

Research Article

Green Synthesis of Gold Nanoparticles with Self-Sustained Natural Rubber Membranes

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Green chemistry is an innovative way to approach the synthesis of metallic nanostructures employing eco-friendly substances (natural compounds) acting as reducing agents. Usually, slow kinetics are expected due to, use of microbiological materials. In this report we study composites of natural rubber (NR) membranes fabricated using latex from *Hevea brasiliensis* trees (RRIM 600) that works as reducing agent for the synthesis of gold nanoparticles. A straight and clean method is presented, to produce gold nanoparticles (AuNP) in a flexible substrate or in solution, without the use of chemical reducing reagents, and at the same time providing good size's homogeneity, reproducibility, and stability of the composites.

1. Introduction

The synthesis of noble metals nanostructures for plasmonic applications is a very active field of research [1, 2]. One of the objectives is to develop chemical routes of controlling the homogeneity of nanoparticles formation with desired size [3, 4] and shape [5]. The fabrication of nanostructures follows the demand for specific optical properties [6] allowing potential applications [7]. In particular, we are interested in plasmon enhanced scattering (SERS and SERRS) and plasmon enhanced fluorescence (SEF) [8, 9] applications.

In general, the synthesis of gold nanoparticles is commonly carried out using colloidal chemistry. The latter involves the use of chemicals (reducing/stabilizing reagents), among which are sodium citrate, sodium borohydrate, ascorbic acid, fulvic acid, and so forth [10]. There is a wide range of methods that may be employed to fabricate gold nanostructures such as vacuum evaporation [11] and electrochemical techniques [12, 13]. In addition, arrays of gold nanoparticles can be fabricated using the Langmuir-Blodgett (LB) technique, nanolithography, and layer-by-layer deposition [14].

Currently, the green chemistry, using eco-friendly substances (natural compounds) as reducing/stabilizing reagents, opens a broad range of materials like extracts from different leaves [15, 16], fruits [17, 18], seeds [19], and flowers [20, 21] as well as microbiological compounds from algae bacteria [22], and fungi [23] to develop gold nanoparticle synthesis. These materials minimize the use of chemical compounds and the generation of waste attributed to reagents or solvents included in the chemical synthesis. In some of these cases, the researcher needs a specific knowledge regarding the use of microbiological materials or the extraction of natural products. The natural rubber used here provides a viable alternative: it is accessible and inexpensive natural product. It can now be included in the list of organic compounds used to generate green synthesis, that is, for reduction and stabilization of metallic nanostructures.

Previous work showed that both latex and seed extract from *Jatropha curcas* [24, 25] and latex from *Hevea brasiliensis* [26] are used in solution for synthesis of silver nanoparticles. In addition, cream fraction of latex from ammoniated NR latex and deproteinized natural rubber latex is also used

to synthesize silver nanoparticles [27]. Similarly, epoxidized natural rubber (ENR) is used as polymeric stabilizer of both platinum and gold nanoparticles, after being dissolved in toluene and mixed with colloids prepared by sodium borohydrate [28].

The characterization of the constituents of latex has been previously reported [29, 30]. The studies revealed three phases: rubber solid or latex particles, serum, and bottom phase. The first phase is attributed to the monomers isoprene, the main constituent of natural rubber chain that constitute of near to 60–40% dry rubber. The composition of serum phase is approximately 1.0 to 1.8% protein, 1.0 to 1.2% carbohydrate, 0.4 to 1.1% neutral lipids, 0.4 to 0.5% polar lipids, 0.4 to 0.6% inorganic lipids, 0.4% amino acids, amines among others, and 50 to 60% water [29, 31]. Finally, the bottom fraction contains compounds responsible for the connection between plant and soil, containing a high portion of the monomers with metal ions.

Natural rubber has been the object of research involving a wide range of applications, for example, the fabrication of composites and synthesis of new material [32–34]; it also has been evaluated for its medicinal properties such as induction of angiogenesis and neoformation issue [35]. The composite NR/AuNPs maintains the elastomeric mechanical properties (elasticity and flexibility) increasing the rupture tensile; both materials are biocompatible. Furthermore, gold nanoparticles could work as enzyme support/catalysis or can be used to fabricate sensor devices. Natural rubber membranes with incorporation of gold nanoparticles produced flexible membranes that may be used as substrate for ultrasensitive detection and chemical analysis in plasmon enhanced Raman spectroscopy [36]. These composites membranes can act as a growth inhibitor of *Leishmania brasiliensis* promastigotes in vitro [37].

In this study, we propose a new fast clean green chemistry method for synthesis of eco-friendly and nontoxic gold nanoparticles dispersed in solution, as well as the formation of a flexible substrate of natural rubber with gold nanoparticles, a polymeric biocompatible nanocomposite matrix. The NR membranes are produced by casting the annealed latex (without the traditional vulcanization agent sulfur). The AuNPs were formed at the NR membrane surface through the reduction of gold (III) from AuCl_3 , in aqueous solution kept at 80°C for different reaction times, which leads to diverse NR/Au composites.

