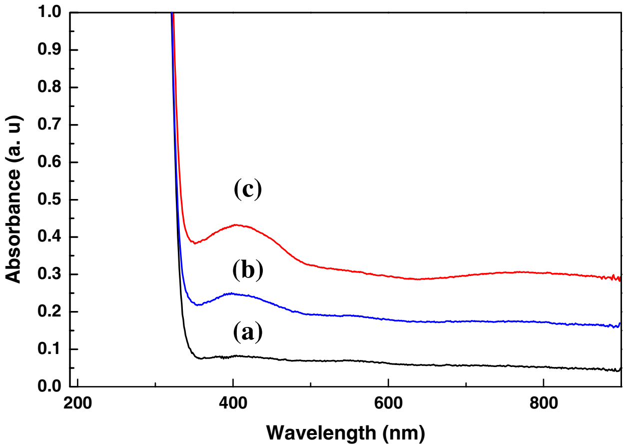


Fig. 1 absorption spectra of a solution of aniline nitrate plus Silver nitrate as a function of the irradiation time (**a**) 1 h of ultrasound, (**b**) 3 h of ultrasound, and (**c**) 5 h of ultrasound

Figure 2 shows XRD patterns of precipitate, obtained by ultrasound method. We can see two intense X-ray peaks; one at $2\theta = 38.3°$ and the other at 44.5°, in which were assigned the [111] and [200] silver particle patterns [23]. Crystallite average size, determined from XRD measurements using Scherrer's equation is 40 nm, which is in agreement with the up limit predicted by absorption and SEM measurements, shown in Fig. 3.

Figure 4 shows FTIR spectra of KBr pellets of precipitate in 400–4,000 cm^{-1} region. Absorption peaks at 1,569 cm^{-1} and 1,493 cm^{-1} can be assigned to quinoid and benzenoid unit stretching modes. Vibration at 1,297 is due to C–N stretch from benzenoid unit stretching mode of PANI. Band at 1,142 cm^{-1} assigned to quinoid unit of doped PANI, confirms the identity of the polymer and is in agreement with published articles in literature [24, 25]. The strong band that appears at 1,345 cm^{-1}, which does not belong to PANI, is assigned to nitrate ions [26].

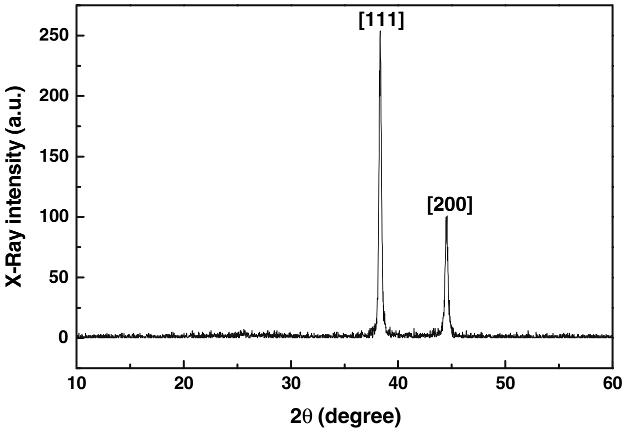


Fig. 2 X-ray diffraction patterns of the polyaniline silver composite prepared using ultrasound

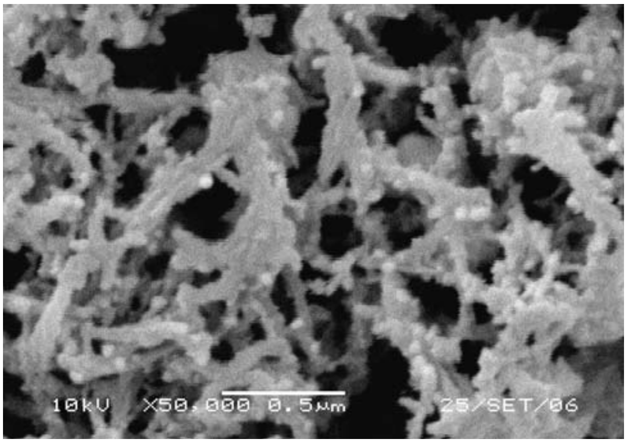


Fig. 3 Scanning electron microscopy images of polyaniline/Silver nano composite grown from a solution of aniline nitrate and silver nitrate irradiated by ultrasound radiation

These results strongly suggest that interaction of ultrasound wave, of high frequency, is able to polymerize aniline monomer and, simultaneously, reduce silver ions. The suggested mechanism to explain the formation of silver nanoparticles and aniline polymerization takes into account radical species that are generated when ultrasound wave interacts with an aqueous solution. Cavitations effects occur and they are responsible for homolytic cleavage of an O–H bond in water molecule. This leads to a highly reactive hydroxyl radical production [27].

$$H_2O \xrightarrow{)))} {}^{\bullet}H + {}^{\bullet}OH \qquad (1)$$

In Eq. 1, the symbol))) indicates ultrasound interaction and, $H^{\bullet}$ is the radical produced that can act as a reducing species and trigger reduction of silver ions (Eq. 2):

