

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).

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 subwavelength 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 chain length of its nanoparticles. Several assays were conducted to find a correlation between concentration crosslink, reaction time and Surface Plasmon Band Absorption (SPBA). Chemical Sciences Journal ISSN: 2150-3494 Chemical Sciences Journal Gradess et al., Chem Sci J 2018, 9:1 DOI: 10.4172/2150-3494.1000182 Research Article Open Access Chem Sci J, an open access journal ISSN: 2150-3494 Volume 9 • Issue 1 • 1000182 Materials and Methods Materials The stabilizer PVA (molecular weight 130 000, 85% hydrolyzed), silver nitrate (AgNO_3), hydrogen tetrachloroaurate (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 Ω .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 5.0×10^{-4} M of AgNO_3 -MeOH and 2.5×10^{-4} M of 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 Ω) 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 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. Figure 1: The formation of Ag NPs assembly. 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 OHterminated Ag and Au NPs [22]. His procedure is based on the domestic MW oven (1000 W, 2450 MHz) -assisted reduction of AgNO₃ and HAuCl₄ by means of polyvinyl alcohol (PVA), which also acts as both a reducing and a capping agent. He 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 AgNO₃ and HAuCl₄, aier 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].

Hen 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.