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Poly(*p*-phenylenediamine)-coated magnetic particles: Preparation and electrochemical properties

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Abstract

Magnetic particles are of great interest in various biomedical applications, such as, sample preparation, in vitro biomedical diagnosis and therapy. For bio-sensing applications, the used functional magnetic particles should answer numerous criteria such as; submicron size in order to avoid rapid sedimentation, high magnetic content for fast separations under applied magnetic field and finally good colloidal stability. Therefore, the aim of this work was to prepare submicron magnetic core and conducting polymer shell particles. The polymer shell was induced using *p*-phenylenediamine as key monomer. The obtained core-shell particles were characterized in terms of particle size, size distribution, magnetization properties, FTIR analysis, surface morphology, chemical composition, cyclic voltammetry and impedance spectroscopy. The best experimental condition was found using 40 mg of PVP (stabilizing agent) and 16 mmol of *p*-phenylenediamine. Using such initial composition, the core-shell magnetic nanoparticles shown a narrowed size distribution around 290 nm and high magnetic content (above 50%). The obtained amino containing submicron highly magnetic particles were found to be a conducting material and superparamagnetic in nature. These promising conducting magnetic particles can be used for both transport and *lab-on-a-chip* detection.

Keywords: Seeded polymerization, Conducting polymer, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy, Sensor, Magnetic emulsion.

1. Introduction

Magnetic nanocomposites have been attracted much attention owing to their promising properties, which can be used in diverse technologies, including, microsystems, lab-on-chip, bio-sensing applications, purification, cancer therapy, nucleic acid extraction and purification and specific capture of analyte in biological samples etc. ¹⁻³. When applied in bio-sensing, these nanocomposites act as concentrator providing good detection sensitivity of the target. In this sense, using superparamagnetic nanoparticles (MNPs) offer a great advantage over normal polymer or silica particles. When superparamagnetic particles are used, the particles are found to be easy to re disperse after applying external magnetic field and no aggregation phenomena have been observed ⁴. Among magnetic nanoparticles, iron oxides and in particular magnetite (Fe_3O_4) and its oxidized form maghemite ($\gamma\text{-Fe}_2\text{O}_3$), have attracted much attention due to their high specific magnetization property, biocompatibility, low toxicity, and easy to preparation at low cost ^{5,6}.

Obtaining superparamagnetic hybrid materials with desired properties, and also with specific functional groups have been reported by several authors using various approaches ⁷⁻¹¹. These approaches can be divided into (i) physical based process (e.g. sequential adsorption of oppositely charged polyelectrolytes) and (ii) chemical encapsulation via polymerization in disperse media (e.g. surface functionalization/modification of MNPs via specific grafting, surface initiated controlled polymerization, inorganic silica/polymer hybridization, or by heterogeneous polymerization in dispersion media) ⁹.

For biosensing applications the MNPs have been combined with conducting polymers to provide a new class of material with both magnetic and electric properties ^{7,12}. Conducting polymers (CPs) are carbon-based molecules, which exhibit electrical, optical, and electronic properties analogous to metals. However, CPs have some advantages compared to metals, such as, flexibility, low toxicity, easy processing, and especially, low cost. All these characteristics make CPs potential materials for applications in sensors, fuel cells, energy storage, and so forth ^{3,10}. In sensors field, the charge transport properties of conducting polymers are changed when exposed to targeted analytes. The captured analyte amount can be directly correlated to the measured signal. Polyaniline (PANI), polypyrrole (PPy), polythiophene, poly(*p*-phenylenediamine) (PPDA) and their derivatives are a class of CPs which are most studied owing to their facile synthesis and flexibility in processing ¹³. Among the CPs, the poly(phenylenediamines) have been attracted more attention, especially in biomedical field, where, the potential toxicity of aniline and its oligomers is feared¹⁴.

In the literature, there are several studies combining magnetic nanoparticles and poly(*p*-phenylenediamine) using emulsion polymerization technique^{15,16}. However, the reported researches consist of producing only magnetic nanocomposites. In order to take advantage of conductive properties of poly(*p*-phenylenediamine) and to improve the accuracy of the biosensing event, we investigated the synthesis route, as well as, the key parameters leading to hybrid submicron core-shell particles containing MNPs-core and PDA-shell. ~~This morphology has found a great deal of interest because of high surface area, π -stacking interaction, and good thermal, chemical, and mechanical stability¹⁷.~~ In addition, The core-shell morphology offers new possibilities for new applications. For example, due to its polymeric core, the surface can be easily modified to interact with a desired analyte enhancing the signal detection and transmission (for biosensor) or even providing fast separations of the analyte by an external magnetic field. Moreover, the core-shell nanoparticles may be used as template for producing new morphologies such as hollow particles.

To prepare core-shell nanoparticles, the magnetic emulsion (ME), containing superparamagnetic iron oxide nanoparticles, was used as seed in a seeded-emulsion polymerization approach. Then, the polymerization of PDA was carried out to obtain NH₂-functionalized CPs on the particle surface. The influence of both the amount of the monomer and the stabilizing agent on the final morphology of the nanoparticles were evaluated. The obtained magneto-conducting core/shell nanoparticles were characterized in terms of chemical composition, particle size and size distribution, morphology, and magnetic behavior. Then, electrodeposition assays, cyclic voltammetry and impedance spectroscopy were performed to ascertain the potential of magneto-conducting core/shell nanoparticles in biosensor applications.

