

# Tuning the surface enhanced Raman scattering and catalytic activities of gold nanorods by controlled coating of platinum

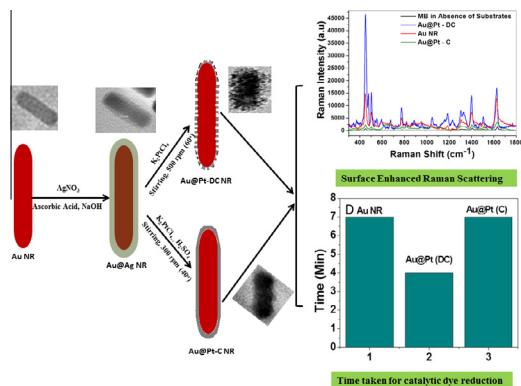


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## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 22 May 2015

Revised 9 September 2015

Accepted 14 October 2015

Available online 22 October 2015

### Keywords:

Core-shell nanorods  
Gold nanorods  
Galvanic replacement  
SERS  
Dye reduction

## ABSTRACT

Galvanic replacement of silver (Ag) by platinum (Pt) on bi-metallic nanorods (NRs) having gold (Au) core and silver shell (Au@Ag) resulted in discontinuous coating of Pt over Au (Au@Pt-DC) NRs. However, a novel method has been developed in this work for the preparation of Au NRs having smooth and continuous coating of Pt (Au@Pt-C NRs) using galvanic replacement reaction of Au@Ag NRs in presence of sulphuric acid. Selective blocking by the bisulfate ions that are adsorbed on Pt surface, preventing Pt on Pt deposition seems to be the mechanism of formation of Au@Pt-C NRs. Effect of the nature of Pt shell (i.e. whether continuous or discontinuous) on SERS activity of the NRs was investigated with methylene blue (MB) as a reporter molecule. The specific enhancement of the Raman signals were in the order Au@Pt-C NRs < Au NR < Au@Pt-DC NRs. Catalytic reduction of MB by NaBH<sub>4</sub> using the NRs also followed a similar trend with Au@Pt-DC NRs showing almost three times better activity than Au and Au@Pt-C NRs.

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## 1. Introduction

Metallic NRs in general are of great interest due to the fact that their localized surface plasmon resonance properties can be tuned by changing aspect ratios. Controlled coating of one metal over the

other is yet another way by which properties of NRs can be tuned. They can be prepared with high monodispersity, yield and precise control of the aspect ratios. Au NRs and core-shell varieties of Au NRs have a number of applications in catalysis, sensing, bioimaging and in nanomedicine due to their localized surface plasmon resonance [1]. Various core-shell nanostructures have been synthesized in recent times with Au as the core material such as Au@Ag, Au@Pd and Au@Pt [2]. Au@Ag core-shell nanostructures

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have different applications in photocatalysis, optics, bioimaging and SERS [3,4]. However, Ag as a shell has limited biological application due to its inherent toxicity [5,6]. Platinum is a candidate for the shell material over Au nanostructures because of its antioxidant potential and minimal toxicity in vivo as compared to other elements [7]. Recently, it was shown that formation of the Pt nanodot shell on the surface of Au NRs provides a versatile way to tune the LSPR band to the red spectral region and the Au@Pt NRs had a higher cell uptake in cancer cells than Au NRs [8]. Moreover, Pt is much more stable against oxidation than other elements and is widely used as catalyst in many important chemical reactions. Au@Pt nanostructures can also be used for operando monitoring of catalysis using surface enhanced Raman scattering (SERS) [9]. This method is a very valuable tool in the study of reaction mechanisms, as real time monitoring of intermediate species is possible using SERS. Thus, the use of Pt as a shell in nanostructures is being explored in the biology oriented applications, in SERS as well as in catalysis.

Novel methods for achieving controlled coating of one metal over the other are of great interest due to the possibility of modulating the properties. Lattice structure, surface and cohesive energies of constituent metals determine the uniformity of the shell. For example, it is difficult to achieve a uniform coating of Pt over Au surface because of the lattice mismatch between the two elements. High cohesive and surface energy of Pt also is unfavorable for the formation of smooth coating of Pt over Au surface [10]. Various attempts to make core-shell Au@Pt NRs in the past via successive reduction method and seed mediated techniques resulted in island like coating of Pt [11–13]. There are only very few methods available for the preparation of Au NRs with uniform and smooth Pt coating. Recently, a method for the controlled deposition of Pt on Au NRs has been reported. This involves sequential deposition steps with selective blocking of surface sites with CO that prevents Pt-on-Pt deposition and thus uniform deposition was achieved [14]. A method based on galvanic replacement of a monolayer of Cu on bulk surface of Au with Pt is also reported in the literature [15,16]. However, it is difficult to deposit a Cu monolayer itself using under potential deposition on nanostructures of gold [17]. Thus, there is interest in developing alternative methods for the preparation of smooth and continuous layer of Pt on Au nanoparticles and this has been one of the objectives of the present work. In contrast to Pt, Ag forms a uniform coating over gold surface due to the similarity of lattice structures. Attempts to use galvanic reaction to replace Ag by Pt over the Au surface also resulted in non-uniform coating [18]. In the present work, we have modified the galvanic replacement reaction to achieve continuous coverage of Pt over Au NRs. We have used selective blocking of Pt surface using bisulfate adsorption and galvanic replacement to successfully achieve our objective. Fenell et. al. reported that Au@Pt NRs with uniform coating of Pt that was prepared using CO has better long term stability than those NRs that were prepared using standard Pt deposition [14]. The Au@Pt NRs with continuous Pt coating also showed enhanced electrochemical activity for oxidation of CO and reduction of oxygen [14]. Thus, it was found appropriate to compare the properties of the Au@Pt NRs with continuous coating of Pt that were prepared in this work with the ones having discontinuous coating. We have explored the potential of the Au@Pt nanostructures in SERS and as catalysts in dye reduction reaction and the results are presented here.

