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# Nanospherical particles of polypyrrole synthesized and doped by plasma

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ABSTRACT

This work presents the synthesis of nano and meso spherical iodine doped particles of polypyrrole using glow discharges of pyrrole. The synthesis produced polypyrrole powder with the purpose of using the polymers in bioelectric applications. The powder was composed of homogeneous spheres of diameter between 35 and 350 nm, which arranged in agglomerates of several micrometers. A molecular simulation approach of polypyrrole nanoparticles was done considering full networking of 12 pyrrole rings joined in hexagonal arrangements. In those conditions, spherical particles can be obtained with a minimum diameter of approximately 1.4 nm. The inclusion of iodine atoms is difficult in such particles, however as the particles grow, iodine compounds produced in the chemical reactions can be trapped or adhered to the particles. The electric conductivity of polypyrrole powder as a function of relative humidity was in the interval $10^{-9}$–$10^{-6}$ S/m.

## 1. Introduction

One important application of polypyrrole is as a biomaterial with potential to transport electric charges. The electric interaction between cells and materials is a wide area to explore because it includes not only the electronic but also the ionic transference of charges. The activity of biopolymers with cells is also strongly influenced by the area in contact with biological fluids and tissues, in such a way that if the material is composed of nanoparticles, their superficial area and mobility should be greater than in other forms, enhancing the function of the polymer in such environment. Another important consideration is that biomaterials used as implants in the body must follow strict rules during the synthesis because they should not be combined with compounds that could leave harmful traces to the biological systems; especially, if the implants are dedicated to the central nervous system which has a very delicate physicochemical equilibrium.

One of the non-contaminant methods that use electric variables instead of chemical reagents to induce polymerizations is by plasmas of electric glow discharges. The electric field ionizes the gases participating in the synthesis forming plasmas with the monomers and dopants. The ions increase their kinetic energy and collision with other particles breaking some chemical bonds in the monomers. This process occurs in such a way that the monomers may join among them through the substitution of H atoms. However, if pyrrole polymerizes losing all H atoms, structures formed only with C and N atoms in different combinations of double and single bonds may appear in the final compounds; and depending on the conditions of synthesis, these compounds can have morphologic structures of single or layered nano-dimensional spheres, wires or tubes. The physicochemical characteristics of these materials compared with other similar polymers with film macromolecular morphology are modified by the regular arrangement and mobility of the particles because of their small size and comparatively great superficial area.

Several nanostructures obtained with combinations of pyrrole and other materials have been reported in the last years. One common method to obtain nanoparticles is to synthesize polymers inside the structure of another material that acts as a template. The desired nanostructure grows inside the template voids, which govern the final dimensions and geometry of the particles. Once the synthesis has finished, the template is removed obtaining the nanostructures. Using template methods, Jerome electropolymerized pyrrole and poly(ethyl acrylate) in liquid phase to produce wires, 600 nm diameter and up to 300 μm length [1].

Plasma methods are also electropolymerizations in gas phase. In these methods, the first chemical reactions occur in the gas and as the polymer grows, it adheres to the surfaces of the reactor, continuing as a solid. There should be a liquid phase in the oligomeric states in the way to the polymers. In this condition, the electric and thermodynamical variables can be manipulated to obtain some kind of alignment in the intermediate compounds that

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result in different geometrical profiles in the final polymers. This possibility was experimentally presented by Yang in nanoparticles of polypyrrole using atmospheric plasmas of Ar. He obtained spheres at 5 W, bars at 10 W and small sheets at 20 W [2].

One study that relates aromatic rings as precursors of hollow spherical nanoparticles was reported by Cao using low temperature plasmas of Ar [3]. Other complex core-shell configurations of nanoparticles with enhanced electrical and magnetic properties were prepared by oxidative polymerization in liquid phase using pyrrole and $Fe_3O_4$, obtaining conductivity in the $10^{-5}$ a $10^{-1}$ S/cm interval [4,5]. Polypyrrole with poly(N-vinylcarbazol) was also used to synthesize core-shell particles by microelmusion polymerization with conductivity in the order of $10^{-1}$ S/cm [6]. Reung synthesized spherical nanoparticles of polypyrrole and ammonium peroxydisulfate via microelmusion polymerization with conductivity up to $10^2$ S/cm in spherical nanoparticles (60–90 nm) [7].

