Optical and morphological properties of Au@Ag core-shell nanoparticles: Influence of different reducing agents

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Abstract. Colloidal suspensions of gold coated with silver core-shell nanoparticles in poly vinyl alcohol were prepared by the seed-mediated growth approach and a comparative study of optical and morphological properties was conducted. Two types of gold seeds were considered. For the first type, a strong reducing agent (NaBH₄) and for the second one, a weak reducing agent (Na₃C₆H₅O₇) were used. Four volumes of AgNO₃ solution were used to obtain silver coatings with different thicknesses. In each case, morphological and optical properties were investigated by transmission electron microscopy and ultraviolet–visible spectroscopy, respectively. Also, numerical calculations of optical absorption were performed with Matlab toolbox for the simulation of metallic nanoparticles, using a boundary element method approach. This study offers practical considerations useful as a route of synthesis at room temperature of this type of nanoparticles, in such a way that a good homogeneity and reproducibility can be achieved. Results here presented show practical details useful in the synthesis of this type of nanoparticles for applications such as catalysis.

1. Introduction

Currently, the domain that exists on the synthesis of bimetallic nanoparticles (NPs) is the result of great scientific efforts, as evidenced by the plethora of researches that exists on their interesting optical and photothermal properties [1,2]. Noble bimetallic NPs have mainly been studied because of their unique optical properties, especially gold (Au) and silver (Ag) have a broad absorption band in the visible region of electromagnetic spectrum [3]. For instance, core-shell NPs of Au coated with Ag (Au@Ag) have attracted special due to possible applications in surface enhanced Raman scattering (SERS), photocatalysis, sensing, medical diagnoses and colorimetric determination of heavy metal ions in water samples [4-6]. There is a great variety of synthesis techniques to produce highly customized NPs; however, there are still a number of fundamental challenges that remain to be addressed and give rise to new directions of work in this field.

One of this is the synthesis of bimetallic NPs containing 10% or less of the secondary metal. This type of NPs is of particular interest for catalysis since the control on the addition of a secondary metal can greatly influence the activity and selectivity of the catalyst for a particular reaction. The small sized NPs encapsulated by a single atomic layer, also referred to as a skin layer (~1.5 nm), are used as
heterogeneous catalysts having the highest possible utilization efficiency and the lowest material cost for the atoms on the surface. On the other hand, nanocrystals with thick coatings (more than six atomic thick layers) have advantages such as the tuning of their optical properties in a wide range and improved thermal and chemical stability [4]. There have been significant advances in the optical and morphological analysis of these Au@Ag core-shell architectures, nevertheless, much of this literature focuses on the synthesis of Au@Ag from Au seeds with ~40 nm of diameter [7-8].

Other studies have been focused on different Ag shell thicknesses of Au@Ag NPs by adjusting the Au seed concentration [9-10]. In an effort to tailor different properties for Au@Ag NPs and improve their performance in catalysis and other applications, scientists have developed a seed-mediated growth approach under a variety of conditions [11]. In this method reducing agents play here an important role in controlling the size distribution of NPs [12]. At present, various reductants are used to synthesize nanocrystals, including bimetallic NPs, such as sodium borohydride, alcohols, gaseous hydrogen, hydrazine, tannic acid and polyvinylpyrrolidone (PVP) [13-14].

In this work, we report a comparative study of optical and morphological properties of colloidal suspensions of Au nanospheres coated with Ag in a poly vinyl alcohol matrix (PVA) based on the seed-mediated growth approach. We study both the influence of the Au core size and the thickness of the Ag shell on the optical and morphological properties of the synthesized NPs when different reducing agents are used. Two types of Au seeds were considered, and four concentrations of Ag were considered in order to obtain Ag coatings with different thicknesses for the two types of Au seeds in the synthesis of the Au@Ag NPs.

2. Experimental details

2.1. Chemicals
Tetrachloroauric acid, Ag nitrate, trisodium citrate dihydrate, sodium borohydride, L-ascorbic acid, sodium hydroxide pellets and PVA were purchased from Sigma-Aldrich and used as received. All chemicals used in the experiment were analytical reagent grade. The aqueous solutions were prepared using ultrapure water.

2.2. Synthesis of gold seeds
The Au NPs were synthesized by the chemical reduction approach, based on the method proposed by Turkevich and Frens [15]. Two types of reducing agents were considered: a strong reducing agent (NaBH₄) and a weak reducing agent (Na₃C₆H₅O₇). The solution reduced with NaBH₄ reached a soft violet color indicating the possible formation of Au seed NPs and solution reduced with sodium citrate turned wine-red (Left and right side of Figure 1(a), respectively). Figure 1(b) and Figure1(c) show transmission electron microscopy (TEM) images of Au seeds using NaBH₄ and Na₃C₆H₅O₇ as reducing agents.