2. Experimental

2.1. Materials

Potassium persulfate 99+% (KPS), Povidone (PVP) were purchased from Sigma-Aldrich. Oil in water magnetic emulsion (ME) (total solid content 7.9%, average size distribution 193 ± 5 nm) consisting of superparamagnetic nanoparticles stabilized with oleic acid, octane, and dodecyl sodium sulfate was from Ademtech S. A (Bordeaux, France). *p*-phenylenediamine (PDA), 99+% was purchased from Acros Organics. All reagents were used without further purification and aqueous solutions were prepared with deionized water.

2.2. Synthesis of poly(*p*-phenylenediamine)-coated magnetic particles

The seeded-emulsion polymerization was performed upon addition of 1.52 g of ME (0.12 g dried extract) into a 25 mL glass reactor being mechanically stirred with a Teflon paddle. Then, the supernatant was removed from the mixture after 3 min of magnetic separation. After that, 7.5 mL of a solution containing known amounts of PVP (as stabilizing agent) and PDA (as monomer) were brought into the reactor. The solution was kept at 300 rpm for 4 h. Later, 7.5 mL of an acidic solution (HCl 0.1 mol L⁻¹) containing 43.2 mg (0.16 mmol) of KPS was added dropwise (0.5 mL min⁻¹), while stirring (see samples composition in Table 1). The mixture was left to react for 20 h under stirring at room temperature.

Table 1. Compositions of stabilizer (PVP) and monomer (PDA) used in the seeded polymerization.^(a)

Sample Name	PVP (mg)	PDA (mmol)
0000 ^(b)	0.0	0.00
0008	0.0	0.08
0016	0.0	0.16
0032	0.0	0.32
1000	10.0	0.00
1008	10.0	0.08
1016	10.0	0.16
1032	10.0	0.32
2000	20.0	0.00
2008	20.0	0.08
2016	20.0	0.16
2032	20.0	0.32
4000	40.0	0.00
4008	40.0	0.08
4016	40.0	0.16
4032	40.0	0.32

(a) 0.16 mmol of KPS was used in the seeded polymerization at RT for 20h; (b) Reference Sample.

Herein, the samples were labeled according to their initial composition: The amounts of PVP (in mg) are indicated at the first two digits while the amount of PDA (in mmol) is

indicated at last ones. For example, sample 2032 means 20 mg of PVP and 0.32 mmol of PDA used in the seeded polymerization. All other reactants concentrations were kept constant.

3. Characterization

3.1. Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) images was obtained with a Philips CM120 microscope at the “Centre Technologique des Microstructures” at the University of Lyon (Villeurbanne, France). A small drop of suspension was deposited on a microscope grid (copper support covered with carbon) and slowly dried in open air. The dried samples were observed by bright field TEM applying 120 kV acceleration voltage.

3.2. Particle size and zeta potential measurements

A Malvern Zetasizer (Nano ZS, Malvern Instruments Limited, UK) was used to measure both the particle size, size distribution and the zeta potential of the magnetic polymer colloidal particles. The magnetic samples were dispersed in a 10^{-3} mol L⁻¹ NaCl solution. Then, the particle size distribution was obtained taking into consideration the average of at least five measurements (10 runs for each colloidal dispersion).

The zeta potential was obtained as function of pH at 25°C. The measurements were performed using a highly diluted dispersion of the colloidal particles in a 10^{-3} mol L⁻¹ NaCl solution. The pH was adjusted using solutions of 0.1 mol L⁻¹ NaOH or 0.1 mol L⁻¹ HCl. The recorded value was considered as the average of three measurements.

3.3. Fourier Transformed Infrared (FTIR)

The surface properties of the samples were investigated using an Attenuated Total Reflexion-Fourier Transformed Infrared spectrophotometer (ATR-FTIR)-Shimadzu, Japan. All samples were wiped off and dried before analysis. The spectra were scanned over a range of 4000-400 cm⁻¹.

3.4. Thermogravimetric analysis (TG)

Thermogravimetric analysis measurements were carried out on a thermogravimetric analyzer (NETZSCH -TG209F1 Iris[®]ASC). The measurements were performed under a N₂ atmosphere (50 mL min⁻¹) starting from room temperature up to 1000 °C at a heating rate of 10 °C min⁻¹. Before analysis, the samples were separated from the supernatant by applying permanent magnetic field, and then washed with deionized water to remove the non-magnetic

materials, such as surfactant and free polymer particles. After that, the samples were left to dry at 40 °C for 24 h before TG analysis.

3.5. Cyclic Voltammetry and Electrochemical Impedance Spectroscopy measurements

Electrochemical characterizations were carried out by using a VMP-3 potentiostat (Biologic CE-Lab VMP3). All measurements for cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were made at room temperature (approx. 24 °C). The electrolyte for both CV and EIS measurements was made from a redox probe using ferro- and ferricyanide $K_3(Fe(CN)_6)/K_4(Fe(CN)_6)$ at 5×10^{-3} mol L⁻¹ in PBS buffer (pH 7.4). Electrochemical measurements were made within a Teflon cell in which the gold working electrode (WE) was sandwiched between the two parts of the electrochemical cell (see Figure S2 - supplementary data). Platinum wire was used as the counter electrode (CE) and a calomel saturated electrode was used as the reference electrode (RE). The gold area exposed to the electrolyte was approx. 3 mm in diameter. The volume of ferrocyanide buffer was affixed for all measurements at 1.3 mL.