In the field of biomaterials, Shi prepared spherical nanoparticles (50–200 nm) of polypyrrole and poly(D,1-lactide) by emulsion polymerization to be applied in the growth of fibroblasts under electrical stimulation. They considered that this material could be useful in tissue engineering and bioelectronics [8].

This work is inserted in a similar biological perspective presenting a study about the synthesis by plasmas of polypyrrole nanospheres with potential application in the central nervous system. Similar polypyrroles synthesized as films have been applied in rats with complete section in the spinal cord with improvement in the locomotor functions [9]. In this work, particles of polypyrrole are synthesized as nano and meso spheres to be applied in contusion spinal cord lesions. The polymers were doped by plasma with iodine simultaneously with the polymerization to increase the transference of electric charges. The structure of the nanopolypyrroles obtained and the influence of the dopant in the electric properties are discussed.

## 2. Synthesis of polypyrrole nanoparticles

According with the application, the synthesis of polypyrrole particles should be without any other chemical reagent or template, except the monomer and dopant, pyrrole and iodine (Aldrich, 98%), respectively. Thus, the syntheses were done by plasma in a reactor made of a glass cylinder of 9 cm diameter and 25 cm length with stainless steel flanges and two flat electrodes of 6.5 cm diameter separated by 7 cm. The total volume was approximately 1500 $cm^3$. The monomer and dopant were deposited in separated containers connected to the reactor.

The process started reducing the pressure in the reactor at 0.1 mBar. After that, the electrodes were set at 13.5 MHz applying a power of 100 W with an Advanced Energy RFX-600 generator combined with a matching network. One electrode was connected to the RF port of the generator and the other was grounded. The thermodynamical and electrical conditions are very important in the synthesis by plasma of polymers. Small changes in one variable immediately influence other variables resulting in different structural and morphological final products [2]. Other syntheses of polypyrroles by plasma at much lower power have produced films and not nanoparticles [10].

Once the electrical discharges started with the residual air, the recipients with the monomer and dopant were opened to the reactor and their vapors mixed inside. The discharges excited the gases forming plasmas of both components which combined chemically to form the polymers. The time of synthesis was 180 min. Several experiments were performed in the study varying power from 40 to 100 W.

Polypyrrole powder adhered to the reactor walls was obtained. Small variations of the conditions of synthesis during the first steps of the polymerizations proved to be very important in the amount of nanoparticles obtained. The powder was collected from

