

Implications on the Tuning of Gold Nanorods Interface: Post-Synthesis Modification Using the Electron Beam in the Transmission Electron Microscope

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Gold (Au) is a widely used material due to its multiple applications [1, 2], which is directly attributed to size under the nano-range (1×10^{-9} m) and morphology [3]. Since the Au was achieved as a nanostructured material, some gold nanomaterials have been proposed to be used in the biomedicine and biotechnology field due to their interesting properties like high electronic conductivity, great biocompatibility, large surface area, the bactericidal effect [4], localized surface plasmon resonance (LSPR) [2], and easy-to-do biofunctionalization procedures [4, 5]. These properties allow some remarkable applications like protein detection [6], biosensors, anticancer activity [7, 8], and enhancement in photocatalytic degradation of water pollutants [9]. In addition, it has been recently proved that some atomic planes located at the interface of metallic nanostructures have a strong influence on the enhancement in properties as catalytic activity [10]. Thus, developing strategies to control the atomic arrangement of Au nanostructures could open the door to novel tools for technology developing toward materials processing.

The chemical synthesis routes, i. e. chemical reduction of HAuCl_4 , allow a high precision in the control of the shape and size of Au nanostructures. The gold nanorods (AuNRs) are complex structures, with large surface areas, that exhibit photoactivity by absorbing the visible light region of the electromagnetic spectrum. This behavior is possible due to LSPR [2]. The post-synthesis modification is a recent proposal to modify features at the interface of nanomaterials to improve the properties by tuning atomic structure [11, 12]. This modification has typically been studied under a focalized energy source such as the electron beam into the transmission electron microscopy (TEM). As the focalized high-energy electron beam can be adjusted about 200~400 keV, allows the modification in atomic network in some materials [12]. This phenomenon can be extrapolated in the future to develop novel post-synthesis techniques toward surface modification in nanomaterials. In addition, post-synthesis modification could be useful for tuning properties linked with applications like catalysis or optical sensing in gold nanostructures. This work contributes to the understanding of the atomic reorganization in AuNRs due to the exposition time to an electron beam. In addition, the implications or the atomic rearrangement on the interface modification are discussed.

The AuNRs were synthesized by the seed-mediated method. This chemical methodology was performed in two steps: (1) preparation of aqueous solutions, and (2) AuNR growing. Three solutions were prepared to obtain a solution 1, labeled as “seed solution”: cetyltrimethylammonium bromide (CTAB, 0.2 M), chloroauric acid (HAuCl_4 , 0.5 mM), and sodium borohydride (NaBH_4 , 0.01 M). Afterward, solution 2, labeled as “growth medium” was formed by mixing four solutions: CTAB (0.2 M), AgNO_3 (0.01 M), HAuCl_4 (0.001 M), and ascorbic acid (7.88×10^{-2} M). All the aqueous solutions were mixed at room temperature. Afterward, the seed solution was added to the growth medium to promote a selective

growing of gold crystals to obtain AuNRs. To clean the AuNRs from remnant reagents in the chemical reaction, the sample was centrifugated and the precipitate was removed. Then, it was decanted and refilled with deionized water. The procedure was done until a pH of 7 was achieved in the solution. Once the sample was cleaned, the AuNRs were observed under the transmission electron microscope (TEM, JEOL ARM200F) with an acceleration voltage of 200 keV. High-resolution TEM (HRTEM) and low-resolution TEM (LRTEM) images were obtained. Also, the electron diffraction (ED) pattern of the samples was recorded in the same instrument. The effect of time exposition to the electron beam on the atomic structure of AuNRs was analyzed.

Figure 1 shows the bright-field TEM micrograph of AuNRs after the cleaning process. The results show that AuNRs were achieved with high control on size and morphology. The average length of the nanoparticles was 51.2 ± 5 nm and the width of 20.6 ± 8 nm. The insert in Figure 1a discloses the ED of AuNRs, which demonstrate that Au is the only element contained in the nanostructures with a face centered cubic structure [8]. As the time of AuNRs under exposition to electron beam was increased, the atomic arrangement was modified. Particularly, Figure 2a shows a single AuNR across 8 seconds of exposition time. This time is enough to completely rearrange a section in the nanostructure. The atomic reordering could be allowed by two steps: (1) loss of crystallinity and (2) recrystallization. The previous idea is supported by the observations made in the circled section of inserts in Figure 1a.

A larger time of electron beam exposure promotes a morphological modification in the AuNRs. Figure 2b shows the modification that underwent the sample across 20 min of exposure time to the electron beam. After 5 min (middle image in Figure 2b) the morphology in the interface was modified in such a way that AuNR lost the original shape. As it can be seen, the AuNRs tend to increment the size and agglomerate when the 20 min were completed. This behavior could be a direct consequence of the atomic rearrangement observed in Figure 2a due to an increment of energy of the environment. This idea has been suggested to be a crucial factor for the stability of AuNRs [2]. The results suggest that high energy sources can promote morphological modification of AuNRs by the effect of TEM.

As concluding remarks, based on the analysis carried out on the AuNRs synthesized by the “seed method”, exposure time to an electron beam with energy of 20 keV promotes an atomic rearrangement in the AuNRs. The atomic rearrangement in the AuNRs appears to be a fast process once the activation energy is provided to the atomic system [13].