![Figure 1](image-url)

**Figure 1.** (a) Colloidal suspensions of Au NPs using NaBH₄ and Na₃C₆H₅O₇ as reducing agents. TEM images of Au NPs reduced with (b) NaBH₄ and (c) with Na₃C₆H₅O₇.
2.3. Synthesis of gold coated with silver core–shell nanoparticles

Au@Ag core-shell NPs were synthesized by the seed-mediated growth method based on the synthesis route proposed by Pyne, et al [3]. The strategy is based on the gradual reduction of Ag⁺ ions by the addition of AgNO₃ to the solution of Au seeds and ascorbic acid (AA) as mild reducing agent. Different amounts (1.25, 2.5, 3.75, 5 mL) of 1 mM AgNO₃ were added to the above solution to obtain Ag coatings with different thicknesses for the two types of Au seeds.

2.4. Characterization and numerical studies

Ultraviolet-visible (UV-Vis) spectra were recorded using an UV-Vis spectrophotometer Evolution 600, Thermo Scientific. Morphology of the NPs was analyzed using TEM with a FEI Tecnai F20 Super Twin operating at an acceleration voltage of 200 kV. Numerical calculations obtained using the Matlab MNPBEM open source simulation package based on the boundary element method (BEM).

3. Results and discussion

3.1. Visual observations

While the starting Au colloid reduced with NaBH₄ was soft violet, upon deposition of 1.25 mL of Ag salt, a pale purple color was obtained, as shown in Figure 2(a). This result is possible because of the agglomeration of Au seeds due to the absence of a stabilizing agent. In contrast, when Ag⁺ ions increases to 5 mL of AgNO₃ the color changes to deep orange, which means that core shell NPs of Au@Ag were obtained. On the other hand, the color obtained for Au seeds reduced with Na₃C₆H₅O₇ was wine-red, and after the addition of the Ag salt the color changes to yellow. This color change indicates the formation of the Ag coating on the Au core, i.e. core-shell NPs of Au@Ag. Figure 2(b) shows the changes in color of the solution, from soft yellow to deep yellow as the concentration of Ag⁺ ions increases, that is, as the thickness of the Ag coating is increased.

3.2. Ultraviolet-visible absorption spectra

Figure 3(a) and Figure 3(b) shows UV-Vis absorption spectra of Au@Ag NPs synthesized from Au seeds reduced with NaBH₄ with varying Ag volume. The wavelength of maximum absorbance was slightly decreased with the increase in concentration of Ag. The position of plasmon resonance (PR) of the Au reduced with NaBH₄ is 538 nm. When Ag is added, blue shifts to 525 nm, 524 nm, 523 nm, 480 nm for 1.25 mL, 2.5 mL, 3.75 mL and 5 mL, are obtained respectively. On the other hand, the optical properties of the Au@Ag NPs for 5 mL of Ag exhibited a PR at 384 nm, which corresponded to NPs that are mostly Ag. Generally, it is known that Ag NPs have plasmon absorbance at about 400 nm.
Figure 3. (a) UV–Vis absorbance spectra of Au@Ag NPs from Au seeds reduced with NaBH₄ having different thickness of Ag (b) Numerical absorption spectra for a 2.6 nm Au nanospheres with Ag coating thickness of 0.11 nm, 0.115 nm, 0.12 nm and 0.4 nm in a medium with relative dielectric permittivity of 2.75.

The UV-Vis absorption spectra of Au@Ag NPs in a matrix of PVA synthesized from Au seeds reduced with Na₃C₆H₅O₇ with varying Ag volume in Figure 4(a) and Figure 4(b) shows that effectively the optical properties of the Au seeds were influenced by the Ag deposition. Before the addition of Ag, the characteristic peak of the Au seeds reduced with Na₃C₆H₅O₇ was centered at 521 nm (not presented). After the addition of Ag, the PR of the Au is blue shifted to 495 nm and 484 nm for 2.5 mL and 3.75 mL respectively. For these NPs with 1.25 mL of Ag, the characteristic peak of Au predominates (522 nm), since the core of Au is much greater than the thickness of Ag. On the other hand, for Au@Ag NPs with 5 mL of Ag, a new peak appears around 401 nm which indicates that over the Ag shell is dominant over Au core. Finally, for both series of NPs (reduced with NaBH₄ and Na₃C₆H₅O₇) the increasing of the Ag coating thickness produces a significant increasing in the absorption cross section of bimetallic nanoparticle from UV to a large part of the visible spectrum between the resonance peaks corresponding to Ag and Au.

Figure 4. (a) UV–Vis absorbance spectra of Au@Ag NPs from Au seeds reduced with Na₃C₆H₅O₇ having different thickness of Ag. (b) Numerical absorption spectrum for a 21.8 nm Au nanospheres with a Ag coating thickness of 0.7 nm, 2.5 nm, 3 nm and 4.2 nm in a medium with relative dielectric permittivity of 2.20.