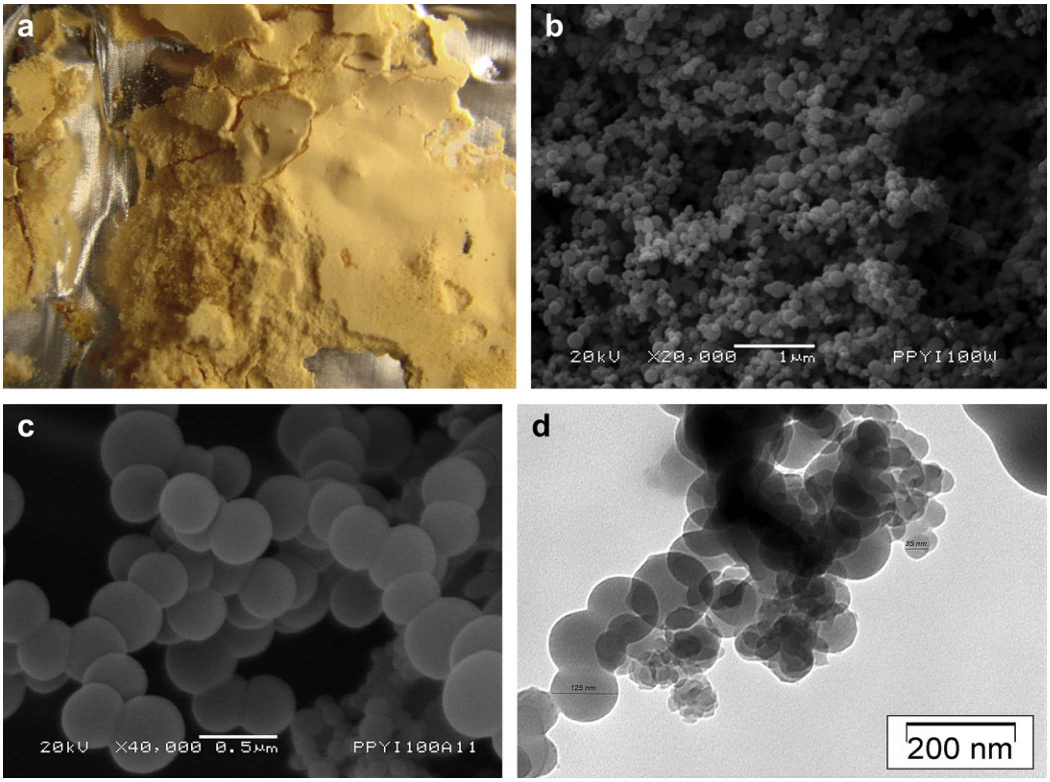

**Fig. 1.** Morphology of PPy/I particles. (a) Photograph of the particles after the synthesis. (b) SEM image of the particles and agglomerates. (c) SEM image of polypyrrole mesoparticles. (d) TEM image of polypyrrole nanoparticles.

the surfaces with a small brush and withdrawn from the reactor, see Fig. 1(a).

## 3. Characterization

The morphology of the powder was studied with a Jeol JSM 5900LV scanning electron microscope (SEM) coupled with an EDS Oxford INCA-XACT probe for elemental analysis. The inner conformation of the material was performed by transmission electron microscopy with a Zeiss EM-910 (TEM) apparatus. The chemical structure was studied by infrared spectroscopy (IR) with a Nicolette 550 spectrophotometer in the 400–4000 $cm^{-1}$ interval and with a Thermo-Fisher K-Alpha X-ray photoelectron spectroscope (XPS). As the polymers have low conductivity, an Ar ion gun was used to compensate static charges during the XPS analysis.

The volumetric electric conductivity was calculated measuring the cross-sectional resistance of the samples in a two-probe device with an OTTO multimeter and with an Alpha-Lab high resistance multimeter. The calculations in the molecular simulation of polymers were done with the Cerius 2 and with the ChemSketch 11 computer programs.

### 3.1. Morphology

Fig. 1 shows different morphologic aspects of the polypyrrole nanoparticles. A photograph of PPy/I powder with small particles and agglomerates after they were collected from the reactor is presented in Fig. 1(a). Two SEM images of the nanoparticles are shown in Fig. 1(b) and (c). In Fig. 1(b), the micrograph shows that the particles are spherical with diameter in the interval between 50 and 300 nm, randomly agglomerated. Fig. 1(c) has a greater amplification of the particles, showing that the spheres appear sufficiently close to press one against the other deforming the spherical profile. At that comparatively small mass, the frictional electrostatic forces could be a strong physical bonding that maintains some particles together. Fig. 1(d) shows a TEM micrograph of the PPy/I nanoparticles, the transmission beam indicates that the spheres are formed with solid and homogeneous materials, polypyrrole and its derivatives.

### 3.2. Structure

The PPy/I particles were analyzed by means of infrared (IR) spectroscopy mixed with KBr in small tablets. Fig. 2 shows the transmittance (adimensional) as a function of the wavenumber ($cm^{-1}$) of the polymers. The IR analysis shows that the PPy/I powder has a structure with a strong presence of O–H, N–H and C–H groups in the wide bands centered at 3615, 3296, 3213 and 2962 $cm^{-1}$. The last two absorptions belong to aromatic and aliphatic C–H bonds, respectively. Groups with multiple bonds, C=O (2360 $cm^{-1}$), C≡C and C≡N (both in the absorption centered at 2216 $cm^{-1}$) appear also in the polymers with different intensity. This effect suggests that the removal of hydrogen atoms is intense in the particles.