3.6. Magnetic properties

Magnetization measurements were carried out using the Automatic Bench of Magnetic Measurements (ABMM) at CNRS-IRC Lyon laboratory, France. Samples were dried and magnetization was investigated at room temperature by varying the magnetic field (H) from -20000 to +20000 Oe.

4. Results

4.1. Investigating the experimental parameters for preparing core-shell particles

Excellent colloidal dispersion of magnetic particles can be achieved when there is a balance between the attractive and the repulsive forces. In case of magnetic emulsions, the repulsive forces are dominating mainly owing to their negatively charged surface¹⁸. However, the intensity of the repulsive forces may be decreased upon addition of an acidic solution. In such a condition, the attractive forces (due to the magnetic interaction) are formed in the emulsion, leading the small particles to coalesce into larger ones.

For preparing core-shell nanoparticles, using poly(*p*-phenylenediamine) (PPDA), an acidic environment is required for solubilizing the PDA monomers (see *section 2.2*). Thus, to avoid the coalescence of the nanoparticles during the experiments, PVP was used as stabilizing agent. We hypothesized that the PVP could act as a steric barrier between the

magnetic particles, preventing their coalescence^{7,19}. Therefore, the influence of PVP amount on stabilizing the magnetic emulsion was investigated. The samples evaluated were: 0000, 1000, 2000, and 4000 (0 mg, 10 mg, 20 mg, and 40 mg of PVP respectively) and the results are shown in Figure 1 (A-D).

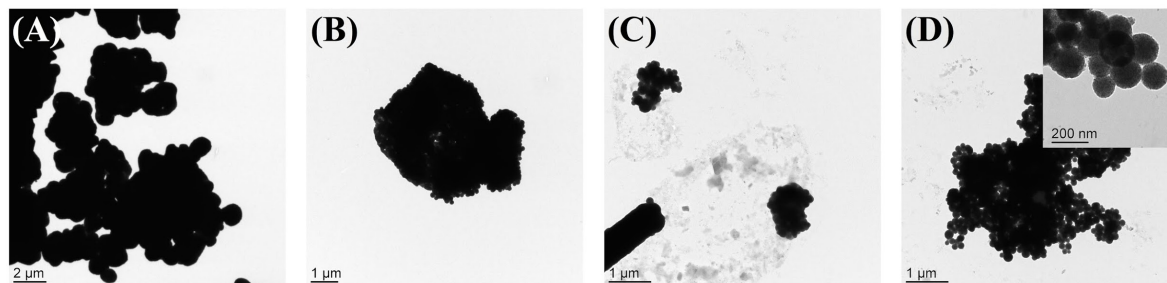


Figure 1. Bright field TEM images of magnetic emulsion after the acidification step. The samples were prepared without PDA and varying the PVP amounts:

(A) 0000, (B) 1000, (C) 2000, (D) 4000.

The magnetic emulsion (sample 0000), Figure 1A, was immediately precipitated after addition of acid solution (see Figure S1 in supplementary information). As explained early, this effect is the result of a decrease in the negative surface charges on the magnetic particles, owing to increased acidity of the magnetic emulsion. At this condition, the attractive forces became more important (by magnetic attraction), leading to coalescence of the particles. In fact, the ME could be stabilized, in acid environment, only when the amount of PVP was higher than 20 mg (Figures 1C and 1D).

In a second test, the influence of PDA in the emulsion stabilization was also investigated. Polymerization reactions containing 0.08, 0.16, 0.32 mmol of PDA were performed without PVP (samples 0008, 0016, 0032, respectively). However, regardless of the concentration, the PDA did not show any significant effect on stabilizing the emulsion. In addition, in such experimental condition, we observed phase separation, where the poly(*p*-phenylenediamine) (PPDA) was polymerized without magnetic core and the magnetic particles remained agglomerated (data not shown).

In fact, core-shell morphology was only observed when the amount of PVP and PDA were, respectively, higher than 20 mg and 16 mmol (samples 2016, 2032, 4016, and 4032). TEM images of the core-shell nanoparticles are shown in Figure 2.