3.3. Transmission electron microscopy studies
The morphology of both series of bimetallic NPs was determined by TEM. Figure 5(a) show Au@Ag NPs in a matrix of PVA synthesized from Au seeds reduced with NaBH₄ with predominant spherical shape. Figure 5(b) show some agglomerations that contribute to the formation of particles having irregular shapes. The core diameter of Au has an average of 2.6 ± 0.1 nm. Moreover, the average diameter of 68% of Au@Ag NPs was 5.8 ± 0.2 nm. However, the thickness of the Ag shell deposited onto the Au surface was not possible to measure reliably from TEM images. These results suggest that a strong reducing agent (NaBH₄) for Au seeds facilitates the formation of small sized NPs.
Moreover, the shape of the Au@Ag NPs in a matrix of PVA synthesized from Au seeds reduced with Na$_3$C$_6$H$_5$O$_7$ is highly uniform. Figure 6(a) show TEM images of these bimetallic NPs with spherical geometry using 1.25 mL of Ag and Figure 6(b) show similar bimetallic NPs with a greater thickness of Ag using 5 mL of Ag. The Au core has an average diameter of 21.5 ± 0.4 nm. Besides, the thickness of the Ag shell deposited onto the Au surface was estimated as 2.3 ± 0.2 nm, 2.7 ± 0.2 nm, 3.0 ± 0.3 nm, and 5.0 ± 0.5 nm for 2.5 mL, 3.75 mL and 5 mL, respectively. According to the particle size distribution the average diameter of these NPs was 21.8 ± 0.3 nm. In contrast with the previous type of NPs, the weak reducing agent (Na$_3$C$_6$H$_5$O$_7$) for Au seeds contributed to the formation of relatively large bimetallic NPs. Additionally, the variation of concentration of Ag was found to affect the shell thicknesses of Ag as seen in Figures 7(a) with 2.5 mL, Figure 7(b) with 3.75 mL, and Figure 7(c) with 5 mL of Ag volume respectively.
3.4. Numerical results

Absorption cross sections of both series of bimetallic NPs were calculated using the Matlab MNPBEM simulation package developed by Hohenester and Trügler [16] which is based on the BEM. The NPs are excited by an incoming electromagnetic plane wave in the UV-Vis region with a wavelength greater than the diameter of the nanoparticle such that the calculations are performed within the quasi-static approximation. Table 1 summarizes the conditions for the numerical calculations.

| Type of NPs | Au core diameter experimental (nm) | Au core diameter theoretical (nm) | Ag thickness experimental (nm) | Ag thickness theoretical (nm) | Relative dielectric permittivity of the medium |
|-------------|-----------------------------------|----------------------------------|--------------------------------|-------------------------------|---------------------------------------------|
| Au@Ag-NaBH₄ | 2.6±0.1                           | 2.60                             | Not available                  | 0.40                          | 2.75                                        |
| Au@Ag-Na₃C₆H₅O₇ | 21.5±0.4                         | 21.80                            | 5.00                           | 4.20                          | 2.20                                        |

In Figure 3(b) numerical results for the absorption spectrum for a Au nanosphere with diameter of 2.6 nm and different Ag coatings in a medium with relative dielectric permittivity 2.75, are shown. This situation represents the Au@Ag NPs from Au seeds reduced with NaBH₄ with different thickness of Ag. Although it was not possible in this case to estimate reliably the thickness of the coatings from the TEM images, the numerical analysis seems to suggest that indeed a thin thickness shell is formed. A good agreement with the behavior of the UV-Vis experimental spectra was obtained by assuming coating thicknesses of 0.40 nm, 0.32 nm, 0.31 nm, and 0.30 nm, as shown in Figure 3(b). The separation between the experimental curves of the three lower thicknesses in comparison with the numerical results is possibly due to different concentrations of NPs in each sample. For these three cases it is observed that the highest resonance remains at the resonant wavelength for Au (525 nm), that is, a significant coating is not achieved. However, for the higher content of Ag (5 mL) an increase in the absorption and a widening of the spectrum towards the Ag resonance, is obtained which indicates a higher Ag coating.

Numerical results for Au@Ag NPs from Au seeds reduced with Na₃C₆H₅O₇ are shown in Figure 4(b). The absorption spectra correspond to an Au nanosphere with diameter of 21.8 nm and different Ag coatings (4.2 nm, 3 nm, 2.5 nm, and 1.3 nm of thickness) in a medium with relative dielectric permittivity 2.20. As seen, numerical results are in very good agreement experimental results. It can be noticed that the absorption increases, and the highest resonance is shifted towards the resonant wavelength for Ag when the coating thickness is increased.

4. Conclusions

We have successfully demonstrated a facile approach to the preparation of Au@Ag bimetallic NPs with different size in a PVA matrix. Smaller and morphologically non-uniform Au seeds were obtained with NaBH₄ and in this case, Au@Ag NPs with thinner coatings of Ag were formed. These NPs would have high surface-to-volume ratio, greater number of uncoordinated atoms on their surface, which would make them more reactive and of great interest for catalytic performance (activity, selectively, and durability). Conversely, greater and more uniform Au seeds were synthetized with Na₃C₆H₅O₇ and Au@Ag NPs with higher thicknesses of coatings were obtained. These NPs would allow adjusting more easily of the spectral characteristics of the localized surface plasmon resonances (LSPR), such as position and profile. Absorption UV-Vis results were compared with MNPBEM simulations and good agreement was achieved. Results here presented showed practical details useful in the synthesis of this type of NPs for applications such as catalysis.

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