**Table 1**
Atomic percentage in polypyrrole particles. The XPS data is based in 1s orbitals.

| Element | %At | |
|---|---|---|
| | XPS | EDS |
| C | 80.01 | 77.36 |
| N | 16.79 | 17.19 |
| O | 3.2 | 5.0 |
| I | – | 0.45 |

The presence of C=C (1634 $cm^{-1}$) can increase with the removal of hydrogen of consecutive carbon atoms and the subsequent rearrangement of radicals. This last absorption is complex because in that region N–H groups in polypyrrole also appear. The other related absorption can be found in the peak centered at 1296 $cm^{-1}$, which can be associated to =C–H bonds in alkenes overlapped with part of the C–N fingerprint indicating a high alkene character in the particles. The absorption at 1455 $cm^{-1}$ can be associated with the substitution of hydrogens in heteroaromatic rings. The plasma doping of iodine can be identified with a small absorption around 500 $cm^{-1}$.

Table 1 contains EDS and XPS data of atomic distribution in the particles collected at $10^{-6}$ and $10^{-9}$ mBar, respectively. Both analyses show C, N and O, but only EDS shows the presence of I. The doping of iodine was exposed in the IR spectra which was taken at atmospheric pressure; however, the iodine atomic percentage barely appeared in the EDS analyses, 0.45% at $10^{-6}$ mBar; and it disappeared in the XPS survey at $10^{-9}$ mBar, see Fig. 3. The XPS survey presents only the signals of C1s (285.8 eV), N1s (399.8 eV) and O1s (532.4 eV) electronic orbitals.

These results suggest that there are only C, N and O atoms in the polypyrrole particles; the first two atoms belong to the pyrrole structure, but the O atoms can be originated in the oxidation of the particles. On the other hand, the iodine doping could result in compounds trapped or adhered to the particles, which were released with the low pressure.

