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Research Article

One-Step Green Synthesis of Metallic Nanoparticles Using Sodium Alginate

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Metallic nanoparticles have been focus of research because of their characteristic properties, specifically the LSPR which can have wide applications in biomedical sciences and engineering. Currently, traditional physical and chemical methods can synthesize these nanoparticles but their disadvantages such as costs, time, effectiveness, and toxicity of precursors provide a wide range of problems for the synthesis of these nanoparticles. Recently, some natural polymers and organic compounds have been used for the synthesis of nanoparticles by green methods. In this study, we synthesize copper, silver, and gold nanoparticles using sodium alginate as reducing and stabilizing agent under microwave irradiation. The LSPR for each system was observed by UV-vis spectroscopy. Particle size distribution and zeta potential demonstrate the size and stability for these nanoparticles. FESEM and TEM microscopies have shown the size and morphology of these systems correlated with UV-vis, particle size distribution, and zeta potential analyses. The study demonstrates a rapid, facile, cheaper, and one-step green method of synthesis for these metallic nanoparticles being an alternative to the conventional methods used for synthesis of metallic nanoparticles.

1. Introduction

Metallic nanoparticles have been investigated because of their characteristic properties and applications in the biomedical sciences and engineering, plus the interest for use in nanotechnology. These nanoparticles such as gold, silver, and copper differ from bulk materials due to the optical response of the excitation of localized surface plasmon resonance (LSPR). This phenomenon is coherent oscillations of conduction electrons in the excited metal surface due to the interaction with electromagnetic radiation.

These oscillations provide a band of extinction in the range of infrared, visible, and ultraviolet spectrum. The spectral position (wavelength) of these phenomena is very sensitive to the type of metal, size, shape, and dielectric surrounding on the media [1].

This field of research is known as "plasmonics" [2–4] and has been under research due to potential applications in small devices such as sensors and photonic circuits and also in medical diagnostics and therapy [5–9].

However, obtaining these nanoparticles by chemical or physical methods is complicated due to the consumption of energy and time, costs of equipment, and the toxicity of chemicals.

There are certain ways of synthesizing metal nanoparticles by physical methods; the most typical syntheses are the nanospheres lithography (NL) [10] and the electron beam lithography [11]. The main disadvantages of these methods are the restriction on nanoparticles' morphology for NL and a low yield and high investment costs for the EBL method. These disadvantages are overcome by chemical methods [12], specifically the chemical reduction.

This method has the possibility of synthesizing nanoparticles with controlled shapes and sizes and it has been characterized by its rapid progress in recent years with synthesis of different morphologies like spheres [13], rods [14], prisms [15, 16], cubes [17, 18], and discs [19, 20], among others [21]. This combination of shapes and sizes provides different response in their optical properties, which can be

Table 1: Considered values for the experiments for each system.

Ion	MW time of reaction [min]			Metal ion concentration [mM]			pH
	High	*Middle*	*Low*	*High*	*Middle*	*Low*	*Maximum*
Gold	3	2	1	10	0.2	0.004	12.9
Silver	3	2	1	10	0.2	0.004	10
Copper	3	2	1	10	0.2	0.004	8

Table 2

Experiment	Time of reaction	Metal ion concentration
1	High	High
2	High	Low
3	High	*Middle*
4	Low	High
5	Low	Low
6	Low	*Middle*
7	*Middle*	High
8	*Middle*	Low
9	*Middle*	*Middle*

used in different applications, depending on the requirement or field of study.

Many of these syntheses are carried out using reducing agents such as sodium borohydride [22, 23], hydrazine [24], N,N-dimethylformamide [25], and other organic compounds [12, 26, 27] providing nanoparticles with a high reactivity. However, many of these compounds are related to the toxicity and biological risk [28]. Similarly, the stabilizing agents used for the synthesis include organic molecules like triphenylphosphine [29], polyvinyl alcohol [30], and polyvinylpyrrolidone [31], which are toxic and difficult to dispose environmentally [32].

