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Solvent co-assisted ultrasound technique for the preparation of silver nanowire/polyaniline composite

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ABSTRACT

Silver wire/polyaniline (Ag^0/PAni) composite was prepared by the sonochemical solvent assisted method. This composite was obtained after sonicating a silver nitrate ($AgNO_3$) and anilinium nitrate aqueous solution in the presence of isopropyl alcohol. The presence of the alcohol decreases the polymerization kinetics of the conducting polymer and allows a more stable dispersion of the polymer composite to be obtained. As a matter of fact, precipitation of the polymer occurs when the reaction takes place in the absence of isopropyl alcohol. Scanning electron microscopy revealed that isopropyl alcohol has a remarkable effect on the growth and the morphological structure of reduced silver. Also, the reaction time is an important parameter which allows us to obtain silver wires with a mean diameter of 120 nm and a medium length of 4 μm instead of the spherical particles ordinarily obtained by synthesis without the alcohol. Additionally, we observed that bigger silver wires with a mean diameter of 1.5 μm and a length of 85 μm were obtained if the reaction medium was left to rest in a dark place after the sonication process ended. X-ray diffraction (XRD) and UV–vis absorption spectroscopy indicate that the reduced silver is highly crystalline and the polymer obtained is PAni in the emeraldine salt form.

1. Introduction

The synthesis of noble metal nanoparticles has been the focus of many scientific and technological studies recently, in part due to the high potential for applications that this material presents, in several areas [1]. Particularly one-dimensional (1D) nanostructured materials, such as nanorods, nanotubes and nanowires, have attracted much interest due to the properties of quantum size effects and the high potential for applications presented by these nano structures in several areas [2]. For example, bifunctional gold/nickel nanorods are potentially attractive carriers for the delivery of DNA into cells [3], gold nanorods have been used as contrast agents for biological imaging to detect diseases at an early stage [4], and highly efficient photovoltaic heterojunctions made of p and n semiconducting regions on a single wall carbon nanotube have been reported [5].

An alternative approach to the preparation of nanostructures preparation is the use of a polymer as a matrix for *in situ* nanoparticle growth. In many cases, the composite prepared combines the properties of the host polymer matrix and the unusual properties sometimes displayed by the nanoparticles formed therein [6]. Such composite materials in most cases present enhanced electrical, optical, magnetic, catalytic and mechanical properties [7,8]. For that reason, several techniques were undertaken in order to prepare the metal- or metal oxide-polymer nanocomposites with the desired properties [9–12]. For example, copper–polymer composite materials were prepared by *in situ* reduction of within a Cu^{+2} in a poly(itaconic acid-co-acrylic acid) complex [13], by the thermal decomposition of a copper formate-poly(2-vinylpyridine) complex [14], by the solvothermal process, where uniform spherical CuO particles coated with PAni were obtained by mixing CuO powder, aniline and poly(vinyl alcohol) in an ethanolic solution in a sealed reaction vessel and heating at 100 °C for 48 h [6], and by the electrochemical method where the electrode comprises copper microparticles dispersed in a PAni film [15]. In this case, the electrode was used as an amperometric sensor for carbohydrates and amino acids. Also, copper, cobalt and nickel particles embedded in PAni matrices were prepared by the polyol process in which reduction of the precursor and polymerization of the monomer was achieved in one step at 180 °C [16], with the use of a nucleating agent.

The use of ultrasound in the synthesis of polymeric materials [17,18] has gained widespread popularity since it tends to be extremely efficient, and in many cases it may be carried out without the addition of external chemical initiators. The propagation of ultrasound waves through a fluid, induce the formation of cavitation bubbles that subsequently collapse, leading to extreme local conditions such as high temperatures (5000 K) and pressures (1000 atm) [19], and cooling rates greater

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than 10^{10} ks^{-1} [19] which are classified as extreme or non-classical experimental conditions. This technique has been used for the polymerization of methylmethacrylate [20], preparation of metal–polymer composite materials [21], conducting polymer colloids [22], microemulsion polymerization [23] and for the preparation of conducting PAni-nanocrystalline TiO_2 [24], all have been accomplished with ultrasound. Most works, however, use ultrasound simply for homogenizing the media; in addition, all cases involving conducting polymers make use of a conventional oxidant such as ammonium persulfate to carry out the polymerization.

Recently we succeeded in preparing Ag^0/PAni nano composite using the ultrasound technique where, simultaneously, silver ions are reduced and, consequently, the aniline monomer is polymerized. These results show that PAni has a fibrillar morphology and the silver metals have a spherical shape with a mean diameter of 40 nm [25]. In this paper, we present an additional methodology to prepare Ag^0 nanowires instead of spherical particles. We found that the solvent used decreased the kinetics of the polymerization reaction, and this fact improving metal reduction, and modifying the crystallization morphology of the metal.

2. Experimental

Aniline (nuclear) was distilled twice and stored in the dark and at low temperature prior to synthesis. All other reagents were used as received. All aqueous solutions were prepared using distilled and de-ionized water. Aqueous stock solutions of aniline in nitric acid (HNO_3) and silver nitrate ($AgNO_3$) were prepared and stored in the dark and at low temperature prior to use.