2. Experimental

2.1. Natural Rubber Membranes Preparation. Natural rubber (NR) forming self-sustainable membranes are prepared using latex collected from different rubber trees of the *Hevea brasiliensis* (RRIM 600 clone) [38] in an experimental farm in Indiana city, in the region of Presidente Prudente, Sao Paulo state, Brazil. The sample was stabilized with 2% of ammonium hydroxide. The NR cis-1,4-polyisoprene has a glass transition at -67°C . NR membranes of 0.5 mm thickness (40–60% of dry rubber) were fabricated by casting latex on glass and annealing for 10 hours at 65°C, 80°C, and 120°C.

2.2. Synthesis of Gold Nanoparticles. The formation of AuNPs was achieved by direct reaction of the NR membrane in a solution of gold chloride (3.1×10^{-4} M) chosen according to colloid preparation methods by chemical reduction [10]. The gold (III) chloride 99.99% (AuCl_3) was purchased from Aldrich. The synthesis was carried out at 80°C for immersion periods of 6, 9, 15, 30, 60, and 120 minutes.

2.3. Characterization. UV-Vis plasmon absorption was recorded using a Varian spectrophotometer, model Cary 50, with a scan range from 190 to 1100 nm. The analysis TG, Netzsch model 209, was used near 15.0 mg mass, deposited in an alumina crucible, and pure nitrogen gas (N_2) was used as carrier gas (15 mL/min). The heating rate was 10°C/min, and the temperature range was between 25 and 600°C. The spectra TG coupled to FT-IR spectroscopy of evaporated components were recorded on a Vector 22 spectrometer from Bruker, with wavenumber that covers the range between 600 and 4000 cm^{-1} with 4 cm^{-1} spectral resolution for detector MCT. SEM measurements from solutions of gold nanoparticles were done using a FEI Quanta 200 FEG microscope with a field emission gun (filament), equipped with an everhart-thornley secondary electron detector, and a solid state backscatter detector. SEM analysis was done at the Great Lakes Institute for Environmental Research in Windsor—Canada. The SEM substrate used is HOPG (highly ordered pyrolytic graphite) disk.

3. Results

3.1. Reaction Kinetics of Gold Nanoparticles. First, gold nanoparticles from on the surface of membranes (reducing agent) prepared at 65°C (thermal treatment) that are characterized by UV-Vis spectroscopy, showing an absorbance band around 560 nm that can be assigned to the localized surface plasmon resonance (LSPR) of gold nanoparticles. The band intensity increased with increasing reduction time. Second, the nanoparticle fabrication is extended to include membranes prepared at different temperatures in the thermal treatment (65, 80, and 120°C) presented in Table 1.

The plasmon absorption bands of AuNPs show an exponential increase in intensity with the reaction (immersion) time of the membrane in the gold chloride solution, which is seen with good reproducibility until 30 min. The reaction kinetics were previously studied [36, 39].

Studies carried out with reaction times of 120 minutes lead to saturation in plasmon absorption intensity due to nanoparticle aggregation.

Furthermore, the higher the temperature of thermal treatment of the natural rubber membranes (reducing agent), the stronger the absorbance intensity of the LSPR band, which is attributed to larger amount of nanoparticles, formed in the natural rubber matrix.

Analysis of the pH changes in the solution used for synthesis of nanoparticles during the reduction process is shown in Figure 1.

A nearly exponential behavior can be seen, where the pH decreases with increasing reaction time, attributed to gold

TABLE 1: Plasmon resonance absorption results at 560 nm for NR/Au membranes prepared with different reduction time. Synthesis using natural rubber membranes prepared at 65, 80, and 120°C.

Reduction time	NR membranes prepared at 65°C		NR membranes prepared at 80°C		NR membranes prepared at 120°C	
	Average abs.	Standard deviation	Average abs.	Standard deviation	Average abs.	Standard deviation
6 min	0.0691	0.0162	0.0911	0.0192	0.0927	0.0183
9 min	0.0957	0.0199	0.1586	0.0179	0.1641	0.0232
15 min	0.1567	0.0174	0.3101	0.1646	0.3205	0.0332
30 min	0.4477	0.0158	0.8631	0.1715	0.8023	0.0699
60 min	1.2073	0.1419	2.2393	0.0883	2.5307	0.3379
120 min	4.2756	3.1723	5.3294	3.0143	5.4489	2.6496

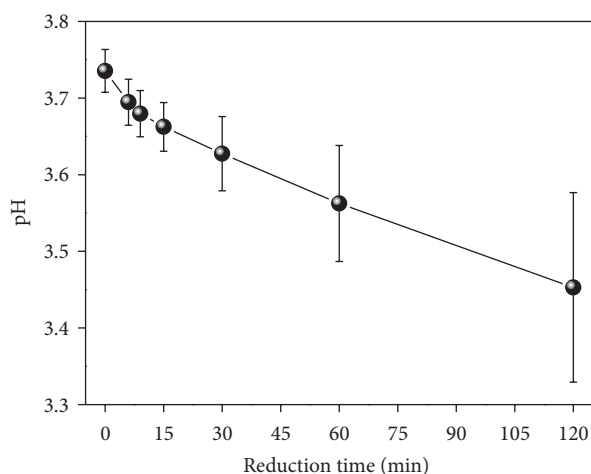


FIGURE 1: pH variation in the solution used for synthesis of NR/Au membranes at different reduction times, using natural rubber prepared at 65°C as reducing agent.

reduction and formation of ions H^+ according to the following reaction:



The kinetic growth of the gold nanoparticles using natural rubber membranes prepared at 65°C was reported [39] showing that increasing the reduction time raises the amount of nanoparticles deposited on natural rubber surface as well as the nanoparticle's size. Here, the natural rubber prepared at different temperatures (annealed at 65, 80, and 120°C) and 15 minutes of reduction reaction time and imaged using SEM microscopy are presented in Figure 2 with micrometer magnification (top) and nanometric resolution (bottom), where nanostructures of ca. 50 nm diameter are clearly seen in the NR/Au membranes.

