A photocatalytic and electrochemical study of gold nanoparticles synthesized by a green approach

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Abstract

Quasi-spherical gold nanoparticles mixed with a controlled amount of gold nano triangles were obtained through a green chemical method using leaf extract of Loeselia mexicana. Moreover, the influence of the extract and HAuCl₄ solution concentration in the morphology of the nanoparticles was studied. The nanoparticle preparation was performed by varying the concentration of the extract and precursor salt. The catalytic activity of the as-prepared nanoparticles was studied by the reduction of methylene blue, rhodamine B, and gentian violet organic dyes. Also, cyclic voltammetry profiles were obtained in order to analyze the electrochemical response of the nanoparticles. The morphology and structural characterization were analyzed by UV–vis, SEM, TEM, FTIR, and XRD. The SEM analysis reveals gold nanoparticles with spherical and triangular morphologies. The UV–vis spectra revealed that the extract concentration influenced the morphology and amount of the obtained gold nanoparticles. The XRD and TEM analysis showed that gold nanoparticles presented a face-centered cubic lattice structure. The cyclic voltammetry analysis confirms a high-sensitivity electrochemical response and stability corresponding to the gold nano triangles. Finally, the presence of gold nano triangles shapes influenced the efficiency of the degradation of the dyes due to their high specific surface area.

1. Introduction

Nanomaterials have recently become of great interest due to the wide variety of technological applications related to their different properties compared to bulk materials [1–3]. Noble metal nanoparticles, such as gold, silver, palladium, have a wide variety of applications [4, 5]. Among them, gold nanoparticles (AuNPs) stand out due to their attractive chemical and optical properties, which make them suitable for applications in catalysis [6, 7].

Chemical reduction methods are effective ways to obtain metallic nanoparticles with different shapes. They employ reducing reagents and stabilizers, such as sodium borohydride and hexadecyltrimethylammonium bromide (CTAB), respectively [8–11]. However, their reaction byproducts are sometimes considered harmful to the environment and health [12–14]. Therefore, obtaining new synthesis methods with low environmental impact continues to be a challenge for the researchers [15].

In recent years, researchers have used biological systems such as plants and fungi for the production of nanomaterials [16–19]. For example, extracts of medicinal plants can be used as both stabilizing and reducing agents for the preparation of metallic nanoparticles [20]. The green method is simple, economical, and can be used on a large scale [21].

Green synthesis employing extracts of medicinal plants has been used to control the obtained nanoparticles shapes, which determines their optical and catalytic properties [22]. Controlling the morphology during the biosynthesis process is essential to achieve consistent properties. Recently, AuNPs have been widely studied in electrochemistry due to their physic-chemical properties [23–25]. The morphology of the AuNPs directly
influences their electrochemical properties. Furthermore, the electrochemical analysis has shown several advantages, such as simple instrumentation and easy signal quantification [26].

The textile industry is one of the highest polluters due to the number of organic dyes discharged into wastewater. Textile dyes are considered toxic and harmful for animals and plants, being poorly biodegradable and resistant to environmental conditions [27–29]. Several methods, including the photo-catalytic technique using metal nanoparticles, can remove or degrade organic dyes at room temperature [30].

Thus, in this work, AuNPs were biosynthesized by changing the concentration of L. mexicana leaf extract. The catalytic activity of the AuNPs was studied using the methylene blue (MB), rhodamine B (Rhb), and gentian violet (GV) dyes degradation. Additionally, an electrochemical analysis was realized using the cyclic voltammetry technique (CV). L. mexicana is used in traditional medicine to treat gastrointestinal problems [31].

2. Materials and methods

2.1. Green synthesis

L. mexicana extract was prepared by mixing 10 g of leaf powder in 100 ml of distilled water at 70 °C for 10 min. The extract was filtered and allowed to cool at room temperature. The first experimental part was carried out by setting the HAuCl₄ concentration at 2 mM and varying the L. mexicana leaf extract concentration from 100 to 1.2 mg ml⁻¹. The second part was done by setting the L. mexicana leaf extract concentration at 5 mg ml⁻¹ and varying the HAuCl₄ solution concentration from 10 to 0.1 mM. The HAuCl₄ solution was mixed with L. mexicana leaf extract in a volumetric ratio of 1:1 and kept at 40 °C water bath for 25 min.

2.2. Characterization

The formation of the products was monitored by UV–vis spectroscopy (Ocean Optics USB 4000). The size and morphology were analyzed in a scanning electron microscope (JEOL JSM-7600F SEM), and the elemental composition by energy dispersive spectroscopy (EDS). Size, morphology, crystalline phases, and orientation were analyzed in a transmission electron microscope (Philips Tecnai F20 TEM). In order to examine the crystalline phases, a Bruker D8 advance diffractometer DAVINCI Lynx eye was employed, using CuKα radiation. Meanwhile, Fourier transform infrared spectroscopy (FTIR) was used to obtain functional groups information of the dry leaf extract by using a Bruker Tensor 27 spectrophotometer in the range of 750 to 4000 cm⁻¹.

