

Surface Modification of Au Nanoparticles Induced by Time Exposition Under the Electron Beam in TEM: Understanding the Formation of Self-assembled Au Nanoporous Structures

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The gold nanoparticles (AuNPs) have carried great attention in the last years due to the promising application in several fields, such as colorimetric sensing for fast detection [1], detection of molecules by surface-enhanced Raman scattering [2], enhancement of photocatalytic degradation [3], or photothermal therapy [4]. The presence of nanoporous in the Au has opened a new range of possible applications of this material particularly, those related to the optical behavior, such as biomarkers detection [5]. Among the nanoporous configurations in the Au structures, those conformed by nanoparticles have carried great interest in the latest years due to the possibility to control the pore size [6]. There have been efforts for controlling the porous size between the AuNPs group (also known in the literature as gaps) due to a homogeneous optical behavior that can be achieved by controlling the gap size in the nanoporous Au structures [7]. Thus, understanding the path followed by AuNPs to the formation of nanoporous structures could open the doors toward the design of homogeneous gaps in Au-based materials for the application previously mentioned. In addition, this research represents a contribution to the understanding of Au nanoporous structure formation assisted by the energy of the electron beam under a transmission electron microscope.

The methodology of this work is divided into 2 parts: (1) synthesis of AuNPs, and (2) TEM beam interaction analysis. To obtain the AuNPs, 400 μL of chloroauric acid solution (1 mM) was diluted into 3.6 mL of deionized water to set a total volume of a 4 mL aqueous solution. Separately, 1.1 mL of ascorbic acid solution (10 mM) was added to 0.9 mL of sodium borohydride solution (10 mM) to make the so-called precursor solution. Afterward, 250 μL of the precursor solution was added to the chloroauric acid solution previously obtained. The mixing was stirred for 45 s and, finally, the AuNPs were obtained. The as-synthesized AuNPs were placed on a copper grid (for TEM analysis) and observed into a JEOL-ARM200F transmission electron microscope. The sample was imaged under an acceleration voltage of 200 keV. Electron diffraction (ED) of the sample was performed into the same electron microscope. The effect of time exposition (the sample under electron beam) on the structure and morphology of AuNPs was studied.

The AuNPs were obtained with an average diameter of $14.3 \text{ nm} \pm 1.5 \text{ nm}$ as is shown in Figure 1a by a BF-TEM image. The ED of the sample, shown in the insert of Figure 1a, confirms the Au face-centered cubic as the unique phase that constitutes the nanoparticles, this result is in good agreement with other reports of AuNPs [8]. An image of a group of nine AuNPs (Figure 1b) demonstrates that the nanoparticles were obtained as polyhedrons-like particles. From this group of AuNPs, one was selected for being exposed to the electron beam across time. As can be seen in Figure 2a, the atomic arrangement in the AuNP changed in such a way that interplanar distance was 2.17 Å, 2.21 Å, 2.29 Å, and 2.34 Å after 0 s, 2 s, 4 s, and 6 s of exposition time, respectively. The atomic reordering suggests that the energy

supplied by the energy beam is enough to promote atomic migration. Thus, an AuNP was imaged for the same intervals of time to see the effect of atomic migration on the surface. Figure 2b shows that AuNPs modify their morphology across time exposition to the electron beam. In addition, when exposition time is equal to 0 s, the nanoparticle presents a definite morphology like a circle. When the exposition time increases to 2 s, the circle-like shape changes. Then, after 4 s, the asymmetry is more evident and finally, after 6 s of exposition to the beam, the nanoparticle has lost the circle-like shape. Note that the yellow circle in Figure 2b is a visual guide for distinguishing the change in morphology of AuNP, and the diameter of the circle is 16.13 nm in each figure. On the other hand, Figure 2c demonstrates that AuNPs start to agglomerate when the exposition time is equal to 10 s. This behavior continues when the time increase to 30 s, and after 90 s of exposition, both the average size and stacking of AuNPs have notably increased. Note that the stacking behavior allows the formation of gaps (spaces between the nanoparticles). Similar gap structures have been reported by other systems of AuNPs stimulated by energy supplies like temperature increase [5]. Thus, the same phenomena observed in this research could explain the formation of gaps in other Au synthesis methods.