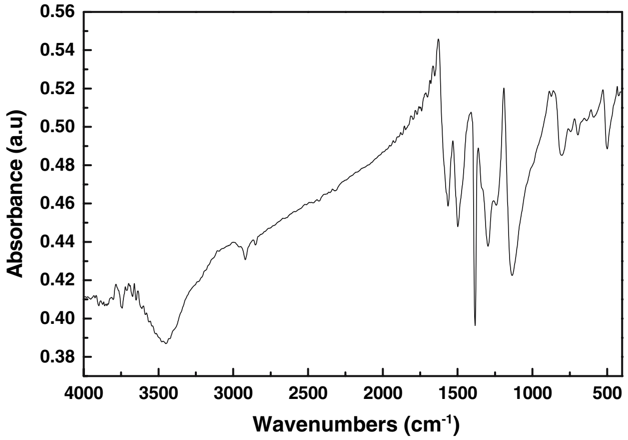
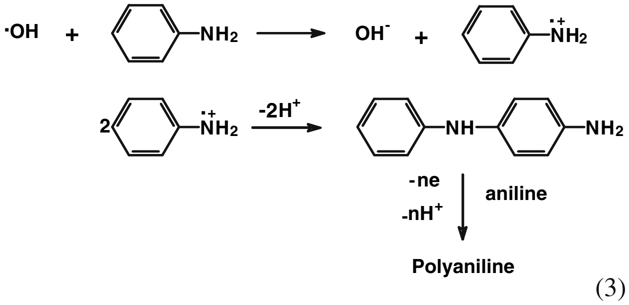


Fig. 4 FTIR spectrum of polyaniline prepared by ultrasonication of a solution of aniline nitrate plus Silver nitrate

$$Ag^{+} + {}^{\bullet}H \rightarrow Ag^{o} + H^{+} \quad (2)$$

On the other hand, hydroxyl radical ${}^{\bullet}OH$ attacks aniline monomer (Eq. 3) starting the polymerization process.



(3)

In order to prove that the mechanism suggested above is responsible for the polymerization process of aniline monomer, we have repeated the same experiment in the presence of a radical scavenger [28]. In this case, we have used a small amount of DMSO together with aniline and silver nitrate solution, and have left the experiment to run during the same time as in conventional procedure. After this time, no polymer precipitation occurred; only the yellowing of the solution was obtained. This yellowing of the solution is due to the appearance of Plasmon band, which is a characteristic of silver particles growth due to silver ions reduction. Since DMSO solvent is a recognized ${}^{\bullet}OH$ radical scavenger, this result strongly suggests that ${}^{\bullet}OH$ is responsible for monomer polymerization.

Polyaniline synthesis and the simultaneous reduction of silver ions with γ-ray radiation were performed using a slight modification of the technique developed by Zhu for the preparation of nanocrystalline silver powders [23]. The developed procedure proposed by Zhu, uses isopropilic alcohol as a scavenger for hydroxyl radicals. Decomposition of water molecule by γ radiation results in the formation of hydroxyl radical ${}^{\bullet}OH$, hydrogen radical $H^{\bullet}$ and hydrated electrons. Since isopropilic alcohol is used in the process, the only available radical is hydrogen radical $H^{\bullet}$, which acts as a reducing agent for silver ions. In our process, instead of isopropilic alcohol we have used aniline monomer as a scavenger, and the resulting interaction is the oxidation of aniline monomer by hydroxyl radical ${}^{\bullet}OH$, leading to the preparation of polymer PANI. On the other hand, free $H^{\bullet}$ radical will interact with silver ion reducing it to silver metals. Figure 5 shows FTIR spectra for the composite silver/PANI obtained after irradiation of silver nitrate and aniline nitrate solution with a dose of 10 kGy. The presence of absorption peaks at 1,569 cm^{-1} and 1,493 cm^{-1} assigned to quinoid and benzenoid unit stretching modes, the vibration mode at 1,297 cm^{-1} assigned to the C–N stretch from benzenoid unit stretching mode of PANI, and the vibration mode at 1,142 cm^{-1} assigned to quinoid unit doped PANI, confirm the identity of the polymer and is in agreement with published reports in literature [24, 25]. The strong band that appears at 1,345 cm^{-1} and which does not belong to PANI is assigned to nitrate ions [26].