2.3. Electrochemical analysis

The electrochemical experiments were performed using a BioLogic VSP potentiostat at room temperature. The employed electrodes were the glassy carbon (GC) as the working electrode, saturated calomel (SCE) as the reference electrode, and graphite carbon as the counter electrode. GC was polished with alumina slurry and rinsed with distilled water. 150 μl of each sample was dispersed with 1 mg of carbon powder, with the aid of ultrasonic agitation. Then, 10 μl was dropped with 7 μl of nafion on the cleaned GC electrode and let dry at room temperature. The electrochemical analysis of the modified electrodes and the GC bare was performed at 25, 50, 75, 100, 150, 200, 250, and 300 mV s⁻¹ in 0.5 M of H₂SO₄ and 0.3 M of KOH media. Also, 10 CV cycles of the modified electrodes at 50 mV s⁻¹ were performed in both media.

2.4. Catalytic activity

The catalytic activity was evaluated by taking 5 mg of washed products and mixing with 3 ml of MB, Rhb, and GV solutions with moderate agitation. The dye solutions without AuNPs were maintained as control samples. Dye degradation was monitored by UV–vis spectroscopy.

3. Results and discussion

The reduction of the Au³⁺ ions was performed by using the L. mexicana leaf extract. It could be seen that the solution changed from yellowish to purple after 20 min of reaction, which indicates that the Au³⁺ ions were reduced to Au⁰ and grown to form the AuNPs. Figure 1 shows the UV–vis spectra of the variation of L. mexicana leaf extract concentration on the synthesis of the nanoparticles. An SPR-peak situated at 537 nm corresponding to the typical quasi-spherical gold nanoparticles (AuNSs) was observed [32]. The highest absorbance value indicating a high performance of nanoparticle formation occurs for 30 mg ml⁻¹ extract concentration. Thus, the amount of AuNSs decreased for extract concentration values below (figure 1(a)) or above 30 mg ml⁻¹ (figure 1(b)).
From the extract concentration of 10 mg ml\(^{-1}\), an SPR peak is observed in the wavelength range between 860–740 nm corresponding to triangular gold nanoparticles (AuNTs)\([33, 34]\). This SPR-peak shifted to shorter wavelengths as the extract concentration increased up to 30 mg ml\(^{-1}\) and disappeared at a concentration of 60 mg ml\(^{-1}\) (figure 1(b)). It has been reported that a blue-shift indicates the presence of smaller particle sizes. Thus, as the concentration of the extract increased from 10 to 50 mg ml\(^{-1}\), AuNSs, and AuNTs coexisted.

It is essential to mention that a mixture of AuNPs and AuNTs was obtained at relatively short reaction times (20 min), which indicated higher reaction rates compared to other works\([35]\). Also, these mixtures were obtained using only 10 mg ml\(^{-1}\) of the plant extract, which meant a substantially less amount than the previously used, implying a low-cost method\([36]\).

Figures 2(a)–(c) show SEM images of the formation of AuNTs coexisting with AuNSs, which decreased in size after increasing the extract concentration. For example, an insignificant amount of AuNTs having \(\sim 42\) nm was observed for 60 mg ml\(^{-1}\) extract concentration (figure 2(a)). Figure 2(b) shows that the obtained AuNTs increased in quantity and size up to \(\sim 136\) nm for 15 mg ml\(^{-1}\) extract concentration. Finally, figure 2(c) shows AuNTs with \(\sim 420\) nm in size for 10 mg ml\(^{-1}\) extract concentration. Furthermore, figure 2(d) shows the EDS chemical analysis of the obtained products, showing that the AuNPs are composed of the Au element.

Similarly, the HAuCl\(_4\) concentration influenced the absorbance intensity of the SPR-peak and the formation of the AuNTs (figure 3). For example, for 3 mM of HAuCl\(_4\), the formation of AuNSs was greater. Below (figure 3(a)) or above (figure 3(b)) 3 mM, the AuNSs production decreased, and the SPR-peak absorbance was reduced. However, there was no direct relationship between the concentration of the precursor and the AuNTs.
Figure 2. SEM images of the AuNPs synthesized with (a) 60 mg ml$^{-1}$, (b) 15 mg ml$^{-1}$, and (c) 10 mg ml$^{-1}$ of L. mexicana leaf extract concentration. (d) EDS chemical analysis.