In conclusion, the results suggest that single Au nanoparticles, obtained by chemical reduction methods, can form nanoporous Au structures by the effect of the energy contained in the beam of the electron microscope. The global effect of AuNPs under the electron beam exposition is the surface modification, due to nanoparticle growing, and the stacking between nanoparticles. These phenomena could be responsible in the formation of self-assembled Au nanoporous structures in systems assisted by energy like the thermal [9].

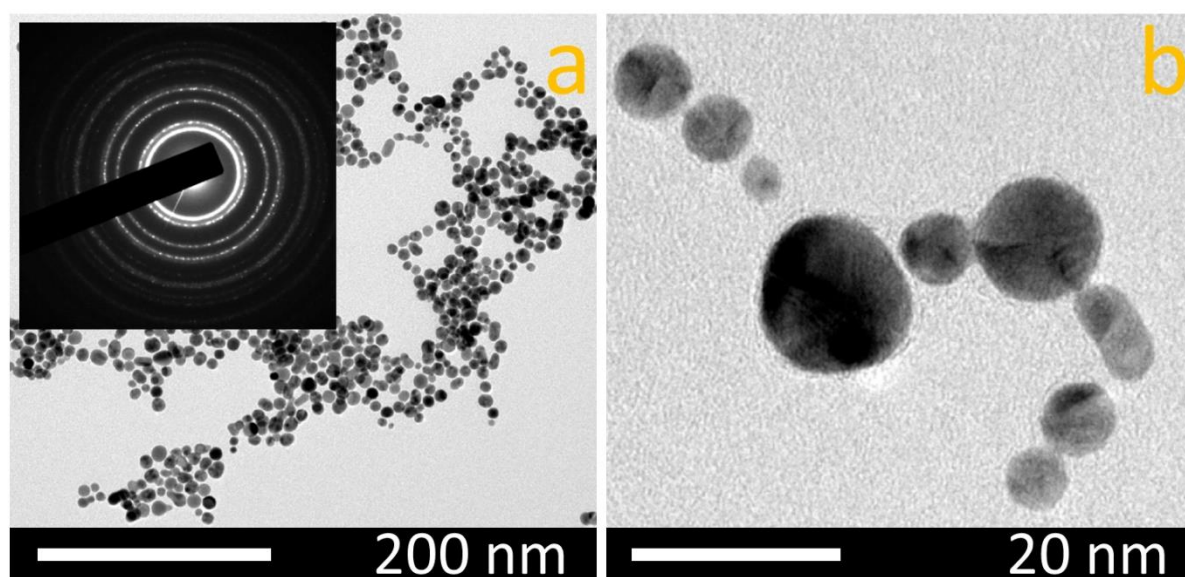


Figure 1. AuNPs imaged by bright-field TEM in (a) a survey view, and (b) a close view of the sample. The insert in (a) shows the ED of the sample.

