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Au–Ag hollow nanostructures with tunable SERS properties

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ABSTRACT

Fabrication of hollow Au–Ag nanoparticles is done by the sequential action of galvanic replacement and Kirkendall effect. Polyol synthesized silver nanoparticles were used as templates and the size of cavities is controlled by the systematic addition of the $HAuCl_4$. Au–Ag nanoparticles carved in different depths were tested for application as substrates for surface enhanced Raman scattering. Two medically important Raman active analytes-Nile blue chloride and Crystal violet were used in the surface enhanced Raman scattering (SERS) performance analysis. A systematic study has been made on the Raman enhancement of hollow nanoparticles fabricated with different cavity dimensions and compared with that of the silver templates used. The enhancement observed for these hollow substrates with cavities is of interest since Au protected hollow nanostructures are vital and an active area of interest in drug delivery systems.

1. Introduction

Engineering plasmonic metal nanostructures with well-defined morphologies and unique tunable properties for diverse applications such as surface enhanced Raman scattering (SERS), photocatalysis, nanophotonics, biomedical detection, imaging, drug delivery, etc. is an active area of research [1–22]. Among the various morphologies, metal nanostructures with hollow or porous interiors have remarkable applications especially in the field of drug delivery systems [5,6,8]. The galvanic replacement reaction is generally applied to synthesize nanoparticles with hollow features [3]. It is necessary that for galvanic replacement reaction to take place for the formation of hollow nanostructures, the reduction potential of a sacrificial metallic template should be sufficiently lower than that of the metal composing the final hollow structure. In this regard, silver nanocrystals (AgNCs) have frequently been used as sacrificial templates to produce Au–Ag hollow nanostructures owing to the much lower reduction potential of Ag compared to Au [12].

Surface enhanced Raman scattering is an effective molecular imaging optical technique for various biomedical applications owing to its characteristic ability to generate enhanced Raman spectra from trace amount of chemical and biological analytes, when it is in close proximity of nano-sized noble metal surfaces like that of silver and gold [4,8,9]. Among the various SERS substrates, silver nanostructures are widely explored and highly SERS active substrates [19]. Gold made substrates are less SERS active compared to silver but are less toxic. In such a situation, one strategy for overcoming the toxicity and chemical stability without much compromise on the SERS activity is to form a thin outer coating of Au on Ag nanostructures. To realize such an output, an appropriate synthesize method is necessary. The characteristic features and the applications may double if the nanostructures are synthesized with an outer covering and having a hollow interior. To fabricate such nanoparticles galvanic replacement mechanism is a feasible choice [23].

In this work, Au–Ag hollow nanostructures were synthesized using galvanic replacement mechanism with slight modifications. Polyol synthesized silver nanoparticles were used as sacrificial templates. The presence of poly (vinyl pyrrolidone) and polyethylene glycol in the synthesis make a further veneer around nanostructures unnecessary if these substrates are used as carriers or SERS substrates in biomedical field. Attempts were made to make the dimension of cavity in tune with the best possible enhancement of Raman signal. A systematic investigation on the influence of cavity size on SERS enhancement has been done. Suitable Raman molecules and nanoparticles with excellent plasmon characteristics are vital in designing efficient SERS substrates. In this work SERS activity of the Au–Ag fabricated hollow structures were tested with two different dye molecules viz., Nile blue chloride (NBC) and Crystal violet (CV).

2. Experimental

2.1. Materials

The reagents, Silver nitrate (99.99%, Sigma-Aldrich, $AgNO_3$), Gold(III) chloride trihydrate (99.9 + % - Aldrich, $HAuCl_4$), Polyethylene glycol 200 (Merk, PEG), poly (vinyl pyrrolidone) MW-1,300,000 (Alfa Aesar, PVP), Sodium chloride (99.9%, NICE Chemicals Pvt.Ltd., NaCl),

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Sodium Bromide (≥99.5%, Sigma-Aldrich NaBr), Nile Blue chloride (Sigma-Aldrich, NBC), Gram's Crystal violet solution for microscopy (Merck, CV), and Hydrochloric Acid (NICE Chemicals Pvt.Ltd., HCl) were used as received without further purification. Double distilled water was used throughout the experiment.

2.2. Synthesis

2.2.1. Polyol synthesis of Ag nanoanodes

The Ag nanoanodes were prepared using the basic polyol synthesis with some minor modifications [13]. Briefly, 5 mL polyol (polyethylene glycol 200) is taken in a beaker and heated at 150 °C. After 1 h heating, 40 μL of 0.242 M HCl was added into it. Then 5 mL of polymeric capping agent (PVP) having 6 μM concentration was added with 1 mM each of NaCl and NaBr in a beaker. An aliquot of precursor salt $AgNO_3$ (0.0390 g, 0.045 M) was dissolved in 5 mL of deionized water. Then 3 mL each of precursor salt and the mixture containing capping agent were taken separately and injected to the refluxing PEG at a rate of 0.3 mL/min. This was done subsequently 15 min after the addition of HCl. The solution was then brought to reflux for 4 h.

Upon injection of precursor and capping agent, the colour of the solution became milky white with an orange hue. Later it became reddish orange, chocolate brown, greenish brown and finally thick greenish gray. The final product was centrifuged and washed thrice with acetone (to remove excess PEG) and then twice with deionized water (to remove excess PVP) at 9000 rpm for 30 min each. The precipitate was then carefully removed and re-dispersed in 4 mL deionized water for further use.