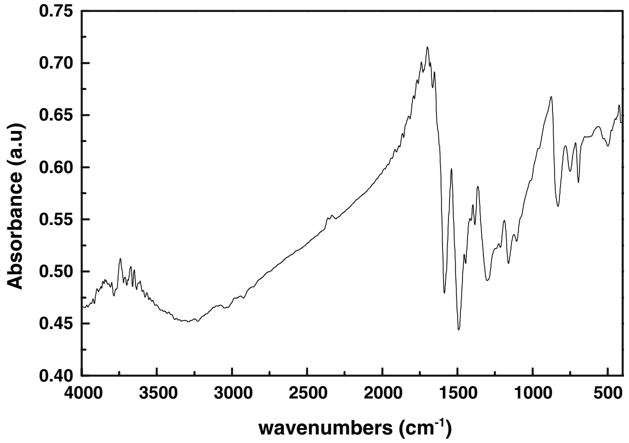


Fig. 5 FTIR spectrum of polyaniline prepared by the radiolysis of a solution of aniline nitrate plus Silver nitrate

Figure 6 shows X-ray diffractograms of composite silver PANI composite powders synthesized by the γ radiation applying a dose of 10 kGy. We have observed that peaks at 2θ values of about 38.6 and 44.2, representing [111] and [200], Bragg's reflections of fcc silver structure of diffraction peaks, is in agreement with literature values of silver particles [23]. According to Scherrer formula, peaks broadening of XRD patterns is inversely proportional to the average crystallite size (L):

$$\beta = K\lambda / L\cos\theta \quad (4)$$

where λ is the wavelength, θ is the Bragg angle and K is the Scherrer constant which is considered dependent on the (hkl)

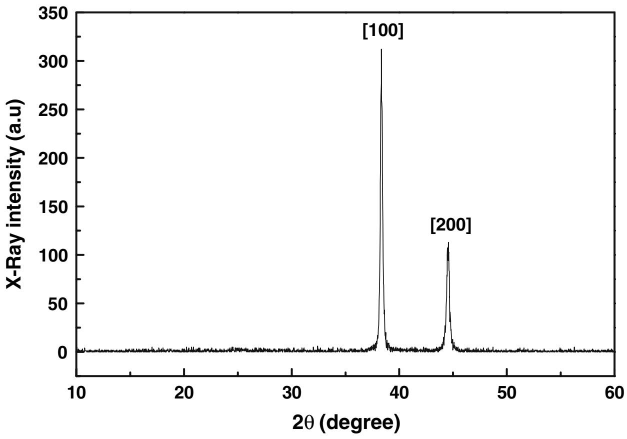


Fig. 6 X-ray diffraction patterns of the polyaniline silver composite prepared using a γ radiation dose of 10 kGy

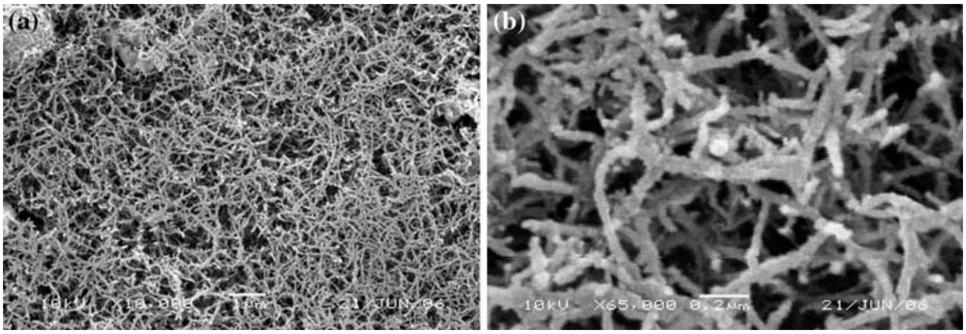


Fig. 7 Scanning electron microscopy images of polyaniline/Silver nano composite grown from a solution of aniline nitrate and silver nitrate at dose of 10 kGy (**a**) low resolution (**b**) high resolution

index and on the crystallite shape [29]. With experimental error of about 10% and for relative determination of size in a series of samples rather than the absolute values, it may be assumed $K = 1$ [30]. We have used K = 1 in particle size calculation. The line broadening β contribution to the particle size is obtained from the Warren and Biscoe equation [31]:

$$\beta^2 = B^2 - b^2 \qquad (5)$$

where B and b are the observed angular half width for the sample under investigation and for a standard sample, respectively. Silver particle size calculation from XRD patterns of Fig. 6 is about 60 nm.

A scanning micrograph of dried PANI/silver composite growth from a solution of aniline and silver nitrate irradiated with gamma radiation dose of 10 kGy is shown in Fig. 7. Instead of a micro compact spheroid surface morphology usually found for pure PANI [32], results clearly show a fibrillar morphology with sub micron dimension, a fibril diameter of 60 nm. In addition, we have noticed that fibril is highly networked as it has been found in the preparation of PANI electrochemically synthesized on indium oxide conducting glass [32]. The reason of this morphology is still under investigation.

Conclusions

It has been shown that PANI/silver composite can be obtained either by ultrasonic waves or by γ radiation ionization interaction with an aqueous aniline nitrate and silver nitrate solution. In both cases, the mechanism proposed to explain the polymerization process is based on the hydroxyl radical $^{\bullet}$OH produced by the interaction of radiation with water molecule or other radical in solution such as nitrate ion. In the case of γ radiation ionization process, the obtained materials are nano structured. Silver particles of about 60 nm particle diameter average are obtained, whereas highly networked and nano structured PANI materials are prepared.

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