Figure 3. UV–vis spectra of the obtained AuNPs by 5 mg ml$^{-1}$ of L. mexicana extract and HAuCl$_4$, varying the HAuCl$_4$ solution concentration between (a) 0.10–3 mM and (b) 4–10 mM.
SPR-peak. Therefore, there was no suitable control in the amount and size of the AuNTs, which indicates that varying the concentration of the HAuCl₄ solution is not a suitable option.

Figure 4 shows SEM images corresponding to the variation of the HAuCl₄ solution concentration. As observed, there was a higher production and size enhancement of AuNTs for low precursor salt concentration. Figure 4(a) corresponds to the sample obtained with 3 mM, wherein a low production of nano-sized AuNTs was observed. On the other hand, figure 4(b) shows a significant number of AuNTs with larger sizes, corresponding to the sample obtained with 0.8 mM. However, it is necessary to mention that no AuNTs were obtained without the presence of AuNSs in any case.

The TEM images shown in figure 5(a) illustrate the HAADF analysis of the sample of 60 mg ml⁻¹ extract concentration with 2 mM of HAuCl₄ (S1). The bright-field TEM image (figure 5(b)) shows only the presence of AuNSs. These nanoparticles have an average size between 10 and 30 nm. The HRTEM image (figure 5(c)) shows fringes with a separation of ~0.23 nm corresponding to the Au fcc crystalline phase with the preferential growth direction along the [111] direction. In the same way, the TEM image, illustrated in figure 5(d), shows a HAADF analysis of the sample of 15 mg ml⁻¹ extract concentration with 2 mM of HAuCl₄ (S2), wherein a mixture of AuNSs and AuNTs was observed. However, the contrast of the AuNTs is lower than the AuNSs due to their low thickness. The bright-field TEM image (figure 5(e)) shows that the AuNTs have an average size of 60–80 nm. In the HRTEM image (figure 5(f)), it was observed that the AuNTs are also composed of the Au fcc phase with fringes separated at ~0.23 nm, revealing that the preferential growth direction was along the [111] direction.

The x-ray diffraction patterns (figure 6(a)) were matched with the reported data corresponding to the face-centered cubic gold phase (JCPDS File No. 00-004-0784). Both the S1 and S2 showed the same diffraction peaks in the same positions. These peaks are located at 2θ = 38.08°, 44.44°, 64.60°, 77.72°, and 81.71°, and were indexed as (111), (200), (220), (311) and (222), respectively. Also, no peaks corresponding to byproducts or impurities were found. The Debye–Scherrer equation was used to obtain the average crystallite size by the full width at half maximum (FWHM) of the (111) peak. The average size of the S1 and S2 was 27 and 21 nm, respectively. For S1, this result matches with the measurements made by TEM; however, the result
corresponding to S2 does not match. The Debye–Scherrer equation calculated the average between the length, height, and thickness of the AuNTs, unlike the value obtained in TEM, where only the size of the edges was measured.

Figure 6(b) corresponds to the FTIR spectra of the dry L. mexicana leaf extract and the dry AuNPs. The band located at 3307 cm\(^{-1}\) corresponds to O–H stretching vibrations, which is characteristic of biomolecules such as flavonoids and terpenes. The band at 2934 cm\(^{-1}\) corresponds to stretching vibrations of C–H, functional groups of alkanes. The band situated at 1616 cm\(^{-1}\), generated by stretching vibrations, indicates the presence of C=O functional groups, which are characteristic of carboxylic acids like citric acid. Also, the band located at 1039 cm\(^{-1}\) corresponds to stretching vibrations of C–N functional groups that belong to the group of amines. It can be observed that the O–H band is more differentiated than the others. Thus, it can be established that compounds, such as flavonoids and terpenes, helped in the reduction of the Au\(^{3+}\) ions.

Due to the high sensitivity of the catalytic sites, CV profiles of the modified electrodes were recorded at 25, 50, 75, 100, 150, 200, 250, and 300 mV s\(^{-1}\) (figure 7). Figure 7(a) shows the scan rate variation of S1 in 0.5 M of H\(_2\)SO\(_4\). First, the bare GC voltammogram recorded at 25 mV s\(^{-1}\) was attached and compared with the modified electrode. It was noted that this voltammogram presented a weak and characteristic signal between −0.3 and −0.5 V versus SCE. Additionally, a peak was observed between −0.3 and −0.5 V versus SCE corresponding to the bare GC electrode, and as observed, a typical peak of Au (111) was present in the region between −0.1 and 0.1 V versus SCE in reverse scan \([37, 38]\). Figure 7(b) illustrates the scan rate study of S1 in 0.3 M of KOH. Similarly, the characteristic peak of the bare GC was observed between −0.3 and −0.5 V versus SCE, and the typical peak of Au (111) between −0.1 and 0.1 V versus SCE. In figure 7(c), the scan rate study of S2 in 0.5 M of H\(_2\)SO\(_4\) is schematized. It was observed that the GC bare signal is negligible. On the other hand, several peaks in
forward and reverse scan corresponding to Au (100), (110) and (111) were observed \[39\], confirming the presence of several Au planes from the different shapes. Figure 7(d) shows the scan rate variation of S2 in 0.3 M of KOH. The presence of the characteristic peaks of GC bare and Au (111) was observed in reverse scan as well as a peak in forward scan between 0.4 and 0.6 V versus SCE. The S2 showed a great variety of electrochemical signals in the acidic media compared to the S1 due to the different nanoparticle shapes of the sample. On the other hand, S1 only generated signals from a single orientation of the AuNSs.

