



The use of gum Arabic as “Green” stabilizer of poly(aniline) nanocomposites: A comprehensive study of spectroscopic, morphological and electrochemical properties



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ABSTRACT

Herein we show the synthesis and characterization of water dispersible composites formed by poly(aniline) and the natural polymer gum Arabic (GA), used as stabilizer. The materials were synthesized via a rapid and straightforward method and were fully characterized by different techniques such as UV–Vis, Raman, FTIR, TEM, SEM and cyclic voltammetry. TEM and SEM images revealed that the proportion of stabilizer highly influences the growth mechanism of the nanostructures. It was found spherical particles, elongated structures and large agglomerates at the lower, intermediate and at the higher GA amount, respectively. Accordingly to fluorescence spectra, different hydrophobic structures are formed depending on the GA amount in aqueous solutions, possibly acting as hosting sites for the PANI growth. In order to further study the PANI polymerization in the presence of GA, kinetics experiments were performed and showed that nucleation is the limiting step for the composite growth and a model is proposed. Spectroscopic experiments showed that the presence of GA affects the PANI conformation, avoiding the formation of phenazine structures which highly impairs the electroactivity of PANI. The material integrity is achieved by strong hydrogen bond interactions between PANI and GA as evidenced by the study of specific N–H bands in FTIR and Raman analyses. The intensity of the hydrogen bonds decreased upon higher amounts of GA, probably due to steric impediment around the NH sites. Cyclic voltammograms showed a good electroactivity behavior of the modified electrodes presenting distinguishable diffusional processes through the adsorbed composites. By this way, we have thoroughly investigated the formation and properties of new conducting polymer composite materials. Taken into account the low toxicity of GA and the excellent dispersity in water, the materials can successfully be applied in bioelectrochemical applications or as green corrosion inhibitors.

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1. Introduction

The stabilization of metallic nanoparticles by natural polymers has been growing very quickly along the past years. Xanthan gum, chitosan, guar gum, among others were successfully employed on the synthesis of copper, silver and gold nanostructures [1]. In the same way, the development of polymer composites (or blends) based on natural and conductive polymers can be seen with great enthusiasm by the scientific community. The combination of these two different classes of polymers is a reasonable idea to overcome the primary disadvantages of conducting polymers, such as, low solubility in common solvents (particularly water), low mechanical strength and infusibility [2].

In an optimistic view, the synergistic effect may produce a unique material which combines the electrochemical activity presented by the conducting polymers and the good processability in water, sustainability, biodegradability and low toxicity showed by natural polymers [3]. The possibilities of study of this kind of composite material covers the development of biological applications based on electrochemical reactions such as artificial muscles and nerves, [4] “*in vivo*” electrochemical sensors and biosensors [5] and controlled drug release [6]. Besides, this composite material can also be applied in “smart” corrosion protection paintings [7] with the advantage of the high water dispersibility, which is indeed of great importance regarding environmental issues. Nowadays, all these applications are directly limited by the stabilization of the conducting polymer in aqueous media.

The stabilization of conducting polymers with petroleum-based synthetic polymers is most commonly found in the literature when

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compared to natural polymers. Stabilizers such as polyvinyl alcohol, poly(N-vinylpyrrolidone), acrylic resin, poly(styrenesulfonate), methyl cellulose, and many others are reported [8]. Regarding the utilization of natural polymers, as commented, they are much less mentioned in literature although some important polysaccharides are more extensively studied such as chitosan [9], cellulose [10] and agarose [11].

Among the natural polymers field, polysaccharides are very promising in a variety of applications, mainly due to their high natural abundance. Gum Arabic (GA) is a class of polysaccharide naturally exudated from the trunks and barks of acacia trees [12]. GA is one of the most important gums in the industry and acts as emulsifier and stabilizer [13]. The African countries are the largest producers of GA, obtained from *Acacia seyal* and *Acacia senegal* trees. However, there are about 1200 species that could produce GA spread around the world, and in most cases, GA is not commercially exploited. For instance, Brazil cultivates *Acacia* trees from *Acacia mearnsii* and its utilization is solely for the use of wood to produce charcoal and the bark for tannin extraction, with no further utilization of GA which is simply wasted away. Hence, a proper study of GA composites could draw up the attention of this important stabilizer and boost the interest of reusing it in another application and develop many others, by this way diminishing the disposal and adding new commercial insight into this biopolymer. GA is chemically described as a combination of branched polymers and oligomers containing arabinose, galactose, rhamnose and uronic acids as monosaccharide components that can be associated with some proteins [14]. Due to the presence of ionizable groups from the uronic acid moieties and from the proteinaceous fractions, GA can be seen as a polyelectrolyte, positively or negatively charged, depending on the pH.