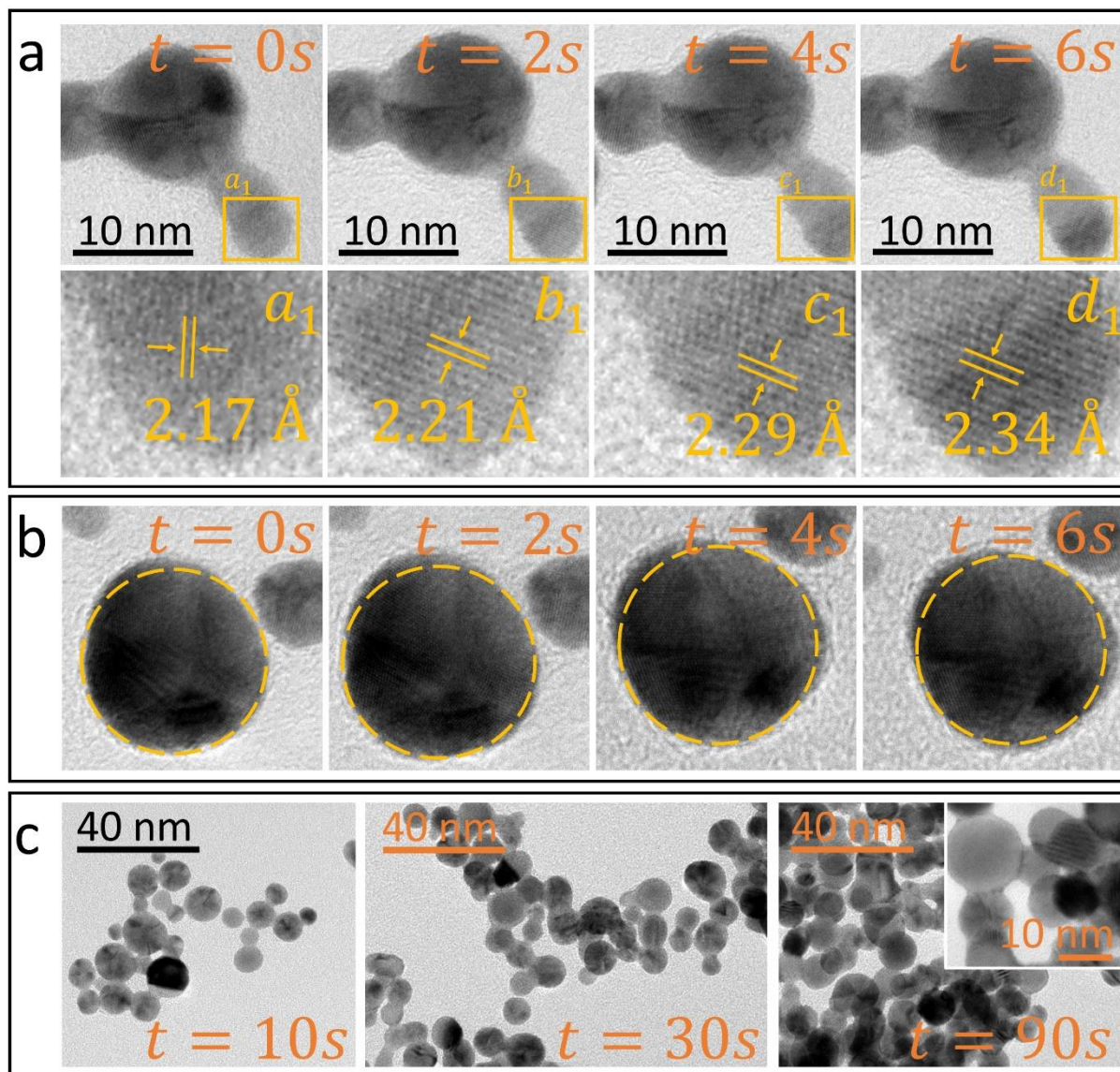


Figure 2. Bright-field TEM images of AuNPs exposed to electron beam across time: (a) shows the evolution of atomic arrangement, (b) shows the modification of AuNPs surface, and (c) shows the formation of the gaps between AuNPs.

References:

- [1] R. Li, et al, *Anal. Methods*, **13** (2021), pp. 5749-5755, <https://pubs.rsc.org/en/content/articlelanding/2021/AY/D1AY01809D>
- [2] D. Zhang et al., *Analytical Chemistry*, **92-23** (2020), pp. 15379–15387, <https://pubs.acs.org/doi/10.1021/acs.analchem.0c02781>
- [3] E.F. Vázquez-Vázquez et al., *Materials Letters*, **290** (2021), p. 129464, <https://doi.org/10.1016/j.matlet.2021.129464>
- [4] A. Al-Kattan1 et al., *J. Phys.: Conf. Ser.*, **2058** (2021), p. 012008, <https://iopscience.iop.org/article/10.1088/1742-6596/2058/1/012008>

- [5] O.E. Cigarroa-Mayorga, S. Gallardo-Hernández, P. Talamás-Rohana, *Appl. Surf. Sci.*, **536** (2021), p. 147674, <https://doi.org/10.1016/j.apsusc.2020.147674>
- [6] K. Sun et al., *J. Mater. Chem. C*, **1** (33) (2013), pp. 5015-5022, <https://pubs.rsc.org/en/content/articlelanding/2013/TC/c3tc30669k>
- [7] P. Pandey et al., *J. Alloys Compd.*, 888 (2021), p. 161504, <https://doi.org/10.1016/j.jallcom.2021.161504>
- [8] H. Ma et al., *Colloids Surf., A Physicochem. Eng. Asp.*, **582** (2019), p. 123889, <https://doi.org/10.1016/j.colsurfa.2019.123889>
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