Increasing the annealing temperature in the preparation of the natural rubber membranes improves the formation of nanoparticles synthesized on the surface of the natural rubber membranes. That latter may be attributed to the higher density of both organics and, particularly, organic acids generated during the degradation of proteins of the protein phase of the natural rubber membranes. Membranes annealed at 65°C show a distribution of shapes close to that found in colloidal solutions. However, membranes of natural

rubber prepared at 80 and 120°C show good homogeneity of nanoparticle aggregates on the surface (see top of Figure 2).

3.2. Evaluation of the Compounds Released from Natural Rubber into the Solution. The compounds released from natural rubber in solution were studied by insertion of about 2 g of natural rubber inside of 50 mL of water, kept at 80°C, for 120 minutes. The UV-Vis spectrum of the solution is provided in the supporting information (see Figure S1 in Supplementary Material available online at <http://dx.doi.org/10.1155/2013/710902>). Two absorption bands observed at 217 and 264 nm can be assigned to aromatic compounds. To identify these compounds, the NR + H_2O solution was lyophilised, and the solid compound was analysed by TG/FT-IR (Figure 3). The assignment of the observed vibrational bands is given in the supporting information Table S1 [29, 31, 40, 41].

It is possible to identify the functional groups from esters (1040–1080, 1596, and 1755 cm^{-1}) and also amides (characteristic to link between amines and aromatic carboxylic acids) (1620 and 3265 cm^{-1}); both are compound types (nonrubber) that can participate as reducing agent in synthesis process of gold nanoparticles. Peaks (928, 972, 1001, 1336, 1379, 2877, and 2965 cm^{-1}), found in TG/FT-IR analysis, can be attributed to CH- and CH_2 - groups mainly found on isoprene structure, the main constituent of natural rubber chain. The released of amides from polymeric chain can be attributed to polymer's hydrolysis in water [42, 43] and also to α -terminal groups compounds of mono- or diphosphate linked with phospholipids [44].

TG/FT-IR analysis of latex phase constituents separated by centrifugation is shown in Figure 4.

Characteristic vibrational bands at 2933, 1456, 1388, and 887 cm^{-1} seen in Figure 4(b) correspond to the rubber phase and bottom fraction, containing mainly isoprene. In fact, they are not seen in the analysis of the serum phase or substances released by natural rubber membrane in water. In addition, there are obvious similarities between components released into solution by natural rubber and those in the serum phase (Figure 4(a)), in particular, compounds containing ester (1534 cm^{-1}), amides (1672 cm^{-1}), and carboxylic acids (1737 cm^{-1}). It is important to point out that the rubber phase has a single region of degradation that appears around 361°C (Figure 4(b)). Figure 4(a) shows that at a temperature of 268°C, there are similar vibrational bands