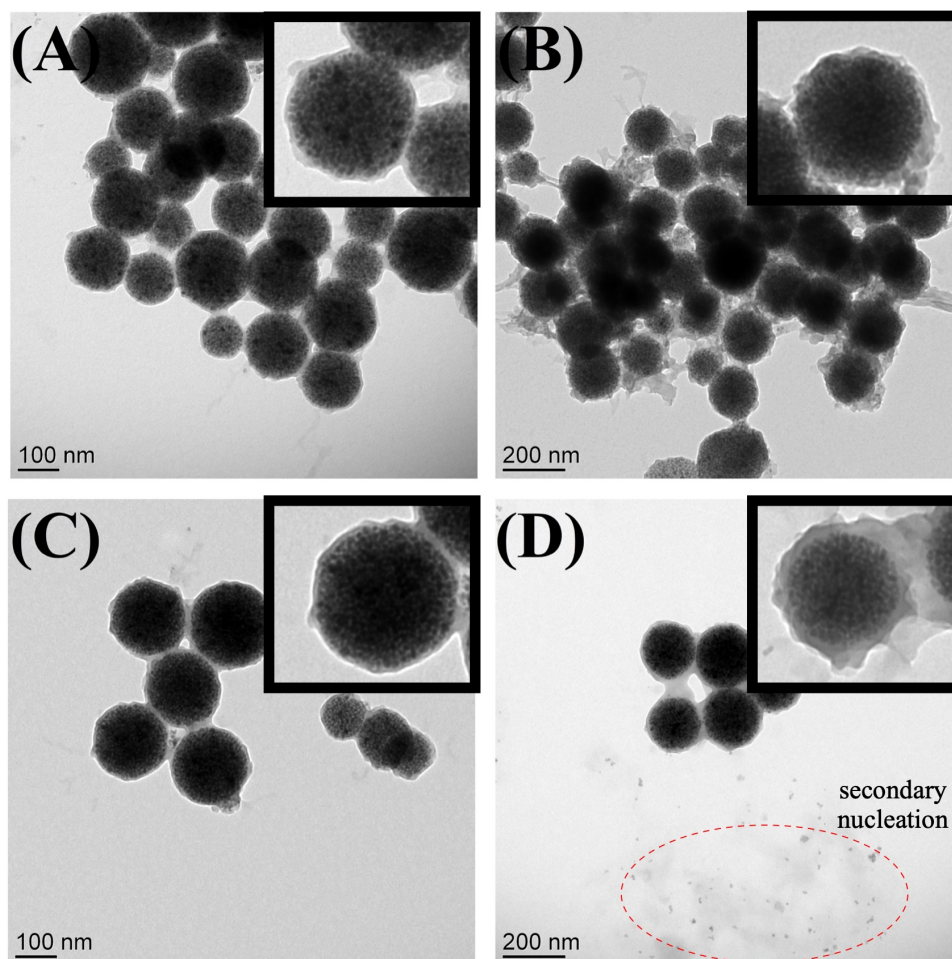


Figure 2. Bright field TEM images of samples obtained after polymerization of PDA using ME as seed: (A) 2016, (B) 2032, (C) 4016, (D) 4032.

For sample 2016 (Figure 2A), a core-shell morphology, with a thin layer of PPDA, was observed. If compared with sample 4016 (Figure 2C), the final morphology was shown to be almost the same. This result suggests that PVP did not play any influence on the final morphology, since, being only necessary for stabilizing the ME. However, when the amount of PDA was increased from 0.16 mmol (sample 2016 - Figure 2A) to 0.32 mmol (sample 2032 - Figure 2B), the polymeric layer became thick and rough. Moreover, polymeric particles, without magnetic core, were observed. The formation of such particles has been thought to be the result of secondary nucleation (Figure 3)¹⁸.

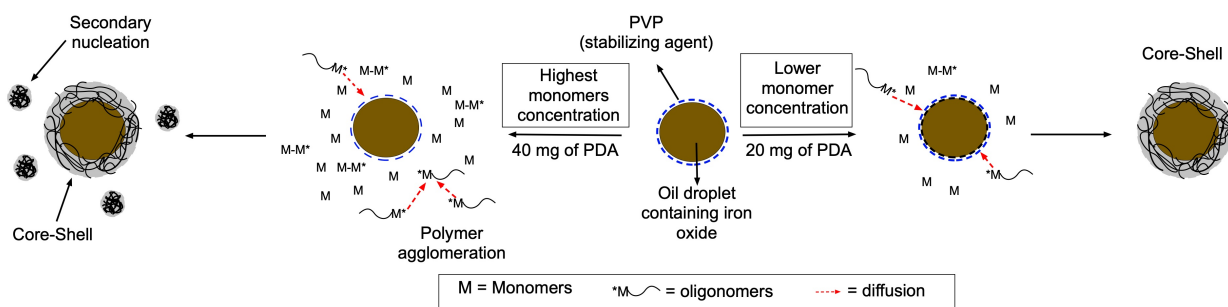


Figure 3. Schema suggesting the different ways for producing core-shell nanoparticles by seeded-emulsion polymerization.

During the initial stage of emulsion polymerization, the oligomeric radicals of PDA diffuse into the oil droplets leading to the formation of core-shell nanoparticles. However, when the concentration of monomer is high, the oligomers may undergo homogeneous nucleation generating polymeric particles without magnetic core^{20,21}. This effect is better observed in the samples 2032 and 4032, both with the highest concentration of PDA (0.32 mmol - Figures 2B and 2D). Based on the observations described above, the samples 2016 and 4016 were chosen as those from the best experimental condition in the production of core-shell type particles.

4.2. FTIR

Figure 4 shows the FTIR spectra of magnetic emulsion (ME), sample 2016, and sample 4016 in the spectral range of 2000 cm^{-1} to 400 cm^{-1} . ME was obtained after the emulsification of ferrofluid (oil phase) in aqueous solution with surfactant. Moreover, in the oil phase, the iron oxide particles were stabilized with oleic acid (OA).

In the ME spectra, an absorption band appeared at $\sim 1700\text{ cm}^{-1}$, owing to C=O stretching vibration of free OA. In addition, a high-intensity band at $\sim 570\text{ cm}^{-1}$ (ascribed to Fe-O stretching vibration), which was observed in all the spectra, is associated to the magnetic phase in the polymer particles⁷.