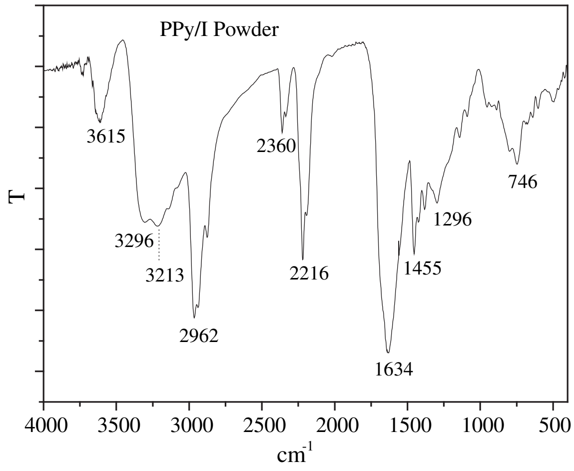

**Fig. 2.** Infrared absorption of polypyrrole particles.

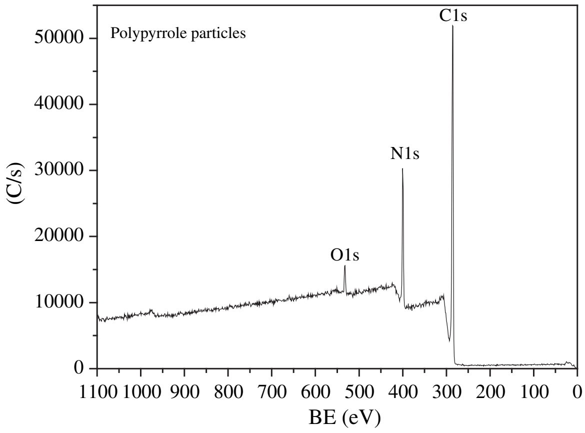

**Fig. 3.** XPS Survey spectrum of polypyrrole particles.

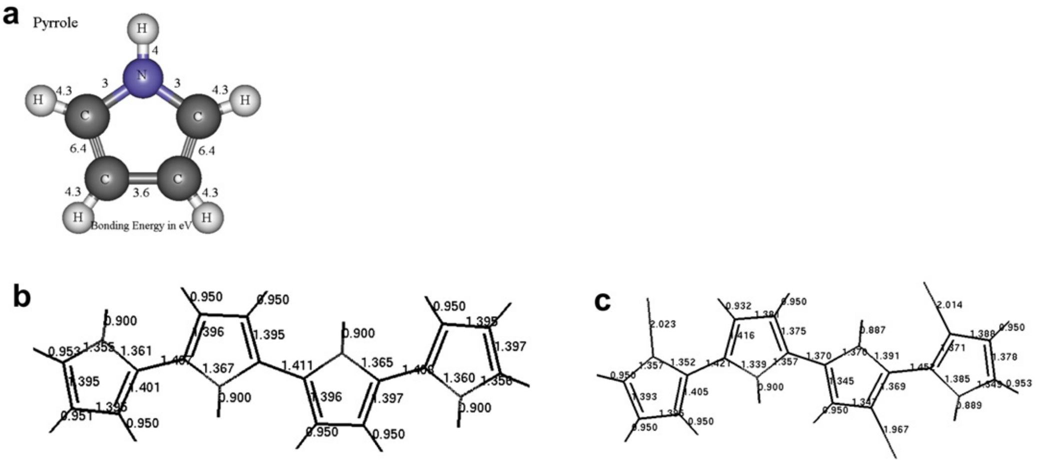

**Fig. 4.** Structure of pyrrole and polypyrroles, bonding energies in eV, distances in Ǻ. (a) Structure of pyrrole with bonding energies. (b) Chain of polypyrrole. (c) Chain of polypyrrole doped with iodine.

### 3.3. *Molecular simulation of polypyrrole nanoparticles*

Pyrrole forms a planar cycle of $NC_4H_5$, see Fig. 4(a) which shows its structure and bonding energies. Under a rain of energetic electrons and ionized particles, this molecule would be more reactive in the neighborhood of the nitrogen atom, because the lowest energies of the ring are located in this place making it more vulnerable to energetic collisions. However, from a spatial point of view, the H atoms look also highly vulnerable to the collisions of particles because of their terminal position. As a result, the breaking of the pyrrole rings and the removal of H atoms are two combined ways to synthesize polypyrroles by plasma with nanodimensional morphology.

When pyrrole polymerizes linearly, it forms structures similar to that in Fig. 4(b) (PPy). The distance between two consecutive pyrrole rings in these structures is around 1.4 Ǻ, which is approximately the side of each pyrrole ring, with small differences due to the different diameters of C and N atoms. This similarity produces regular arrangements when the pyrrole rings are chemically surrounded by other equal rings.

If additionally to the polymerization, an iodine doping is applied with sufficient energy to build C—I bonds (2.47 eV), the structure would be as that showed in Fig. 4(c) (PPy/I). The distances of C—H and C—I bonds are 0.95 and 2 Ǻ, respectively. Iodine atoms have a large size and for the same reason, they have a large cross-sectional area for the collisions of particles in the plasma.

A highly crosslinked polypyrrole would lose all H and iodine atoms becoming in extreme cases networks of pyrrole backbones (rings of —N—C═C—C═C—). This configuration may generate spherical nanostructures based on C and N atoms. Fig. 5 shows two representations of spherical particles derived from polypyrrole. Fig. 5(a) illustrates the growing of a sphere joining pyrrole backbones by hexagons. Although the pyrrole rings are planar, because of the double bonds, their freedom of rotation produce curved surfaces as more rings are added to the network. The process continues until the surface forms a sphere. Fig. 5(b) illustrates the complete sphere. The diameter of the sphere considering only the center of the atoms would be approximately 0.7 nm and with the cloud of electrons would be approximately 1.4 nm. This would be the theoretical minimum diameter in a spherical polypyrrole particle. However, the final diameter of a particle varies according with the space left among the pyrrole rings, the greater the polygons inside, the greater the diameter. Combinations of other polygons in the same particle would generate different profiles.

The smallest spherical particles found in the powder of polypyrrole, 35 nm, have diameter 20 times greater than the minimum discussed before. Considering the presence of C—H bonds discussed in the infrared analysis, it is possible that these particles grow starting in the process discussed before from seeds of nanoparticles and increase the diameter with polymeric layers with hydrogen and iodine atoms.

