

# A Simple Procedure to Assemble Silver and Gold Noble Metal Nanoparticles

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## Abstract

In this study, we are going to report a simple procedure to prepare and assemble noble metal nanoparticle chains using *in situ* synthesis of dicarboxylic acid (tartaric acid). The objective of this study is to investigate the effect of tartaric acid on silver and gold Nanoparticles (NPs). To address this issue, the optical properties, the morphology of silver, gold nanoparticles and their assemblies were investigated by Ultraviolet-Visible (UV-Vis) spectroscopy and Transmission Electron Microscopy (TEM). In addition, Fourier-Transform Infrared (FTIR) was also used to assure the formation of metal nanoparticles assemblies by means of esterification reaction. Gold and silver NPs colloids showed the typical local surface Plasmon resonance of isolated NPs with a symmetric absorption curve. This symmetry did not hold after the addition of the cross link. Moreover, two Plasmon modes were observed for both NPs, the one with longer wavelengths is a characteristic of the assembled NPs due to the near field Plasmon coupling. Furthermore, we observed a great correlation between concentration crosslink, reaction time and Surface Plasmon Band Absorption (SPBA).

**Keywords:** Silver nanoparticle; Gold nanoparticle; Tartaric acid; Plasmon; Optical properties

## Abbreviations:

NPs: Nanoparticles; TEM: Transmission Electron Microscopy; UV-Vis: Ultraviolet-Visible; FTIR: Fourier-Transform Infrared; SPBA: Surface Plasmon Band Absorption; CVD: Chemical Vapor Deposition; NCs: Nanocrystals; PVA: Polyvinyl Alcohol; TA: Tartaric Acid; MW: Microwave; LSPR: Localized Surface Plasmon Resonance; SPR: Surface Plasmon Resonance.

## Introduction

Plasmonic materials are emerging as key platforms for many applications that rely on the manipulation of light at small length scales such as [1-3], optoelectronic nanodevices [4], optical biosensors [5,6], biomedical application [7-10]. Materials that possess sub-wavelength metallic features support surface Plasmons – collective excitation of the free electrons in a metal, they can locally amplify incident electromagnetic fields by magnitude orders at the metal surface [11-13]. However, exploiting the field enhancement offered by Plasmonic materials for practical applications is limited by the lack of a convenient method that can generate these nanostructures with controlled geometry. So far, several methods to synthesize various sizes and shapes of nanoparticles, such as Chemical Vapor Deposition (CVD) ablation laser, sputtering and reduction method in liquid phase were reported respectively [14-17]. All these methods need expensive and specialized machines or hard experimental conditions such as ultra-high vacuum system, high temperature and inert gas atmosphere. Thus, there is an unmet need to develop new methods to synthesize, stabilize metals and assemble NPs. In the last decade, chemical

reduction method was most extensively used in the liquid phase, including aqueous and non-aqueous media [18-20]. Although the reduction method in the liquid phase is rather simple and low cost. It has been used in the structural nanocomposite to produce larger particles and nanosized materials [21]. However, to achieve the reduction in particle size, the chemistry reaction must be selected to give a spontaneous fast reaction and to be able to limit the subsequent growth of the particles after nucleation.

The assembly is emerging as an elegant, "bottom-up" approach to fabricate nanostructured materials from individual metallic elements. Furthermore, combining assembly based on organic materials with special electronic and photonic properties of inorganic components allows us to achieve a powerful new functionality. Colloidal Ag and Au Nanocrystals (NCs) can be easily synthesized with controlled shapes, sizes and surfaces. NCs are ideal building blocks for rationally designed Plasmonic materials. In addition, they generate Plasmon-mediated evanescent fields near their surfaces when irradiated with light.

In the present study, we are going to report a simple procedure to assemble Ag and Au NPs. The system is based on the nanocomposite of noble metal nanoparticles and the polymer producing aggregate nanoparticles with different sizes. The crosslinking reaction of a polymer Polyvinyl Alcohol (PVA), with a dicarboxylic acid (Tartaric Acid) was performed. Moreover, we demonstrated that Plasmon coupling of silver and gold nanoparticles can be attained to any wavelength in the visible spectrum by controlling the assembly size and chains length of its nanoparticles. Several assays were conducted to find a correlation between concentration crosslink, reaction time and Surface Plasmon Band Absorption (SPBA).