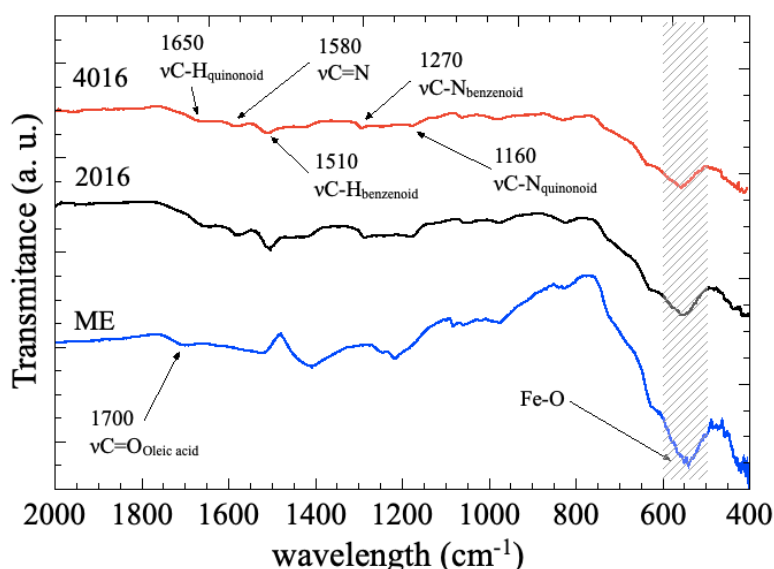


Figure 4. FTIR spectra of magnetic emulsion (ME), samples 2016, and sample 4016 in the spectral range of 2000 cm^{-1} to 400 cm^{-1} .

The samples 2016, and 4016 showed same spectral profile, which is more likely to be from the same polymer shell. The absorption bands at 1650 cm^{-1} and 1510 cm^{-1} are associated, respectively, with C-H stretching from quinonoid and benzenoid rings²², while the band, at 1580 cm^{-1} , was attributed to C=N stretching²³. In addition, the bands at 1270 cm^{-1} and 1160 cm^{-1} were attributed to C-N stretching from benzenoid and quinonoid rings and the band at 1508 cm^{-1} is the result from C=C stretching²².

4.3. Magnetic properties

Magnetic curves for the dried latexes obtained by seeded polymerization are presented in Figure 5. According to the papers published elsewhere, saturation magnetization (M_S) of iron oxide can be found between 60 emu g^{-1} and 80 emu g^{-1} depending on the predominant crystalline phase^{24,25}. In our work, oil in water magnetic emulsion (ME) was used. The magnetic emulsion was obtained dispersing iron oxide in octane followed by dispersion in water using surfactants (i.e. Sodium dodecyl sulfate). Therefore, magnetic emulsion has a significant percentage of non-magnetic material on its composition (see TG measurements), which, in turn, contributes to decrease saturation magnetization to ca. 40.0 emu g^{-1} .

Both samples 2016 and 4016 showed superparamagnetic characteristics at room temperature. Furthermore, the saturation magnetization (M_S) for the samples 2016 and 4016 was approx. 35 emu g^{-1} and 15.0 emu g^{-1} . In addition, for all samples, the M_R/M_S ratio is

found to be below 0.5 which is the expected value for randomly packed single domain particles, which is related to the superparamagnetic behavior.

The sample 4016 has the smallest value of M_S which is associated to a high polymeric content. In core-shell nanoparticles, the percentage of non-magnetic material was increased after coating the magnetic emulsion with PPDA. As a consequence, the M_S values of core-shell particles decrease. This result is in agreement with the observed in TG measurements.

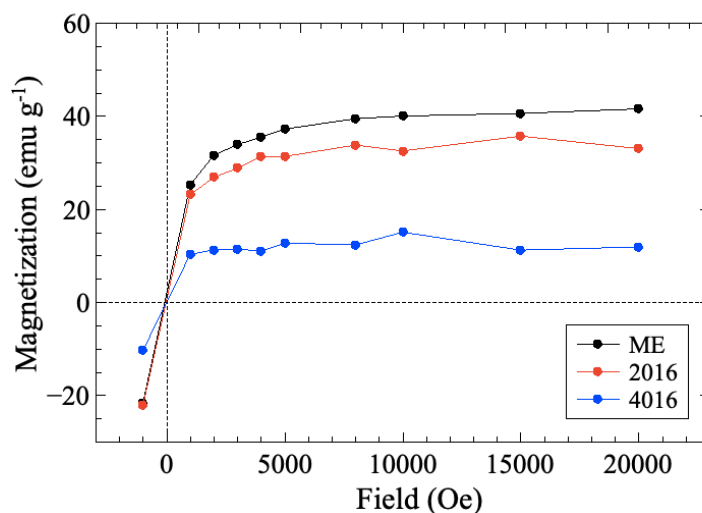


Figure 5. Magnetization curves of superparamagnetic polymeric particles obtained by seeded polymerization.