There is a significant increase in research activities recently on the development of noble metal nanostructures for SERS. This is because, rough surface of noble metal nanostructures can be used as the substrates to increase the Raman signal of the Raman active analyte molecules up to  $10^{12}$  times theoretically [19]. Most of the research on the SERS substrates is directed towards the gold (Au) nanostructures, especially for biological applications [20,21].

Change in morphology, particle size, coatings and assembly of Au nanostructures is known to affect the Raman enhancement [22,23]. The rise in the enhancement factor is usually attributed to the presence of 'hot spots' over the surface of the metal that electromagnetically enhance the Raman signal of the analyte [22]. Coating the Au nanostructures by plasmonic metals such as silver (Ag) has been used as a strategy to enhance the SERS signal [24]. Interestingly, it was found that the overall electromagnetic enhancement of the Raman signal can be improved by coating the surface using non SERS active materials also [25,26]. Hence it was found interesting to compare and find out how the nature of the surface coating affect the Raman signal of gold nanorods (Au NR). We have compared the SERS enhancement of a reporter molecule on Au NRs and Au@Pt core-shell NRs in the present work. We have also investigated the effect of continuous Pt coating (Au@Pt-C) versus discontinuous (Au@Pt-DC) Pt coating on SERS and the results are presented in this paper.

Dyes are a major source of environment contamination in the vicinity of food and textile industries. They have carcinogenic effect on human health apart from causing other health hazards and high toxicity to aquatic creatures [27,28]. Therefore, their safe disposal is widely studied by different methods like chemical reduction, photo degradation, reverse osmosis and coagulation [29–31]. Chemical reduction of dyes is a relatively more economic route. Unfortunately, chemical reduction of dyes is insignificant in the absence of a catalyst and large amount of reducing agent [32]. Therefore, there is a need to develop catalysts which can catalyze the reduction of dyes at ambient conditions with less amount of the reducing agent. Here, we report very high catalytic activity of the Au@Pt-DC for the dye reduction reaction.

## 2. Experimental section

### 2.1. Materials and methods

For the synthesis of gold NRs, cetyltrimethyl ammonium bromide (CTAB), gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) and silver nitrate ( $\text{AgNO}_3$ ) were purchased from Sigma-Aldrich. Sodium chloride (NaCl), L-ascorbic acid (AA) and sodium borohydride ( $\text{NaBH}_4$ ) were purchased from Merck. For the synthesis of Au@Ag NRs, polyvinylpyrrolidone (PVP) was purchased from Alfa Aesar and sodium hydroxide (NaOH) was purchased from Merck. Reagents for the synthesis of Au@Pt NRs such as potassium tetrachloroplatinate(II) ( $\text{K}_2\text{PtCl}_6$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ) were purchased from Sigma-Aldrich and Merck respectively. MB dye for the SERS and catalytic studies was purchased from Merck. All the chemicals were used as received. All the stock solutions were prepared in ultra-pure water ( $18.2 \text{ M}\Omega\text{-cm}$ ) from double stage water purifier (ELGA PURELAB Option-R7).

### 2.2. Synthesis of Au NRs

Au NRs were synthesized in 10 mL batches using a non-seeding method [32,33]. Typically, to the aqueous solution of CTAB (8.33 mL, 180 mM) aqueous solutions of NaCl (225  $\mu\text{L}$ , 0.1 M),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (180  $\mu\text{L}$ , 0.05 M) and  $\text{AgNO}_3$  (180  $\mu\text{L}$ , 0.01 M) were added. The solution mixture was yellowish brown in color. After light agitation, AA (180  $\mu\text{L}$ , 0.1 M) was added and agitated by inversion for 30 s. The color of the solution changed from yellowish brown to colorless. Ice cold  $\text{NaBH}_4$  (10  $\mu\text{L}$ , 3.14 mM) was added to the solution and again agitated by inversion for 30 s. The solution was left at room temperature for 12 h. Samples were washed thrice with water to remove excess reagents and concentrated by centrifugation. After centrifugation, the supernatant was removed and replaced by 1 mM CTAB to obtain the Au NR solution.

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