## Materials and Methods

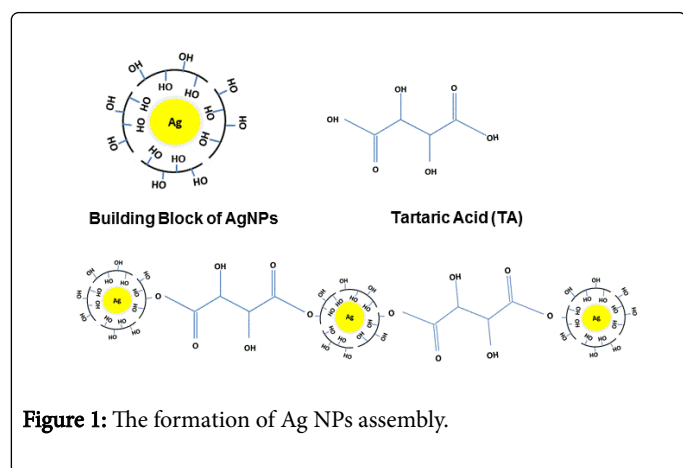
### Materials

The stabilizer PVA (molecular weight 130 000, 85% hydrolyzed), silver nitrate ( $\text{AgNO}_3$ ), hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ), crosslink tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ), methanol (MeOH) were purchased from Sigma Aldrich and used in this study as received. Domestic Microwave (MW) oven (1000 W, 2450 MHz) was used for preparation. Deionized water was purified using a Milli-Q system (18.2 M  $\Omega$ .cm).

### Synthesis of OH-terminated metal nanoparticles

OH-terminated Ag and Au NPs were synthesized as described previously [22]. Briefly, the synthesis is based on the preparation of  $5.0 \times 10^{-4}$  M of  $\text{AgNO}_3$ -MeOH and  $2.5 \times 10^{-4}$  M of  $\text{HAuCl}_4$ -MeOH solutions. Then 10 mg of PVA was suspended in the mixture of the prepared solutions under ultra-sonication. The milky suspension was kept under domestic MW irradiations at 300 W during 30 s giving a yellow suspension. The final solution was purified by centrifugation and resuspended in 20 mL of Milli-Q water (Millipore, 18 M $\Omega$ ) to form a yellowish colloidal solution of Ag NPs. The same preparation protocol was applied to obtain a red- purple solution of Au NPs from the  $\text{HAuCl}_4$  under MW exposure time for 120 sec.

The assembly of OH-terminated NPs (Ag and Au) was favorably carried out using dicarboxylic acid: tartaric acid (TA), as illustrated in Figure 1. The reaction takes place in a slow process and can be fastened by heating. The reaction can be controlled by the concentration of cross linker and time. Therefore, the PVA chains were cross-linked with TA generating amorphous agglomerates of Ag or Au NPs. In order to follow the silver and gold agglomerates process, several samples of 20 mL of Ag and Au NPs were prepared using different amounts of tartaric acid at different reaction times at room temperature.



### Characterization techniques

Ultraviolet-Visible (UV-Vis) spectroscopy (Perkin- Elmer Lambda 20 spectrophotometer) was used to characterize the optical properties of prepared colloidal NPs in water and to follow the assembly reaction in the 250-900 nm range. Light absorbance was measured through quartz cuvette of 1 cm light-path. The size, shape and the morphology of Ag NPs, Au NPs and their assemblies were investigated by Transmission Electron Microscopy (TEM) (Hitachi 600 microscope

operating at 100 kV). Samples were prepared by placing a drop of a dilute colloidal solution of NPs on carbon-coated grids and dried under air at room temperature. Thermo Nicolet spectrometer (NEXUS 870 FTIR) was used to characterize the surface structure of Ag NPs and their assemblies with tartaric acid. TEM images were analyzed using Image Pro Plus 6.0.