4.4. Thermogravimetric analysis

Figure 6 shows the TG curves of magnetic emulsion seed (ME), and samples 2016 and 4016, respectively. In the magnetic emulsion thermogram (Figure 6A), two main thermal degradation events could be observed: (i) at the temperature range from 25 °C to 500 °C, and (ii) above 500 °C. In the first event, an initial weight loss of ca. 20% was observed. As indicated by dTG curve, at this temperature range, a large amount of organic matter (which consists of oleic acid surfactants) is expected to be degraded. When the temperature is between 500 °C and 700 °C, the second thermal degradation event, it was found an additional weight loss of 2.5%. This one is associated to the phase transition from Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3$. Above 700 °C, $\gamma\text{-Fe}_2\text{O}_3$ is converted to FeO as demonstrated by Ayyappan, S and co-authors²⁶.

The samples 2016 and 4016 exhibited the same degradation profile (Figure 6B). PVP degrades totally at ca. 600 °C²⁷, while PPDA starts to degrade at temperatures higher than 250 °C^{22,28,29}. In addition, the weight loss of sample 2016 was clearly less pronounced than

sample 4016. Since the greater weight loss, thicker is the polymer shell. This result indicates the sample 4016 has more polymer covering its surface than sample 2016.

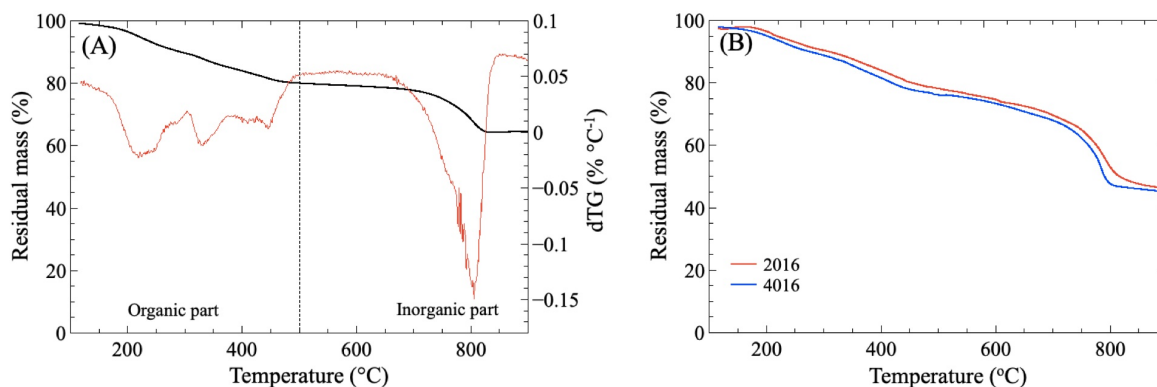


Figure 6. Thermogravimetric curves of dried samples: (A) TG and dTG of the magnetic emulsion seed, (B) TG of polyPDA magnetic latexes (samples 2016 and 4016).

4.5. Particle size

Figure 7 shows the particle size distribution obtained for samples 2016, and 4016. According to the observed, by TEM images, it was expected both samples exhibit almost the same size distribution. However, the sample 2016 exhibited a log-normal distribution with an average size of 319 nm, while sample 4016 shows a normal distribution with an average size of 395 nm.

Furthermore, the sample 2016 has a size distribution wider than the sample 4016 (Figures 7A and 7B, respectively). The widening of the size distribution may be associated to the particle agglomeration. After increasing the amount of PVP from 20 mg (sample 2016) to 40 mg (sample 4016) the narrowing in size distribution was observed. This result suggests that the PVP may act as steric barrier, avoiding the agglomeration of particles, even after the polymerization process.

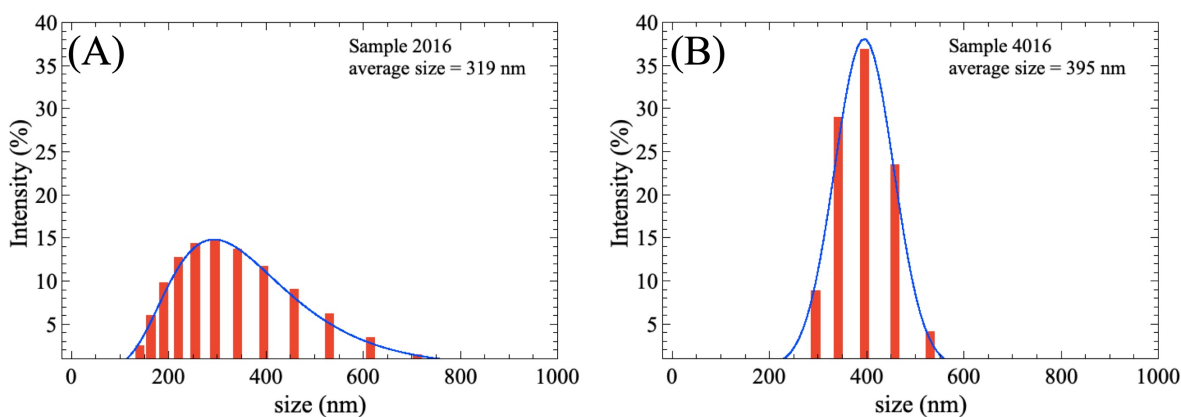


Figure 7. Particle size distribution of (A) sample 2016, and (B) sample 4016.