2.2.2. Synthesis of Au–Ag hollow nanostructures by galvanic replacement reaction

A solution with 0.4 mM $HAuCl_4$, as oxidizing agent (cathode) was prepared. PVP (6 μM) is dissolved in 5 mL deionized water and heated at 100 °C for 10 min. A volume of 200 μL of the Ag nanoanodes (S) obtained in the previous step (2.2.1) was then added into preheated PVP. After 5 min, 1 mL of the prepared $HAuCl_4$ was injected into the solution at a rate of 0.2 mL/min. Stirring and heating was continued for 5 min and it was observed that the colour of the solution became greenish violet. The prepared sample was cooled at room temperature and centrifuged twice with deionized water at 9000 rpm for 30 min, to collect the products. The product was carefully removed and re-dispersed in 3 mL water. The same procedure was repeated by changing the volumes of $HAuCl_4$ such as 2, 3 and 4 mL to prepare hollow nanostructures having cavities with different dimensions and was indicated by dark blue, sky blue and faint blue colours respectively for the resulting solutions.

2.3. Sample preparation for SERS

The samples for SERS measurement were prepared by adding the analytes per mL of different substrates to reach a final concentration

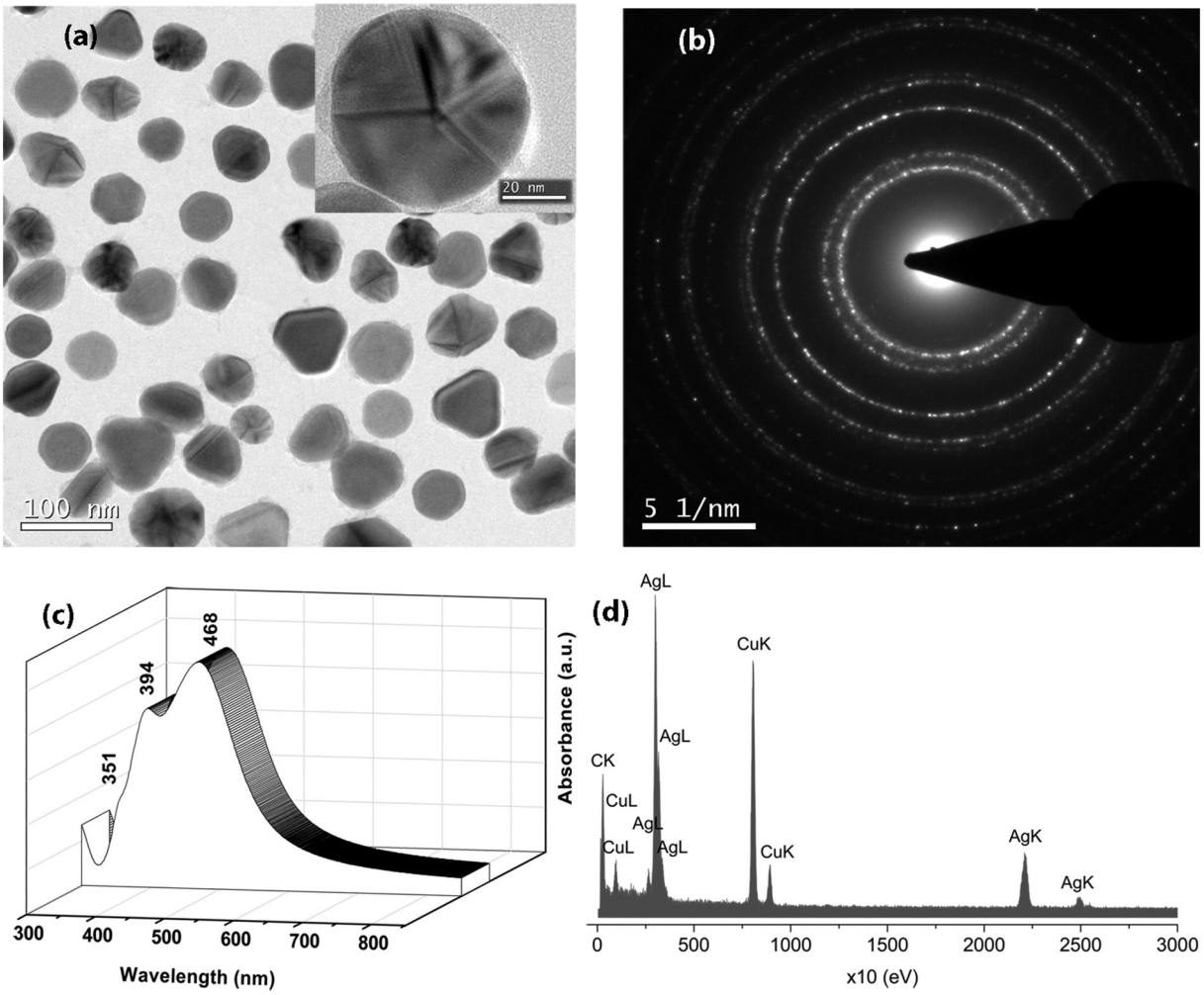

Fig. 1. Sacrificial silver templates: (a) TEM image; inset shows spherical profile of the four-fold twinned particles. (b) SAED pattern, (c) absorption spectrum and (d) EDAX spectrum.