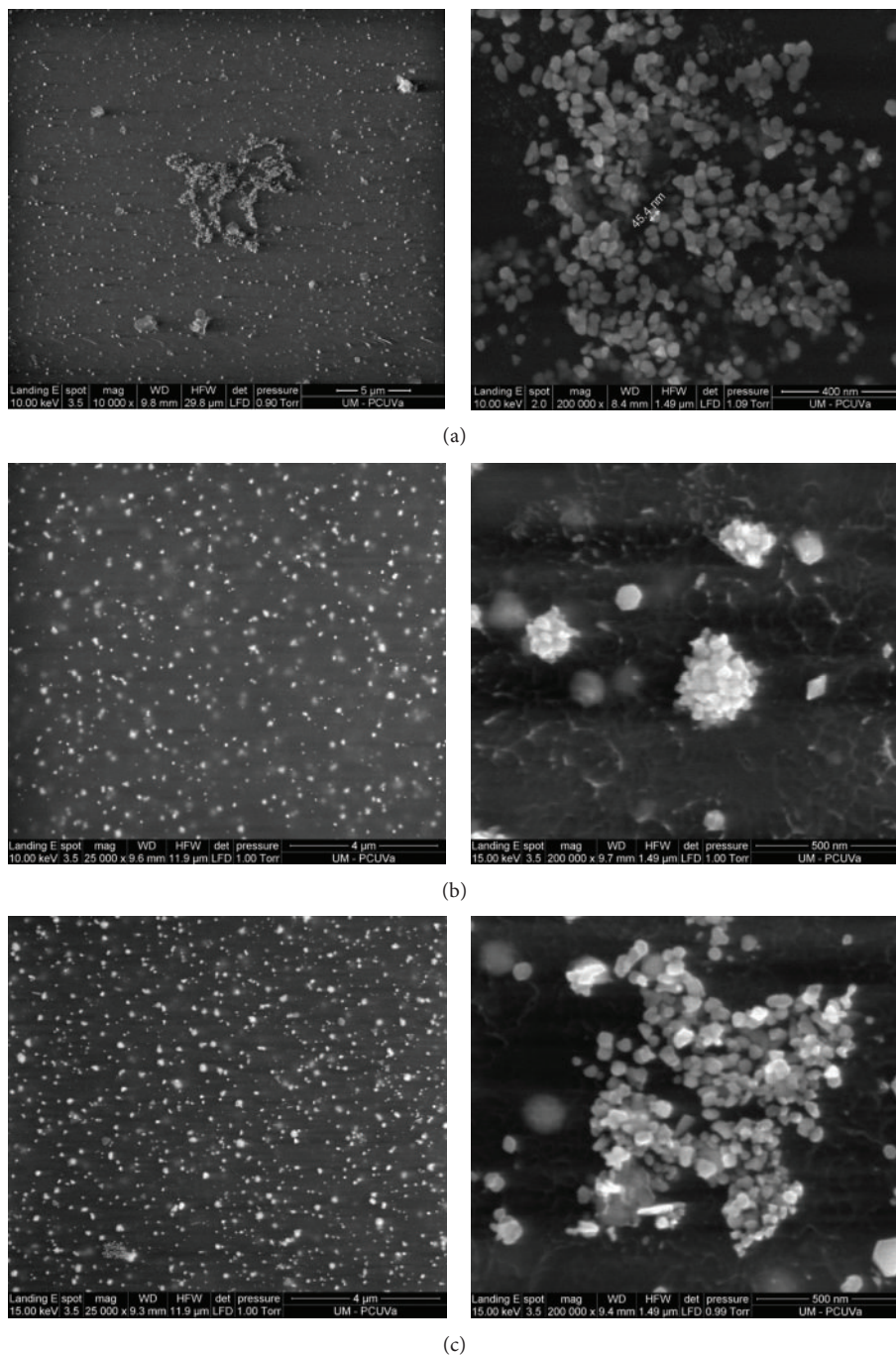


FIGURE 2: SEM images from NR/Au membranes prepared with 15 min reduction time, using natural rubber membranes annealed at (a) 65°C (b) 80°C, and (c) 120°C (thermal treatment casting).

in the spectra of the serum phase, the bottom fraction, and the components released in water by NR membranes, which is attributed to protein constituents (1741 and 1517 cm^{-1}) and constituents relative to isoprene at 1058, 967, and 928 cm^{-1} . The serum phase provides good agreement with the components released into solution, since characteristic vibrational bands at 2961, 1461, and 1394 cm^{-1} of the natural rubber are not observed. It is concluded that the

solid membrane from natural rubber latex, prepared through thermal treatment, releases constituents weakly bound to the main chain of the polymer (isoprene monomer). These constituents are mainly from the latex serum phase and become the reagents responsible for the reduction of gold to form nanoparticles in solution.

To complete the chemical analysis and a study of the vibrational properties of NR and NR/Au membranes has