Aniline polymerization synthesis using ultrasound waves was carried out in a test tubes, where a solution of aniline (0.5 M in 1.0 M of HNO_3) was added to a 0.5 M $AgNO_3$ solution of (mass ratio: [aniline]/[Ag] = 0.50). The mixture was added to the same volume of water or alcohol as required and treated with ultrasound waves in air atmosphere at 25 °C, using a home-made ultrasonic equipment (475 kHz, 50 W cm^{-2}). At regular time intervals, an aliquot of the solution was taken for analysis. After the total reaction time, the solutions were centrifuged and the precipitated material washed with water and acetonitrile several times until the remaining solution became clear.

Spectroscopic characterization in the UV–visible and infrared regions was performed with a Perkin–Elmer spectrophotometer model Lambda 6 and with a FTIR Bruker model IFS66 spectrophotometer, respectively. Scanning electron microscopy (SEM) analysis and X-ray diffraction (XRD) patterns were performed using a JEOL microscope model JSM 5690 and a Rigaku DMAX model 2400 X-ray diffractometer with a Cu target (Cu Kα radiation, λ = 0.154178 nm), respectively.

3. Results and discussion

The sonication effects on a mixture of aniline and $AgNO_3$ solutions in the absence or presence of isopropyl alcohol presents similar color change of color effects: the solution is initially is colorless; and as the reaction proceeds, the solution becomes yellow and finally it turns green. However, These visual color changes, however, seem to be faster in the absence of isopropyl alcohol. This visual observation can be better seen in Fig. 1, where the absorption spectra of the solution in the UV–visible region are presented as a function of the reaction time during the ultrasound irradiation. From these results, we observe that for a short reaction time, the absorption spectra in both cases present only one absorption band near 400 nm, which is attributed to the surface plasmon resonance absorption of electrons in the silver conduction band [26]. As the irradiation times increase, two new absorption bands appear a

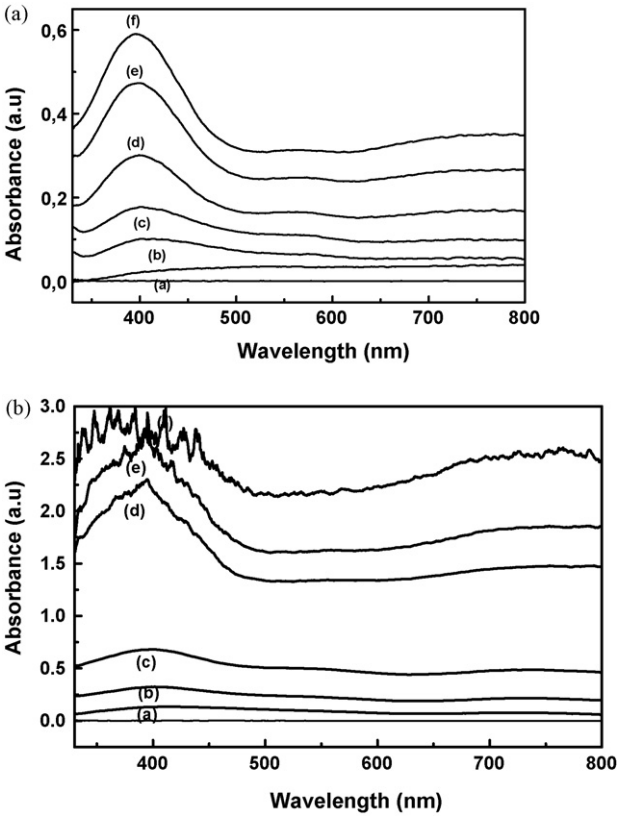

Fig. 1. Optical absorption spectra of solution as function of irradiation time: (a) solution containing 0.130 mol of isopropyl alcohol and (b) solution without isopropyl alcohol.

shoulder at 420 nm and a band near 800 nm, which are attributed to polaron-π* and polaron-π transitions respectively. These absorption bands are characteristic of polyaniline in the conducting state [27,28]. When we now compare the intensity of the absorption band at 800 nm for the same time for both cases, we observe in Fig. 2 that the intensities of this the band grows fast for the mixture without isopropyl alcohol, indicating that, in this case, more conducting polymer has been obtained. Fig. 3 shows a typical photograph of the mixture taken after 3 h of sonication. We observe that the products of the reaction remain stable in the solution containing isopropyl alcohol (on the right), whereas the precipitation of the polymer occurs in the solution without isopropyl alcohol (on the left).

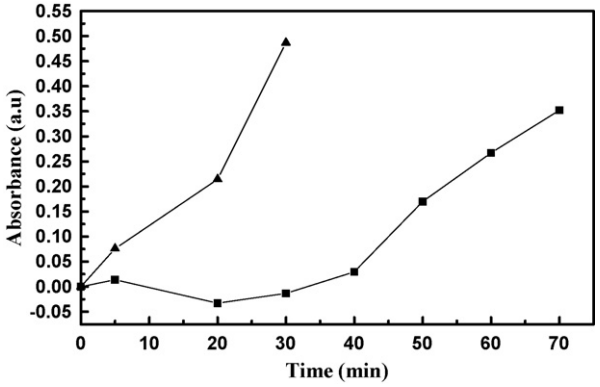

Fig. 2. Absorbance intensity of the band at 800 nm as function of irradiation time. (◄) With isopropyl alcohol and (■) without isopropyl alcohol.