Figure 8 illustrates the stability study of the chemical species performed to 10 cycles recorded at 50 mV s\(^{-1}\). Figures 8(a), (b) correspond to S1, wherein a minimal variation in the intensity of the Au (111) peaks was observed in acidic and alkaline media. Figure 8(c) corresponds to S2 in acidic media. It can be seen that all Au peaks presented almost null intensity variation. Finally, figure 8(d) shows the cycles corresponding to S2 in alkaline media, where once again, a minimal variation in the intensities of the Au (111) peak was observed; however, the Au (111) peak in forward scan disappeared as the cycles were performed, indicating an unstable phase. The modified electrode species corresponding to Au in reverse scan was stable in all analyzes. On the other hand, peaks related to the GC bare showed more significant variation in intensity due to the GC is not entirely inert in electrochemical analyzes, forming thin layers of hydrophilic oxidized carbon that dissolved in the media \[40\].

The electrochemical analysis showed the characteristic signals of Au, which have been previously reported using Au nanoplates and AuNTs synthesized by a green approach \[41, 42\]. However, in acidic media, S2 showed a variety of additional electrochemical signals not previously found (figure 7(c)), indicating that the modified electrode exhibited a high saturation of AuNTs.

UV–vis spectroscopy measured the catalytic activity of the products, as shown in figure 9. The MB (figure 9(a)), RhB (figure 9(b)), and GV (figure 9(c)) dyes have a maximum SPR-peak at 664 nm, 553 nm, and 581 nm in an aqueous medium, respectively. When the AuNPs were added to the dye solution, a gradual decrease reached a minimum at 24 h of the reaction was observed.
Table 1 shows the degradation values of the dyes by the addition of the S1 and S2. The dyes themselves presented stability under normal conditions without the AuNPs addition. When the AuNPs were added, a notable decrease in the SPR-peaks was observed, which indicates that the three dyes showed considerable degradation. Nevertheless, the S2 degraded the organic dyes better compared to the S1. These results can be attributed to the higher specific area of the AuNTs from the S2 in comparison with the AuNSs from the S1. Larger AuNTs have a triangular plate shape and, consequently, a more significant interaction area. Furthermore, these materials were obtained at low concentrations of both leaf extract and precursor salt.

4. Conclusion

In the present investigation, AuNSs mixed with a controlled amount of AuNTs were synthesized using a green approach by L. mexicana leaf extract as a reductant and stabilizer agent. The products were characterized using UV–vis, SEM, TEM, XRD, and FTIR. SEM analysis illustrated a mixture of spherical and triangular morphologies. XRD showed that the Au products have an fcc lattice structure. UV–vis showed that the proportion of AuNSs and AuNTs could be controlled by varying the extract concentration. However, Au nanoparticles with only AuNTs were never obtained. TEM analysis revealed that the obtained AuNSs presented sizes between 10–30 nm, while AuNTs were in the range of 60–80 nm in size. The catalytic study revealed that the higher proportion of AuNTs in the sample improved the degradation efficiency of the dye due to the increase in the specific surface area. Besides, the cyclic voltammetry analysis showed high sensitivity and stability of the AuNPs. However, the sample with nano triangles reveals a wide variety of electrochemical signals showed multiple catalytic sides.
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Figure 9. UV–vis spectra of dyes reduction. (a1) A control sample of MB and its degradation by (a2) S2 and (a3) S1. (b1) A control sample of RhB and its degradation by (b2) S2 and (b3) S1. (c1) A control sample of GV and its degradation by (c2) S2 and (c3) S1.

Table 1. Catalytic degradation of MB, RhB, and GV dyes by the S1 and S2.

| Absorbance decrease | MB (%) | RhB (%) | GV (%) |
|---------------------|--------|---------|--------|
| Control             | S2     | S1      | Control| S2     | S1      |
| 70 min              | 6      | 70      | 57     | 5      | 36      | 30     | 6      | 70      | 61     |
| 24 h                | 6.5    | 98      | 92     | 6      | 85      | 77     | 7      | 91      | 82     |

Table 1. Catalytic degradation of MB, RhB, and GV dyes by the S1 and S2.
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