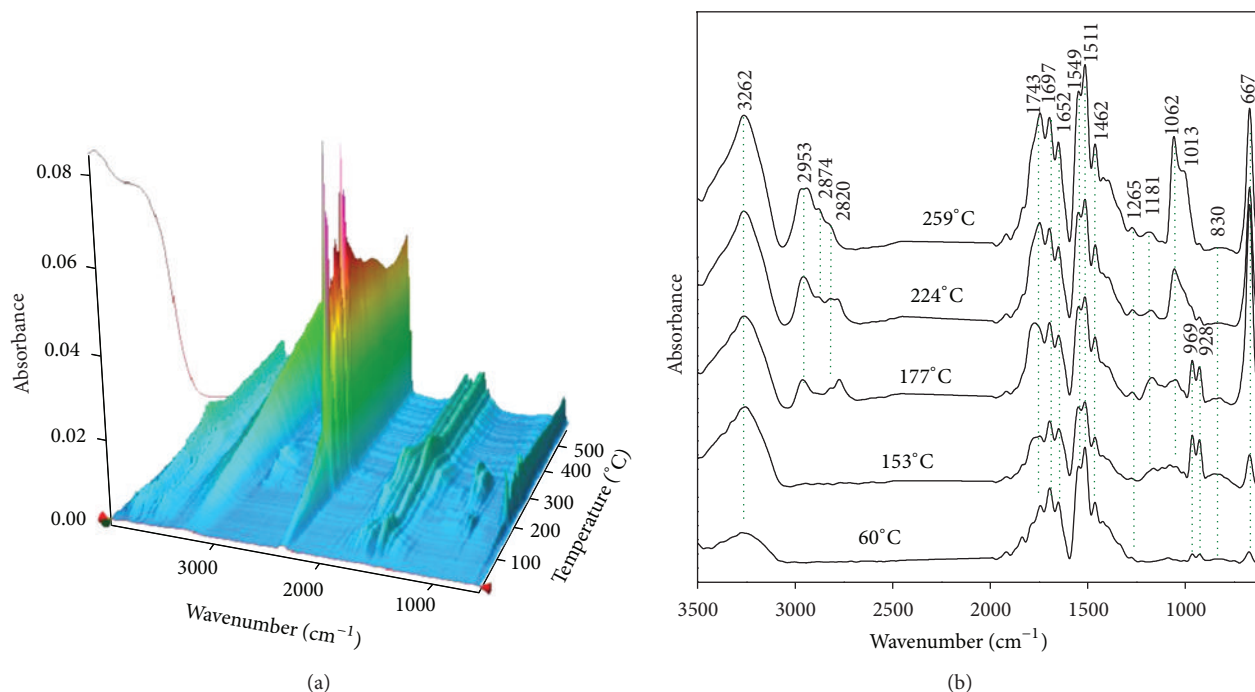


FIGURE 3: (a) 3D TG/FT-IR image from lyophilised solution of H_2O where the NR membrane (2 g) was immersed for 2 hours at $80^\circ C$; (b) spectra extracted from 3D TG/FT-IR image at 60, 153, 177, 224, and $259^\circ C$ obtained for NR + H_2O (lyophilised solution) prepared under the same conditions.

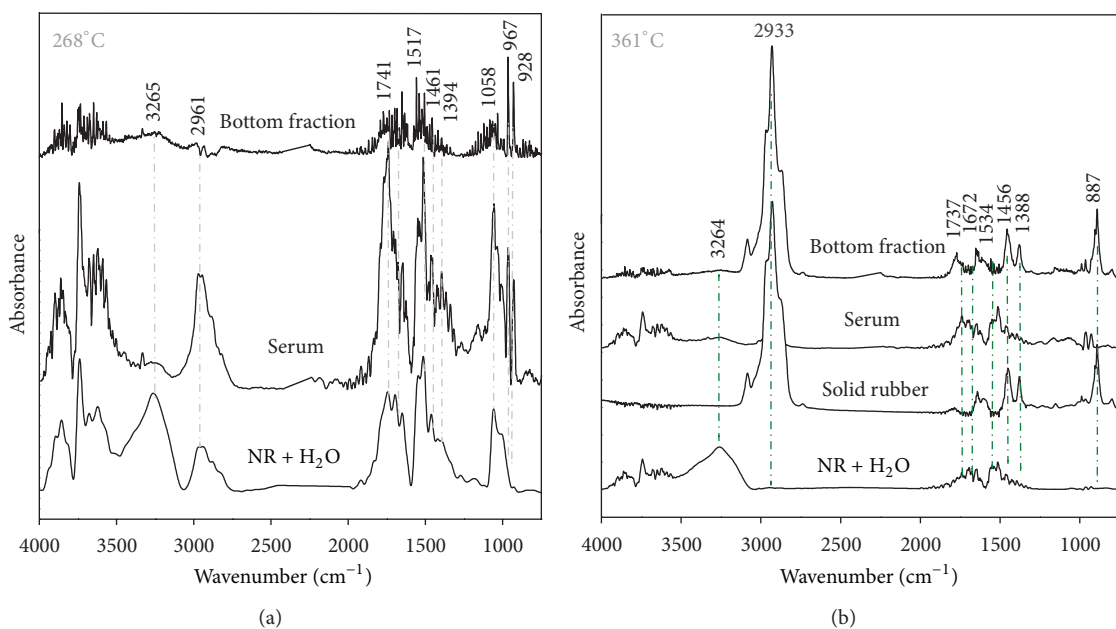


FIGURE 4: Spectra extracted from 3D TG/FT-IR images at (a) $268^\circ C$ and (b) $361^\circ C$. Results obtained analysing the lyophilized solution in H_2O . Also, 2.0 g of NR membrane was immersed for 2 hours at $80^\circ C$. Comparison with different latex phases (bottom and serum phase) after being lyophilised.

been attempted. By thermogravimetric analysis coupled with FT-IR spectroscopy, the components evaporated of the samples during thermal treatment between room temperature and $600^\circ C$ are analyzed qualitatively. Figure 5 shows the graph TG/FT-IR of natural rubber membranes showing that all membranes presented similar behavior.

In the TG curves, there is a first step of 5% loss in mass between 100 and $250^\circ C$ attributed to the release of water molecules and processes of cross-linking and scission of polymer chains, and the main step is assigned to the degradation process starting near $250^\circ C$ and ends around $400^\circ C$, showing a loss of 84% mass, a characteristic of isoprene