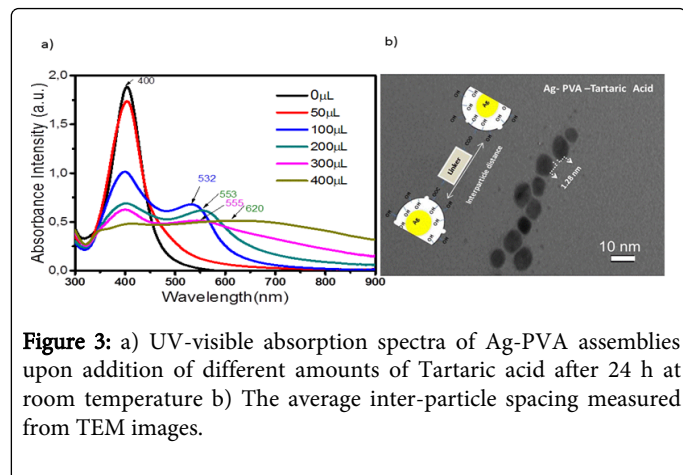
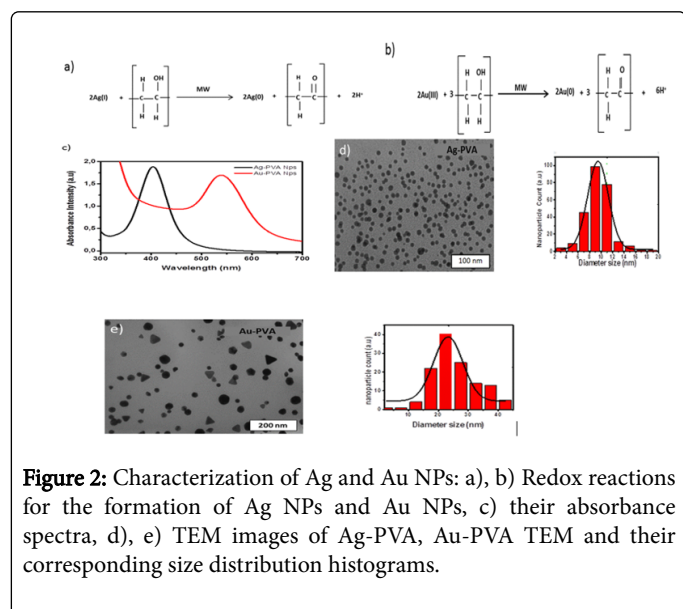
### Results and Discussion

In nanotechnology, the fabrication of complex nanostructures starts with assembling atoms and NPs, which is called bottom up approach. This mechanism is controlled by the polarity and reactivity of the NP surfaces. In this work we have used this approach to fabricate nanostructures based on assembled silver and gold nanoparticles. The synthesis procedure of Ag and Au NPs assemblies is illustrated in Figure 1. The reactions were established by OH-terminated NPs as building blocks and tartaric acid as a bifunctional linker. In a preceding work we reported a novel procedure to synthesis the OH-terminated Ag and Au NPs [22]. This procedure is based on the domestic MW oven (1000 W, 2450 MHz) -assisted reduction of  $\text{AgNO}_3$  and  $\text{HAuCl}_4$  by means of polyvinyl alcohol (PVA), which also acts as both a reducing and a capping agent. The MW assisted reduction of Ag(I) and Au (III) with PVA is achieved from an initial suspension of PVA in methanolic solution of corresponding metal salt. In the beginning, PVA is dispersed in a methanolic solution of  $\text{AgNO}_3$  and  $\text{HAuCl}_4$ , after ultrasonic agitation, the OH groups of the suspended PVA molecules, which are in contact with the Ag(I) and Au(III) solution, coordinate to A(I) and Au(III) ions. Upon MW irradiation exposure, some of ROH groups are oxidized to the corresponding ketone, thus reducing Ag(I) and Au(III) to Ag(0) and Au(0) respectively as demonstrated in Figures 2a and 2b [23]. Then, the resulting solution was purified by centrifugation and resuspended in water to form yellow and red-purple colloidal solutions of Ag and Au NPs, respectively.

The formation of Ag and Au NP was confirmed by UV-Vis spectrometry and TEM analysis. The UV-Vis absorbance of these synthesized metal nanoparticles shown in Figure 2c. The symmetric shape of the LSPR peak of Ag NPs features out the spherical shape and uniform distribution of its NPs. The spectrum exhibits strong and narrow absorption bands localized at wavelength at  $400 \pm 3$  nm, which is the typical Localized Surface Plasmon Resonance (LSPR) of Ag-NPs. The absorbance peak of Au-NPs is less pronounced than that of Ag NPs and is localized at  $540 \pm 5$  nm wavelength that can be explained by greater particles of Au in colloid. Next, the samples of silver and gold nanoparticles were analyzed by TEM. The TEM images and the size distribution histograms are presented in Figures 2d and 2e, the well-dispersed Ag-PVA and Au-PVA NPs are obtained. TEM showed that the majority of Ag-PVA NPs is spherical in shape, with average diameter around  $9.5 \pm 1.8$  nm. However, according to the TEM images of Au-PVA NPs, we could observe clearly different shapes of nanoparticles like triangular prisms and nanospheres. The histogram of the Au-PVA NPs size distribution exhibits a diameter mean size around  $24 \pm 5.5$  nm.