Regarding the electrochemical applications, recent studies have shown the feasibility of GA as corrosion inhibitor itself [15] or acting as stabilizer of inorganic particles, such as γ - Al_2O_3 [16] or Fe_2O_3 [17]. Taken into account electroactive composites, there are very few reports that use GA with conducting polymers [18] and none of them explored in detail neither the kinetics of the composite formation nor the spectroscopic and microscopic characteristics of the formed material at different amounts of stabilizer. Also, the relationship between the GA concentration and the resulting composite morphology is still completely unexplored. By this way, to the best of our knowledge this is the very first report presenting a systematic and comprehensive study of the kinetics, morphological and spectroscopic aspects of GA-PANI composites formation with the corresponding electrochemical behavior. The results presented herein indicate a potential application of these composites on bioelectrochemical modified electrodes as well as for the development of corrosion water soluble inhibitors based on a sustainable and abundant natural polymer.

2. Materials and methods

H_2SO_4 89% and ammonium persulphate (APS) were purchased from Merck and GA was obtained from Sigma-Aldrich (G9752), which is referred in the label as “gum arabic from acacia tree”. Aniline (Aldrich) was distilled under low pressure before use. All solutions were prepared using ultra pure water, resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$.

Poly(aniline) composites (PANI-GA) were chemically synthesized by using a simple and straightforward methodology. The synthetic solutions (35 mL) were prepared by adding aniline (0.15 mol L^{-1}), sulfuric acid (to pH 1) and GA. Three weight ratios of GA:aniline were tested 0.5:1, 1:1, 2:1, giving final concentrations of GA of 7, 14 and 28 mg mL^{-1} , respectively. The solutions were kept at 35°C , under magnetic stirring and the polymerization

occurred by dropping 200 μL of ammonium persulphate aliquots (APS, 0.4 mol L^{-1}) at intervals of 15 min. The syntheses were followed by UV-Vis absorption spectra (Agilent 8453 spectrophotometer) by taking aliquots of 200 μL from the synthetic solutions and diluting in 3.0 mL of water. By the end of the synthesis (indicated by the plateau in the absorbance signal) dark green dispersions were obtained, which were submitted to purification by dialyzing against distilled water through a cellulose acetate membrane (12 kDa, Sigma) during 48 h. The dialysis procedure removes free dissolved ions and low molar weight PANI (oligomers). After that, the colloidal dispersions were centrifuged (14,300 rpm, 30 min) and the obtained solids were dried under low pressure, at room temperature. The supernatants were also verified by UV-Vis.

The samples were characterized by spectroscopic methods. Raman spectra were obtained in a Reninshaw spectrometer by using 632.8 nm incident radiation. Infrared spectra were obtained in a Bio-Rad Excalibur FTS 3500GX spectrometer, using KBr pellets. The study of the aggregation of GA, in water, was performed by fluorescence spectroscopy (Hitachi F4500). GA was first dissolved in water and determined volumes of an ethanolic solution of pyrene were added to a final concentration of $1 \mu\text{mol L}^{-1}$. The samples were excited at 343 nm and the spectra were obtained in the range of 360–500 nm, at room temperature.

The solids were also employed for the preparation of colloidal solutions by their redispersion in aqueous media, at different pHs. Transmission Electron Microscopy (TEM) images were obtained in a Jeol JEM 80 kV instrument by dropping 10 μL of the redispersed colloidal solutions onto carbon-coated copper grids. SEM images were obtained using Tescan Vega3LMU equipment under voltage of 15 kV. Aliquots of the solutions were dispersed onto Al stubs and covered with a thin layer of gold. At least 5 different regions of two independent samples were analyzed. Electrochemical experiments were performed in an Autolab PGSTAT 30 potentiostat using Pt foil and $\text{Ag}/\text{AgCl}/\text{Cl}^-_{(\text{sat})}$ as counter and reference electrode respectively. The ITO electrodes (Delta technologies, sheet resistance $< 12 \Omega \text{ cm}^{-2}$) were modified by simply drop-casting and spreading of 50 μL from the colloidal solutions (labeled as 0.5:1, 1:1 and 2:1 depending on the GA:aniline weight proportion).

Kinetics studies were performed in order to evaluate the polymerization mechanism of PANI in the presence of different GA proportions. To do so, the APS addition occurred at one shot and the variation of absorbance with time was acquired. In order to avoid the overload signal of the absorbance, the total concentrations were lower to the stepwise synthesis, described previously, however, the GA:aniline weight ratios were kept the same. The summary of the experimental procedure is shown in Scheme 1.

3. Results and discussion

The chemical synthesis of PANI has been reported extensively in literature. Many different oxidizing agents were used so far and due to its intense coloration, the PANI reaction can be easily monitored by UV-Vis spectroscopy. Fig. 1(A) shows the UV-Vis spectra taken from the synthetic solution (0.5:1 – GA:aniline) after the successive additions of APS aliquots. The other proportions presented similar behavior. Each spectrum was taken within an interval of 15 min. It is possible to observe the increase of the absorbance at three distinct wavelengths (centered at 280, 390 and 780 nm), indicating the polymerization of aniline.

The band at 390 nm is a combination of two characteristic bands of PANI, the 360 and 440 cm^{-1} assigned to π - π^* transition of benzenoid segment and polaronic transitions, respectively. [19] These two bands are combined at high doping levels of PANI [20]. The 780 nm band is frequently assigned to the localized polaronic transitions [21] and also indicates the formation of high

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