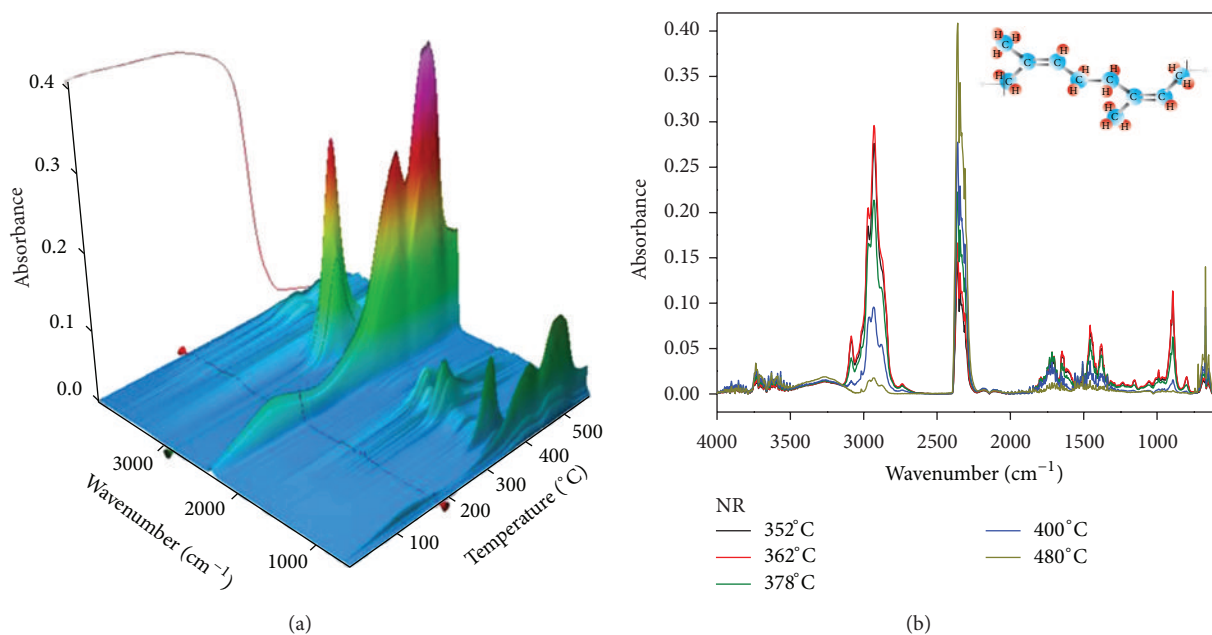


FIGURE 5: (a) 3D image analysis TG/FT-IR for NR membrane (b) 2D Spectra extracted from the analysis TG/FT-IR for NR membrane at different temperatures of thermal analysis. Representation of natural rubber polymer chain (see inset).

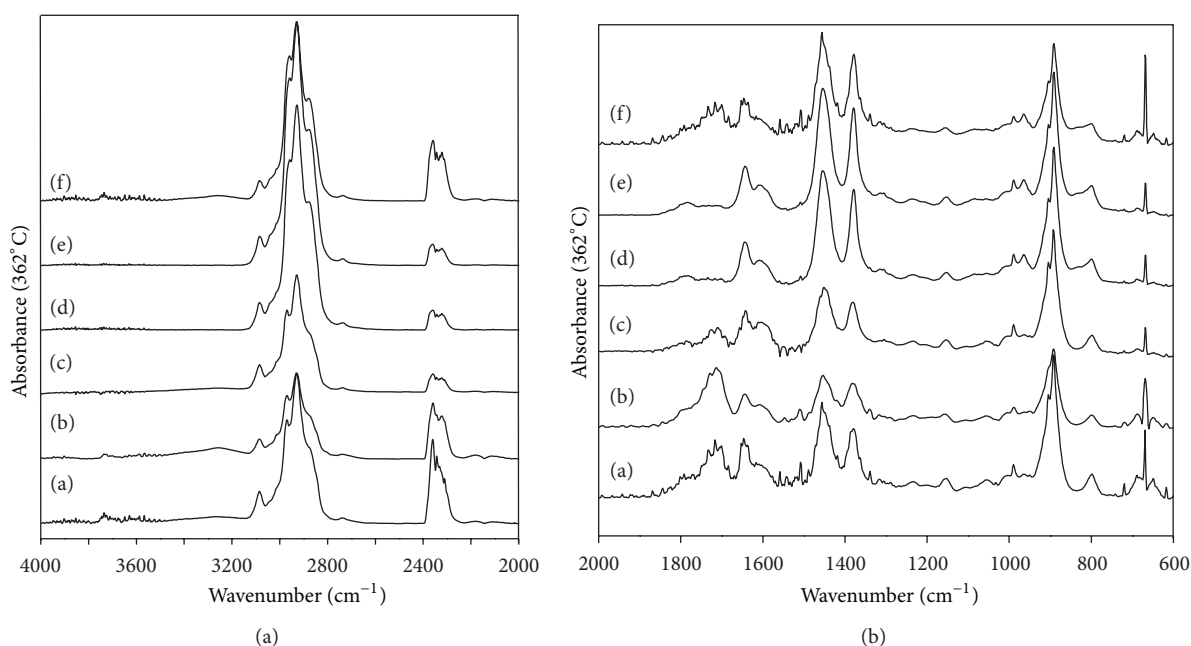


FIGURE 6: (I) 2D spectra (2000–4000 cm⁻¹) extract analysis TG/FT-IR (temperature 362°C) for pure NR membranes compared to NR/Au membranes prepared at (a) NR; (b) 6 min; (c) 9 min; (d) 15 min; (e) 30 min; and (f) 60 min reduction times. (II) 2D spectra TG/FT-IR (600–2000 cm⁻¹).

degradation and subproducts, like amides, amines, proteins, and carbohydrates, among others. The total characterization and analysis of thermal and mechanical properties has been reported [29]. The spectra extracted from the thermal analysis at different temperatures are shown in Figure 5(b). A comparison between the spectra of natural rubber and those

of the NR/Au membranes for different reaction times is given in Figure 6.

The peaks obtained between 2200 and 2400 cm⁻¹ are attributed to the CO₂ and CO molecules released during the thermal analysis. Between 2800 and 3200 cm⁻¹, the compounds relative to C–H (isoprene compounds) are observed.