Recently, some natural polymers and organic compounds such as chitosan [33], starch [34, 35], polypeptides [36], heparin [37], and hyaluronic acid [38] have been used for the synthesis of nanoparticles by green methods. Some of these compounds have a dual role of both reduction and stabilization of metallic nanoparticles, allowing a one-step synthesis [39]. In this work, the synthesis of copper, silver, and gold nanoparticles is presented using sodium alginate under microwave irradiation. This green synthesis method allows a facile, rapid, and one-step synthesis of these nanoparticles.

2. Materials and Methods

2.1. Synthesis of Metallic Nanoparticles. The synthesis of these nanoparticles was planned according to the interaction of metal ions concentration, time of reaction in the microwave, and a specific pH value for each system (see Table 1).

Experiments were carried out considering all the interactions for each system as it is showed in Table 2.

For preparing the 9 experiments, in a beaker, 90 mL of ethylene glycol, 6 mL of sodium alginate 10 mM, and 3 mL of $NaCO_3$ 0.1 M were added. Then the solution was mixed and the pH was adjusted at 11, 10, and 12.5 for copper, silver, and gold experiments, respectively. From this solution, 10 mL was taken and placed in a vial for performing the synthesis. This was repeated for the rest of the experiments.

Then, 1 mL of the solution of $CuSO_4{\cdot}5H_2O$, $HAuCl_4$, and $AgNO_3$ was added for the respective concentration according to Table 2. Then, the beaker was placed in the microwave (MW).

After the heating in MW, the solution for each experiment and system was sonicated for 1 min, and then it was analyzed using UV-visible (Beckman Coulter DU 800). The experiment with the best plasmonic absorption was selected in order to do the following characterizations: using a concentration of 10 mM for all three metal ions and 2 min. for copper and 1 min for silver and gold experiments.

2.2. Particle Size Distribution and Zeta Potential. Particle size distribution and zeta potential were measured using a Zetasizer (Nano-ZS; Malvern Instruments Ltd., Malvern, UK). The nanoparticles solutions were diluted in distilled water placing 50 μL of the sample in 2 mL of distilled water with a pH of 6.58 ± 0.23.

2.3. FESEM and TEM Analysis. The characterization using FESEM was carried out using an aluminum substrate. It was polished and washed with distilled water and acetone for three times; then, a drop of the nanoparticles solution was placed on the substrate and the solvent was allowed to evaporate at room temperature and it was analyzed using JEOL JSM-7401f microscope (JEOL USA, Inc. MA, USA).

TEM analysis was performed using Zeiss EM 10C 10CR TEM (Carl Zeiss Meditec, Oberkochen, Germany) equipment. The nanoparticle solutions were sonicated for 10 seconds, and 10 μL of each one was taken and then placed onto the copper grid (carbon-coated copper grid, 200 mesh) and dried at room temperature, and then it was analyzed by TEM.

3. Results and Discussion

3.1. Synthesis of Metallic Nanoparticles. UV-vis analyses for the synthesis of copper, silver, and gold nanoparticles are shown in Figure 1. The spectra for the experiments of copper at 1 and 3 min of reaction on MW for the three different concentrations of metal ion do not show any characteristic LSPR absorption of copper nanoparticles. However, at 2 min for the middle and high concentrations, LSPR at 600 nm is presented. This result concords with the reports on the literature about the LSPR absorption for spherical copper nanoparticles [40].

The presence of the LSPR absorption on the experiment with 2 min of reaction time is because for 1 min the time is not