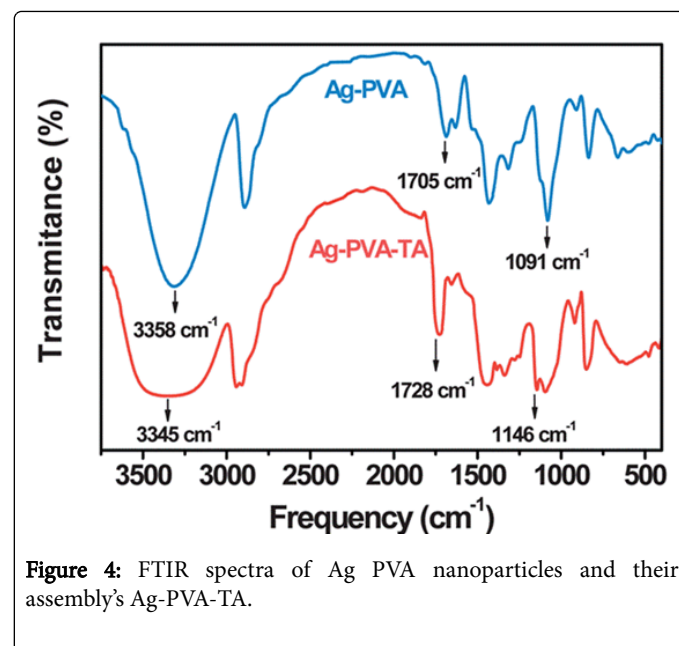
To investigate the influence of Tartaric Acid on the assemblies of Ag and Au NPs stabilized by PVA, different amount of an aqueous solution of TA was added to isolate NPs. Figure 3a shows that the absorption spectra of Ag-PVA nanoparticles are affected by tartaric acid concentrations in dose-response manner after 24 h at room temperature. Figure 3a showed the Surface Plasmon Resonance (SPR) band absorption of assembled Ag nanoparticles with the presence of

tartaric acid at the final state of the reaction with different cross-linking concentration. After adding a low amount of TA (50  $\mu\text{l}$ ), we observed a weak diminution in the absorption intensity accompanied with a small widening in Surface Plasmon Band Absorption, which indicated these Ag-PVA NPs began to form linear-chain aggregates. In addition, increasing the TA amount in the Ag PVA colloids devotes this pronounced decreasing in the fundamental SPR absorbance intensity with a well-marked broadening in the SPBA. This variation in the intensity and the shape of the SPR absorbance was accompanied with appearance of a new resonance peak localized at 532 nm. These changes were thought to be that more monodisperse Ag NPs self-assembled into linear-aggregated Ag NP units. The presence of high TA quantity (400  $\mu\text{l}$  or more) in the Ag-PVA colloid solution, the Surface Plasmon Absorbance Band became broad and broad until the coverage of the infrared wavelengths (300-900). The new absorption band at longer wavelength observed is explained to inter-Plasmon coupling effects [24]. This final result remained unchanged after brooding.



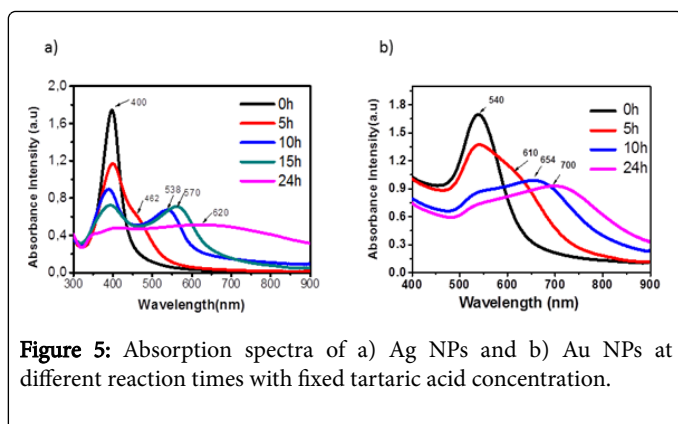
To determine if chemical bonding between the Ag-PVA and Ag-PVA-TA takes place, FTIR was used to assure the crosslinking reaction and confirm TEM images. In fact, the FTIR spectra (Figure 4) of Ag-PVA nanoparticles and Ag-PVA-TA assemblies were collected in