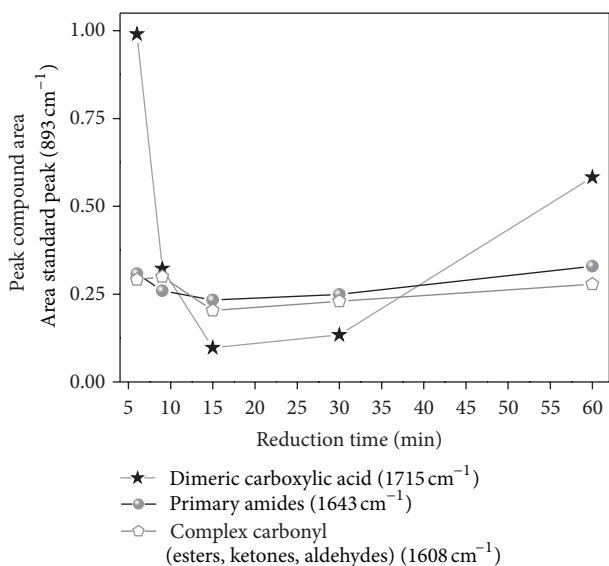


FIGURE 7: Comparison between the areas under the peaks characterized during the TG/FT-IR analysis with respect to the standard peak (relative intensity).

Peaks between 1600 and 1650 cm^{-1} are attributed to the complex carbonyl (esters, ketones, and aldehydes), proteins and primary amides. The peak in 1715 cm^{-1} can be attributed to the stretching symmetric C=O of carboxylic dimer acid ($-\text{COOH}$). It seems reasonable to postulate that the reducing reagents linked to formation of gold nanoparticles are amides, carboxylic acids, and protein constituents in general.

The comparative analysis between intensity of the peaks attributed to reduction of gold nanoparticles was realized by calculating the relation of the area under lines of these peaks with the area of the standard and distinct peak in spectra maintaining an equal measurement interval of wavenumber (Table S2 supporting information) showed in Figure 7.

Compounds presenting an exponential decrease in quantity relative to increase of the reduction time until 15 minutes, act directly in the synthesis of the nanoparticles proportionally to reduction time. However, for reduction times over 30 minutes, a small increase of these compounds is detected, which may correspond to slower reactions kinetics. The concentration of organic groups, like amide and carboxylic acids groups, leads to increase of the relative intensity evaluated by FT-IR spectroscopy.

3.3. Study of the Gold Nanoparticles Dispersed in Solution. After the evaluation of NR/Au substrates, we analyzed the solution to study the formation of gold nanoparticles relative to a different latex thermal treatment. Figure 8 shows the UV-Vis spectroscopy of solution relative to 120 min of reduction time comparing the use of natural rubber membranes as reducer agent prepared at 65, 80, and 120°C by annealing.

The solution's color changes between 15 and 30 minutes, more intense purple color with the increase of the temperature of preparation of the natural rubber membranes (inset).

TABLE 2: Size measurements from SEM microscopy images of gold nanoparticles prepared in solution (120 min). Synthesis using natural rubber membranes annealed at (a) 65°C; (b) 80°C, and (c) 120°C.

Sample	Statistical function—arbitrary line (nm)		
	NR (65°C)	NR (80°C)	NR (120°C)
Count	84	96	280
Mean	138.20	51.25	70.11
Minimum	43.93	23.88	36.55
Maximum	433.68	88.19	158.03
Standard Deviation	88.49	13.36	21.53

The bands around 560 nm are attributed to the LSPR of gold nanoparticles.

Figure 9 presents the SEM microscopy results from gold aqueous solution after the synthesis of nanoparticles at 120 min of reduction time, using natural rubber membranes.

The membranes annealed at 65°C showed lowest absorbance due to gold nanoparticle plasmons. The microscopy shows the presence of small circular gold nanoparticles (Figure 9(a)). These results could be explained by the discharge of reducing agents provided by the natural rubber membranes prepared at 65°C. The amount of nanoparticles increases with the rise of the annealing temperature of membrane fabrication; see, for instance, the results of the synthesis for membranes annealed at 80°C (Table 2). The natural rubber membranes annealed at 120°C produce larger nanoparticles with a more homogeneous size distribution (Figure 9(c)) that is attributed to greater amount of reducing agents released by the membrane into the solution.

According to this, the best annealing temperature of the natural rubber membranes to prepare gold nanoparticles solution should be between 80 and 120°C. However, synthesis of gold nanoparticles on the natural rubber surface, for SERS and SERRS substrate active, should be better when natural rubber membranes annealed at 65°C are used.

4. Conclusion

In this report of a new green chemistry, simple and clean method for in situ synthesis of gold nanoparticles dispersed in solution and on the surface of the flexible substrate is presented. Scanning electron microscopy images show that specific conditions for membrane fabrication can lead to a homogeneous distribution of the nanoparticles on surface of the membranes and colloidal solutions. Managing the reaction time (immersion time) permits to control both the surface coverage and the nanoparticle size. Thermogravimetric analysis coupled with FT-IR spectroscopy and FT-IR/ATR on the membrane surface shows significant variations in the peak assigned to nonrubber components (amines, carboxylic acids) due to gold nanoparticles incorporation, when compared with the spectrum of pure natural rubber membrane, supporting the identification of the components responsible for the gold nanoparticles formation.