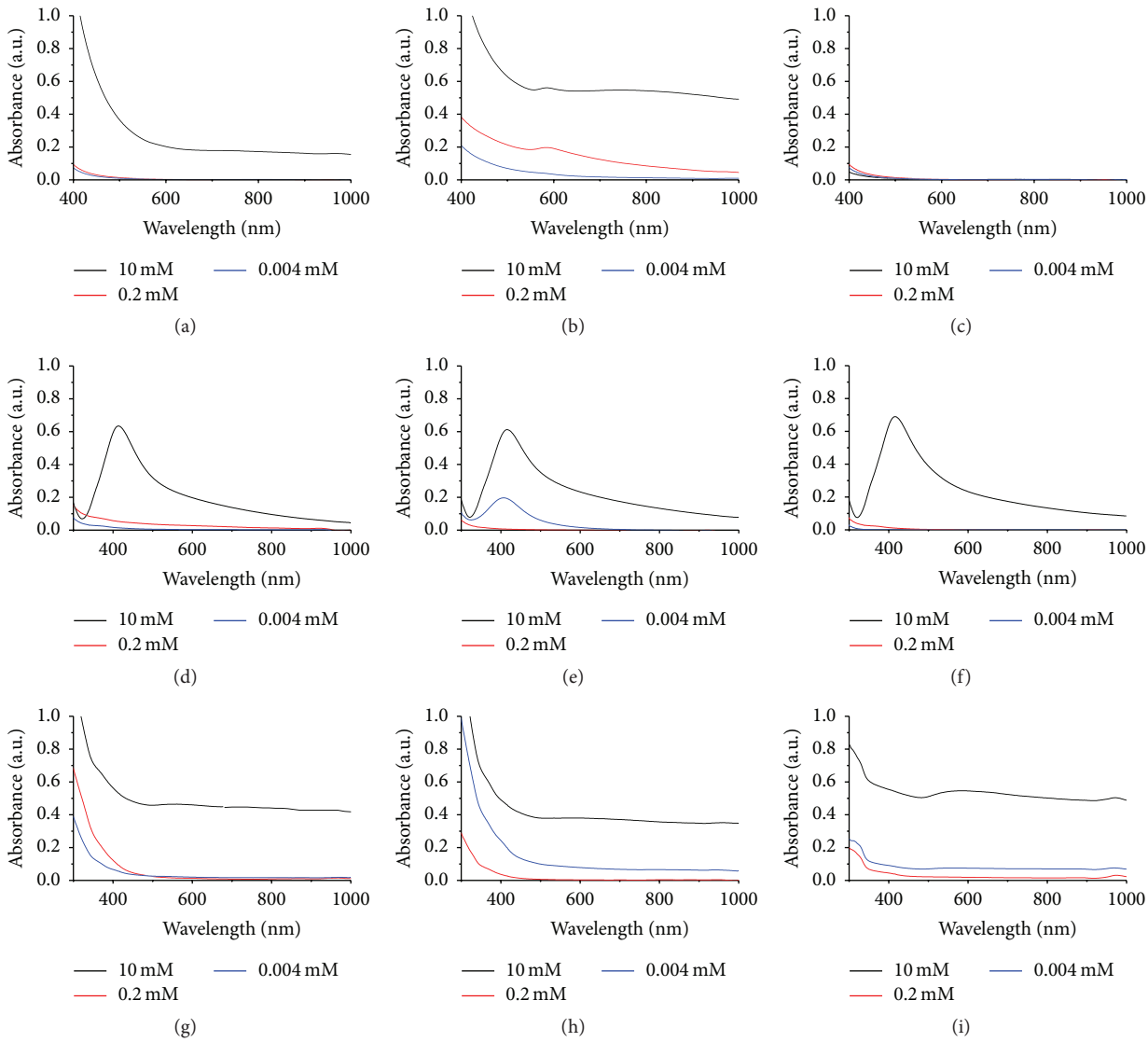

Figure 1: UV-vis analysis for the synthesis of copper (a, b, c), silver (d, e, f), and gold (g, h, i) nanoparticles using sodium alginate with a reaction time on MW of 3 min (a, d, g), 2 min (b, e, h), and 1 min (c, f, i). Black line is related to a concentration of 10 mM, red for 0.2 mM, and blue for 0.004 mM.

enough for the formation of these nanoparticles. The highest time of reaction induces a formation of black pellets and these could be composed of carbon from the decomposition of alginate molecule due to the heat on the reaction.

For silver experiments, the 3 different reaction times with the highest (10 mM) concentration show the characteristic LSPR absorption at 400 nm for spherical silver nanoparticles [41]. Also, the experiment, exposed at 2 min of MW radiation with the lowest concentration, shows the same plasmon absorption.

In the case of gold experiments, the sample that only exhibits a characteristic absorption of a LSPR is when a concentration of 10 mM and a time of 1 min in MW are used. This absorption is characteristic to spherical gold nanoparticles [42]. As well as copper nanoparticles, gold has the same problem at 3 min of reaction time.