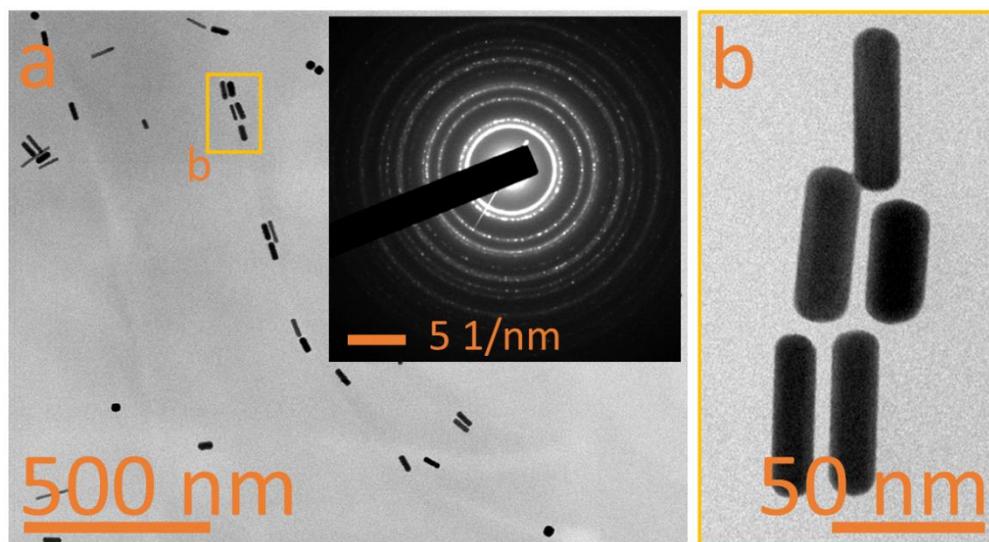


Figure 1. Bright-field TEM image of AuNRs after the cleaning process, (a) shows an image of the AuNRs distribution, and (b) shows an amplified section of AuNRs group. Insert in (a) shows the ED of the sample.

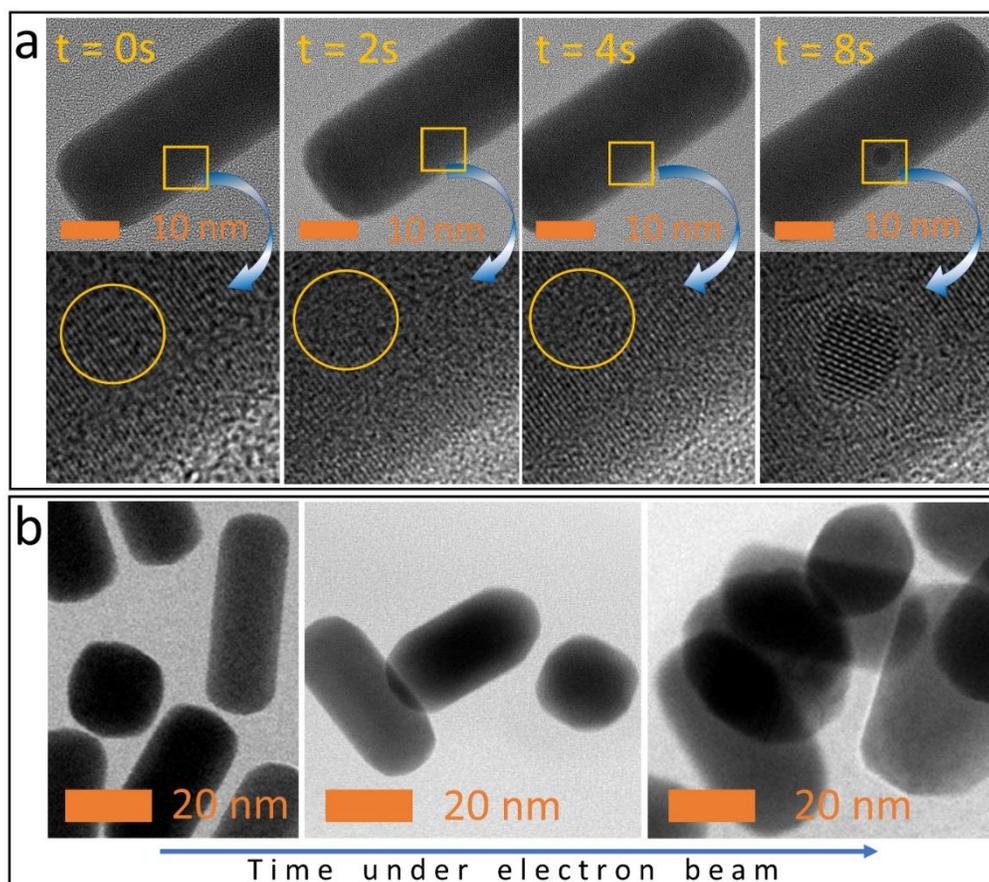


Figure 2. Images of the AuNRs under interaction with the electron beam, obtained across time by (a) HRTEM and (b) LRTEM, both in bright-field mode.

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