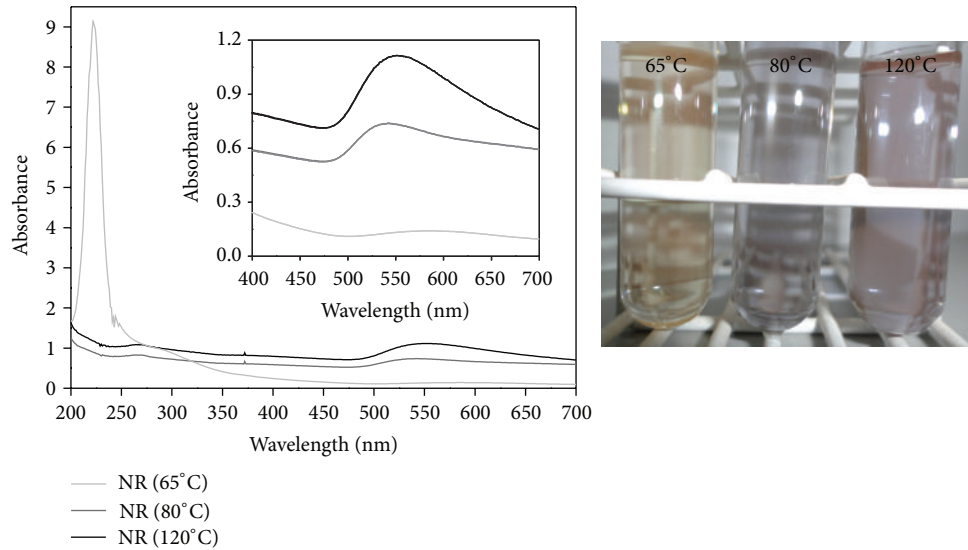


FIGURE 8: UV-Vis spectroscopic analysis of solutions used in the synthesis of gold nanoparticles for 120 min reduction time with natural rubber prepared at 65, 80, and 120°C casting temperature.

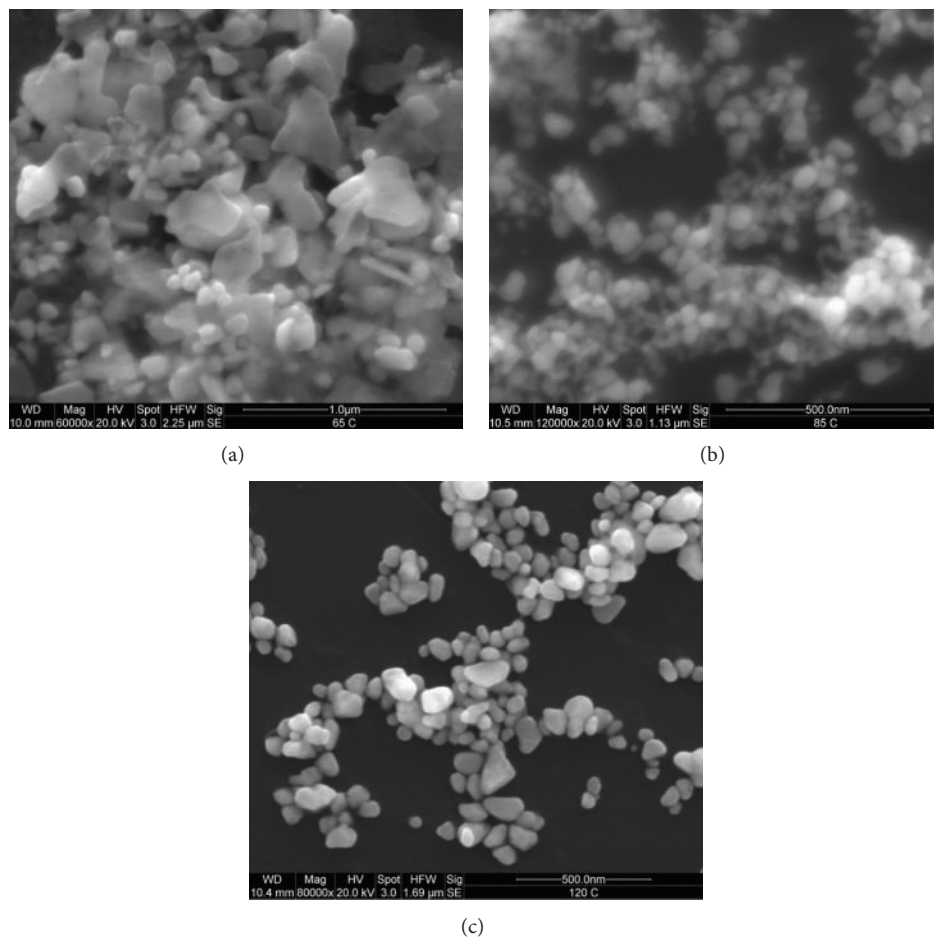


FIGURE 9: SEM microscopy analysis of solution used in synthesis of gold nanoparticles for 120 min reduction time using natural rubber (reducing agent) annealed at (a) 65°C, (b) 80°C, and (c) 120°C temperature. The solution is centrifuged to concentrate the amount of nanoparticles before SEM analysis.

Acknowledgments

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