3.2. Particle Size Distribution and Zeta Potential. The particle size distribution for copper, gold, and silver nanoparticles is shown in Figure 2. Copper experiment exhibits a size of 250 nm and for gold and silver nanoparticles, there is a similar pattern on the size distribution; there are two peaks: one is around 10 nm to 20 nm, and the other one is presented on 150 nm and 185 nm, respectively.

According to the LSPR absorption of copper, silver, and gold nanoparticles (Figure 1), it is not possible to assume that these sizes are related to the real size of nanoparticles. This is explained according to the size of nanoparticles; if these present a size higher than 100 nm (including the three systems), the LSPR absorption would be different and this phenomenon could be presented in a different wavelength [43].

In addition, it is reported that alginate could present hydrogen bonds [44] and this could be important because

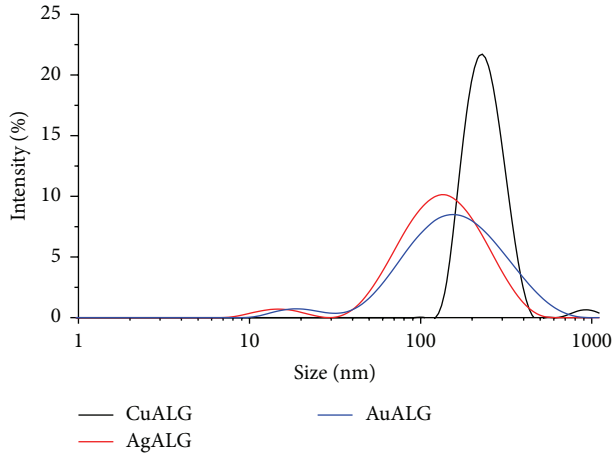

Figure 2: Particle size distribution for copper (black), silver (red), and gold (blue) nanoparticles.

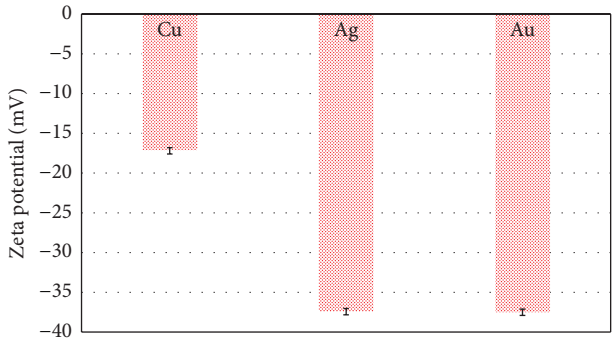

Figure 3: Zeta potential for the synthesized nanoparticles (red) dispensed in distilled water at pH of 6.58 measured at room temperature.

the alginate is presented on the surface of nanoparticles and this interaction could agglomerate more nanoparticles for making a bigger nanoparticle.

Also, for zeta potentials (Figure 3) for silver and gold nanoparticles were -37 ± 2.0 mV and -40 ± 0.4 mV, these values are associated with the stability of these systems; for copper NPs this value was -17.2 ± 3.5 mV. It is important to say that this stability could be related to the agglomeration which occurs in all the systems where at a high zeta potential the agglomeration is less.

3.3. FESEM and TEM Analysis. Figure 4 shows the FESEM and TEM micrographs for copper, silver, and gold nanoparticles. Copper nanoparticles (Figure 4(a)) show a spherical morphology and these nanoparticles had a size less than 100 nm correlated with the LSPR absorption shown on UV-vis analysis. In addition, these analyses demonstrate higher sizes attributed to agglomerates in the sample. The presence of these agglomerates is according to the zeta potential value and particle size distribution.

Silver nanoparticles exhibit an agglomeration (Figure 4(c)) but it is evident that these agglomerates are composed of smaller nanoparticles than 100 nm as it is observed in TEM analysis (Figure 4(d)). Similarly, gold nanoparticles exhibit sizes smaller than 100 nm and agglomerates in a linear way. In addition to copper characterization, these results are correlated with the previous characterizations as UV-vis, zeta potential, and particle size distribution.