4.6. Electrodeposition studies

Based on the aforementioned results, the sample obtained with 40 mg of PVP and 16 mmol of PDA (sample 4016) was chosen as an ideal core-shell nanoparticle, with narrowed size distribution and superparamagnetic properties, to be applied in biosensors. Thus, to check the potential of a device containing our nanoparticles, a fully integrated biosensor platform was used to perform electrodeposition studies. Such biosensor consists of 4 gold working electrodes (WEs) platinum counter electrode (CE) and Ag/AgCl reference electrode (RE) (Figure 8A).

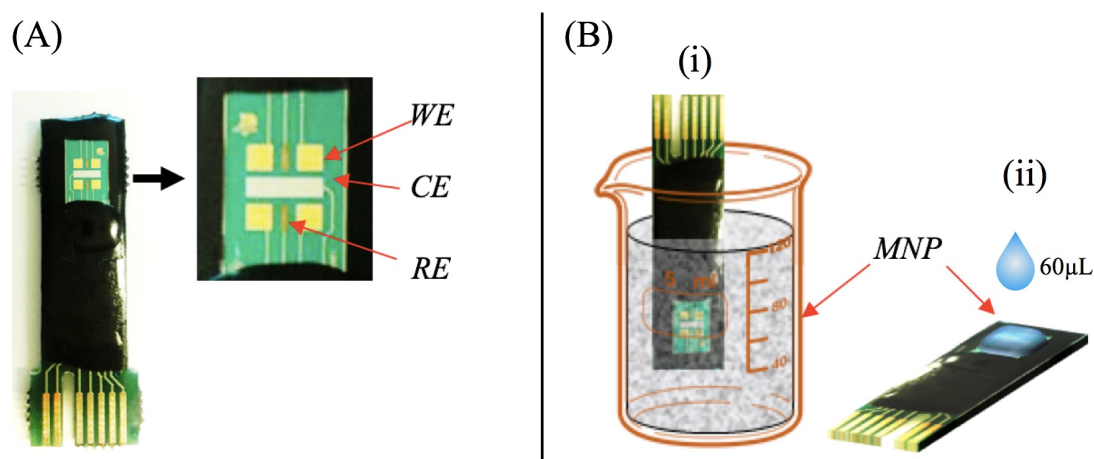


Figure 8. (A) Biosensor device with 4 WEs, CE, and RE (B) Electrodeposition of MNP using (i) vertical position: the biosensor dropped in the MNP solution (ii) horizontal position: a droplet of 60µL of MNP deposited onto gold WE surface.

Electrochemical deposition of sample 4016 was carried out by using cyclic voltammetry technique. The electrochemical deposition was made in two different ways: First, the biosensor platform was dropped in the MNPs solution vertically (Figure 8B – *set-up-(i)*). Here, we considered that the electrochemical deposition of MNPs was not sufficient as there were a little MNPs on gold surface, as can be seen in Figure 9A

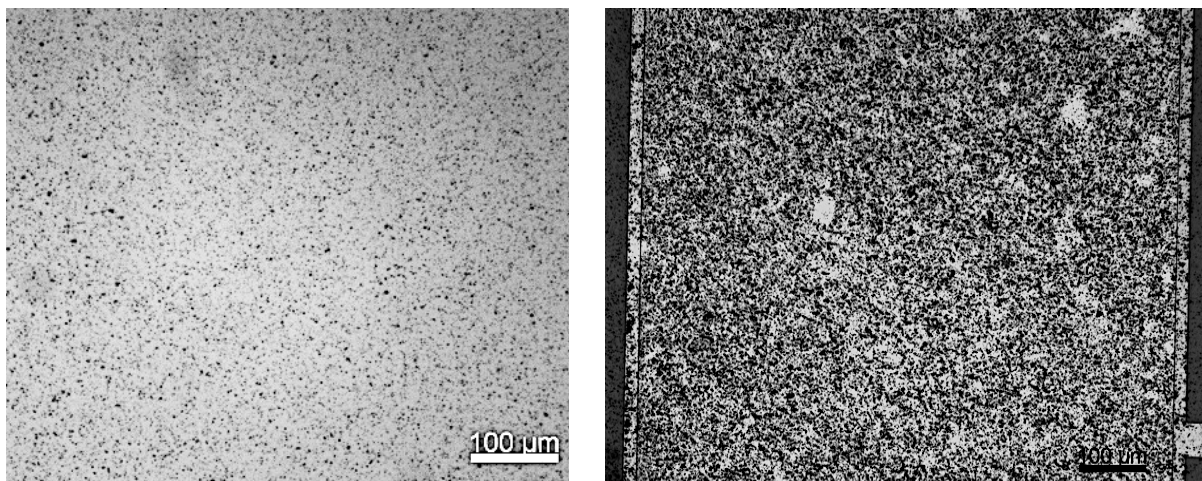


Figure 9. Optical images of sample 4016 electrodeposited on gold WEs using the different experimental approach: (A) *set-up-(i)*, and (B) *set-up-(ii)*.

In order to enhance the electrodeposition of sample 4016, the biosensor was placed horizontally and a droplet of 60 μL of samples was deposited onto its surface using the same optimized electrochemical conditions (*set-up-(ii)*, Figure 9B). Here, the rate of the nanoparticles electrodeposition was higher than the previous experimental configuration (Figure 9B).