transmittance mode in the wavelength range of 4000-400  $\text{cm}^{-1}$ . Comparing FTIR spectra of both Ag-PVA and Ag-PVA-TA, it was found that many peaks obtained by Ag-PVA NPs have been repeated in the FTIR spectrum of Ag-PVA-TA assemblies with changes in the position furthermore in the intensity of transmission bands. Band at 3358  $\text{cm}^{-1}$  was assigned to the O-H stretching vibration mode associated with hydrogen bonds of inter and intra-molecular genre, while one more intense peak is observed at 1091  $\text{cm}^{-1}$  corresponds to the C-OH stretching mode of the hydroxyl groups of PVA. Another peak at 1705  $\text{cm}^{-1}$  could be attributed to the stretching mode of C=O, which due to the oxidation of OH groups of PVA after the reduction of ion Ag(I) to metal Ag(0). The Ag-PVA-TA FTIR spectrum showed that the bands attributed to the C=O and C-OH vibrations are wide and relatively weak, with shifting from 1705  $\text{cm}^{-1}$ , 1091  $\text{cm}^{-1}$  to 1728  $\text{cm}^{-1}$ , 1146  $\text{cm}^{-1}$ , respectively. Also, the O-H stretching vibration mode of Ag-PVA-TA knew a quite narrow and less intense peak as compared to that of Ag-PVA transmittance, which remained to the esterification reaction. These results indicate that the esterification reaction between the hydroxyl groups of PVA and the carboxyl groups of TA has been carried out.



The growth process of the uniform spherical and irregular shape aggregates was inspected in order to pattern the effect of reaction time on the assemblies of Ag and Au NPs. Samples at different reaction times such as those of segregate and aggregate nanoparticles were studied using UV-Vis spectrometer and TEM. Figures 5a and 5b displayed the UV-Vis absorption spectra of Au and Ag nanoparticles aggregates carried out at different reaction times with fixed tartaric acid concentration. At initial time  $t_0$ , the UV-Vis absorption spectra exhibited a strong and a single SPR peak band, with a full width at half maximum around 63 and 105 respectively.



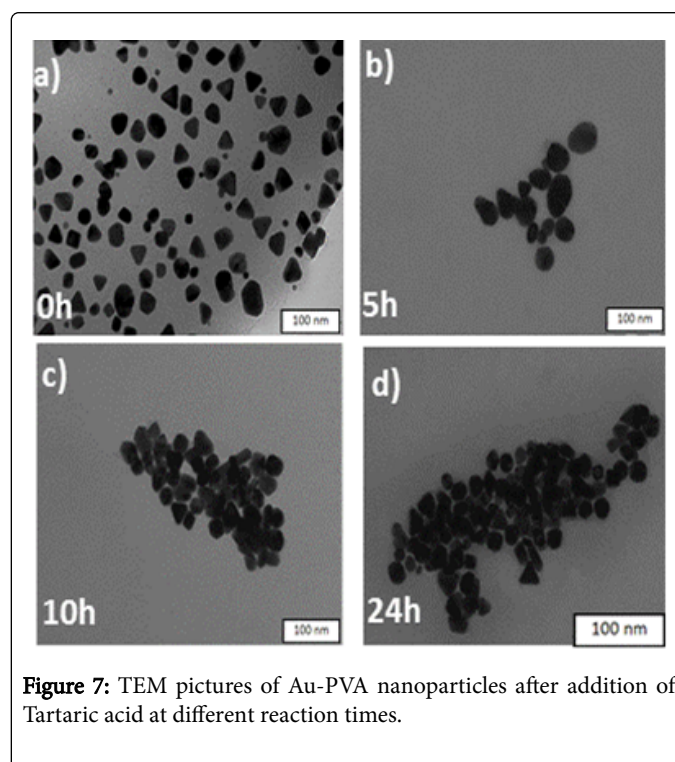
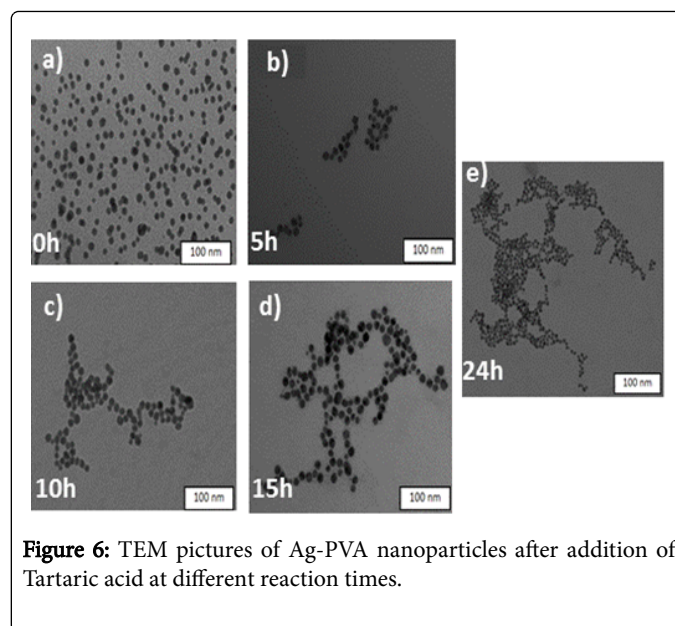