4. Conclusions

An easy and simple one-step green synthesis of copper, silver, and gold nanoparticles using sodium alginate under microwave irradiation was reported. Synthesis was evaluated in terms of reaction time under microwave irradiation as well as concentration of metal ions. The LSPR characteristic for every system was proved using UV-nanoparticles having a correlation with the morphology observed using FESEM and TEM characterization likewise with the particle size distribution and zeta potential. This method proves to be rapid and green with a low cost from the chemicals to the synthesis of these nanoparticles and it could be an alternative to the conventional methods used for synthesis of metallic nanoparticles.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

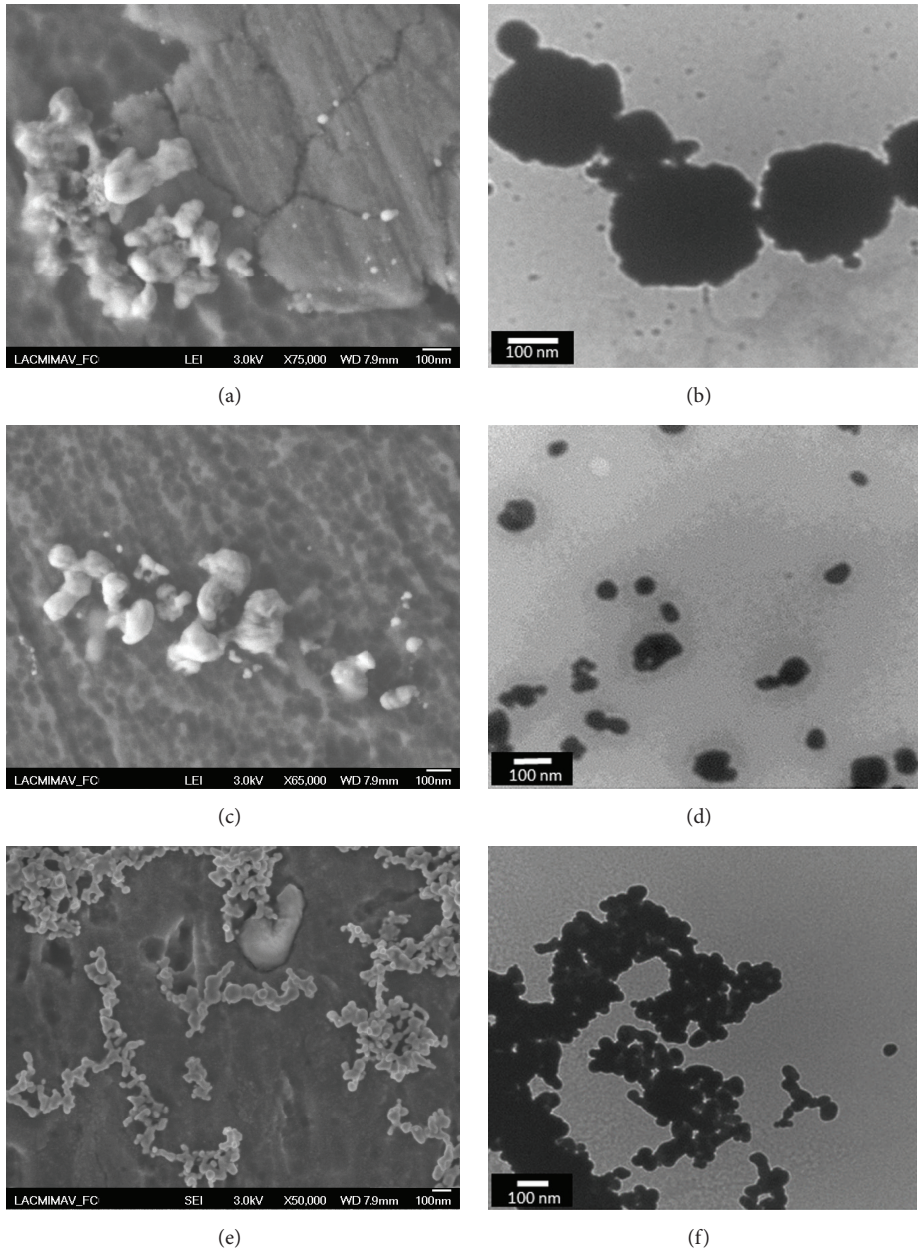

Figure 4: FESEM and TEM analyses for copper ((a) and (b)), silver ((c) and (d)), and gold ((e) and (f)) nanoparticles.

Acknowledgments

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