When the biosensor was vertically placed in the solution (*set-up-(i)*), the core-shell nanoparticles go through the solution to the WEs surface. However, only the nanoparticles at the interface WE/solution are able to be electrodeposited. On the other hand, for the horizontal configuration (*set-up-(ii)*), the nanoparticles go to the surface by gravity and enhancing the electrodeposition.

The solution of sample 4016, containing HCl and NaNO_2 , was left at 4°C for 24 hours and the same experimental parameters for MNPs electrodeposition were used. Here, the aim was to verify if the maximum diazotation of amino groups could enhance the electrodeposition. This sample was called 4016-b. At these conditions, the core-shell nanoparticles agglomerated in the solution, being also electrodeposited onto the surface.

4.7. CV and EIS results

Figure 10 shows the CV and EIS curves obtained for samples 4016 and 4016-b. CV was carried out to characterize gold WE surface before and after electrodeposition of MNPs. The best deposition was observed for sample 4016. However, when compared to bare gold, the redox of sample 4016 peaks were weaker. Finally, for sample 4016-b (left 24 hours in

HCl and NaNO₂ at 4°C), the redox peaks have almost disappeared when compared to bare gold. This behavior is associated to non-homogenous deposition of MNPs.

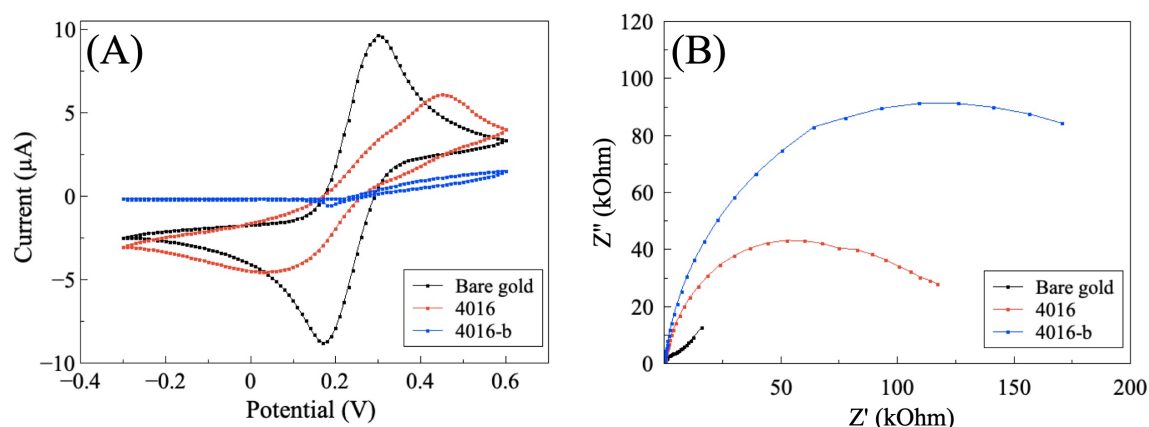


Figure 10. Curves of (A) cyclic voltammetry, and (B) Impedance spectroscopy of samples 4016 and 4016-b.

CV analyses were confirmed by EIS measurement. Comparing the bare gold with samples 4016 and 4016-b, the existence of a single semicircle indicates the presence of a single charge-transfer process, which was slightly affected by the presence of PPDA³⁰. The sample 4016 has an increased impedance which is in complete adequacy with CV due to the homogenous deposited layer. The EIS has increased from 4016 to 4016-b. This is associated to an increase of charge resistance due to the increase of the passivation area onto gold WEs after electrochemical deposition of iron oxide-coated poly(*p*-phenylenediamine).

5. Conclusions

In summary, we synthesized and characterized conducting magnetic particles, based on poly(*p*-phenylenediamine), using magnetic emulsion as seed. Perfect core-shell nanoparticles, with narrowed size distribution and highly inorganic content, could be obtained when 40 mg of PVP and 16 mmol of *p*-phenylenediamine was used. After characterization, we found the core-shell nanoparticles have both superparamagnetic and electric properties with average size of 395 nm and magnetic saturation near to 15 emu g⁻¹. The superparamagnetic property is very important to be used for fast separation, under magnetic field, when used for sample preparation, for instance. On the other hand, the electric property may enhance the signal detection. In addition, due to the presence of -NH₂ groups in the polymer shell, covalent coupling of carboxylate-containing biomolecules (e.g. oligonucleotides, proteins, and antibodies, specific ligands) can be easily performed. These

very interesting characteristics make it possible our particles to be applied in sensors, *lab-on-a-chip*, microsystems, and microfluidics.

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Table 1. Compositions of stabilizer (PVP) and monomer (PDA) used in the seeded polymerization.^(a)

Sample Name	PVP (mg)	PDA (mmol)
0000 ^(b)	0.0	0.00
0008	0.0	0.08
0016	0.0	0.16
0032	0.0	0.32
1000	10.0	0.00
1008	10.0	0.08
1016	10.0	0.16
1032	10.0	0.32
2000	20.0	0.00
2008	20.0	0.08
2016	20.0	0.16
2032	20.0	0.32
4000	40.0	0.00
4008	40.0	0.08
4016	40.0	0.16
4032	40.0	0.32

(a) 0.16 mmol of KPS was used in the seeded polymerization at RT for 20h; (b) Reference Sample.