The evolution of this aggregation process was evaluated at different reaction times: 5 h, 10 h and 15 h at room temperature upon magnetic stirring, the intensity of the transverse band at 400 nm, 540 nm decreased significantly, a new Plasmon band near to 538 nm, 654 nm appeared progressively on the red side of the transverse band of the isolated silver and gold nanoparticles respectively. A marked new peak became visible in the SPBA. After 24 h of agitation, SPAB changed considerably, it was shifted to lower energies. The second Plasmon peak became more intense than the fundamental peak (isolated NPs SPR) and exhibited strong coupling.

Figures 6 and 7 showed the TEM images taken for Au and Ag agglomerates at different times after addition of fixed tartaric acid concentration. TEM images demonstrated that isolated Ag and Au nanoparticles (without tartaric acid) were separated with high interparticle distance and no agglomeration was observed. After 5 h of reaction with TA, we could observe clearly the formation of agglomerates composed by small linear chains. The agglomeration phenomenon became more important with reaction time progress. Experimentally, we determined the interparticle distance from several TEM images of different samples, the interparticle distance was very short with an average value around  $1.28 \pm 0.20$  nm (Figure 3b).

The TEM images help us to understand the appearance of a new peak shown in Figures 5a and 5b. This peak can be attributed to the SPR band which shifted to the red wavelength. The peak position depends on the aggregates size as shown from TEM images. On the one hand, these additional shifts are expected to occur due to electromagnetic interactions between the localized modes [24-26]. For small particles, these interactions are essentially of a dipolar nature, and the particle ensemble can in a first approximation be treated as assembly of interacting dipoles. On the other hand, these shifts which resulted due to the agglomeration and the esterification of PVA on a basic or acid medium, such as the carboxylic groups of the tartaric acid react with the OH groups of PVA to form an ester.

We also observed that the size of aggregate nanoparticles increases when the colour of the solution varies from red solution to deep blue for gold and from yellow to blue colour for silver. Colours change of both gold and silver nano-agglomeration is due to its SPR properties [27,28].



## Conclusion

In this work, we have demonstrated a simple procedure to synthesize assemblies of nanoparticles based on a nanocomposite of noble metal nanoparticles and dicarboxylic acid, as Tartaric acid. We showed that the Plasmon coupling of silver and gold nanoparticles can be attained to any wavelength in the visible spectrum by controlling the assembly size and chains length of its nanoparticles. The formation of Ag NPs and Au NPs assemblies are followed by UV-Vis spectroscopy and transmission electron microscopy. In the beginning, gold and silver nanoparticles colloids exhibited the typical local surface Plasmon

resonance of isolated nanoparticle with a symmetric absorption curve. This symmetry did not hold after addition the cross link, two Plasmon mode are observed for both NPs, the one with longer wavelengths is a characteristic of the assembled NPs. We noticed that the assemblies obtained could be smoothly produced by controlling reaction times and tartaric acid concentrations. Moreover, we demonstrated by means of FTIR spectrometer that the Ag NPs assemblies have taken place by the esterification reaction between Ag PVA NPs and TA. This method has been experimentally shown to produce very stable Ag NPs and Au NPs assemblies.

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## Conflicts of Interest

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

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