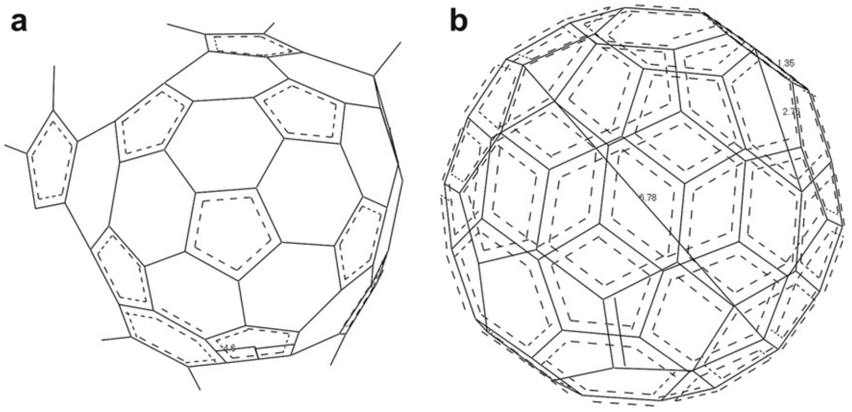

**Fig. 5.** Representation of spherical nanoparticles of crosslinked polypyrrole. (a) A sphere under construction with pyrrole backbones joined by hexagons. (b) The complete sphere.

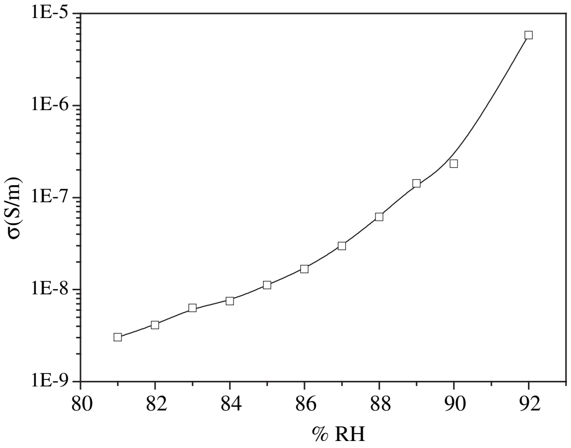

**Fig. 6.** Electric conductivity of PPy/I particles as a function of relative humidity.

### 3.4. Electric conductivity

Fig. 6 shows the electric conductivity of PPy/I particles as a function of relative humidity (RH). In most semiconductor materials the presence of water in the structure increases the conductivity. In a biological application, the PPy/I particles would be surrounded by fluids and salts which most surely stimulate the transport of charges in the wet particles.

The conductivity in PPy/I particles increase with the humidity, from $10^{-9}$ to $10^{-6}$ S/m from 80% to 90% RH. In the same interval of RH, it has been reported before that plasma PPy undoped films have conductivity between $10^{-8}$ and $10^{-7}$ S/m and the similar plasma doped PPy/I films in the order of $10^{-6}$ and $10^{-4}$ S/m [10]. Consequently, the PPy/I powder have conductivity more comparable to PPy than PPy/I films, suggesting the possibility that the plasma doping of iodine in polypyrrole is less effective in the powder than in the polymeric films.

## 4. Conclusions

Powder of polypyrrole was synthesized by plasma to study the formation of nanoparticles with potential application in the spinal cord after a severe lesion. The energetic particles in the plasma were used as promoters of the polymerization to avoid other chemical reagents that could be harmful to the delicate physicochemical equilibrium in the spinal tissues. As the communication in the nervous central system is based in ionic pulses, the polymers were doped with iodine to insert polar sites in the structure.

The synthesis produced powder with pyrrole chemical groups formed with solid and homogeneous spheres of diameter between 35 and 350 nm. The particles arranged in agglomerates of several micrometers. The smallest particles were simulated with a molecular approach resulting in spheres without iodine or hydrogen atoms in the structure. The minimum diameter of such a sphere was approximately 1.4 nm. As most of the particles had diameter 2 orders of magnitude greater, the particles could initiate with the minimum diameter and grow with layers of polypyrrole with hydrogen and iodine atoms to reach the final diameter.

The conductivity increased with humidity, from $10^{-9}$ to $10^{-6}$ S/m, in the 80–90% interval of relative humidity. PPy/I powder has conductivity more comparable to PPy than PPy/I films, suggesting the possibility that the particles of polypyrrole have less capacity to retain iodine atoms than the similar polymeric films.

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