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# Effect of concentration of methanol for the control of particle size and size-dependent SERS studies

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### ABSTRACT

In this paper the effect of concentration of cosolvent (methanol) for the formulation of particles size has been discussed briefly. The binary solvent system has been used which is prepared by simple mixing of two solvents. The morphology of the particles was controlled by varying the amount of cosolvent, keeping the concentration of the stabilizer and reducing agent constant. The polarity of the solvent, transport of the Au(III) ions, and coordinating ability of the solvent play vital roles for nucleus formation and the growth process, which subsequently form different size particles. The particles formed in methanol at lower composition are angular. At higher concentrations of methanol they are spherical. In all the cases the particle size increases as the concentration of the twining of the particles increase with the decrease of methanol content. The particles have been characterized by XRD analysis, UV-visible spectroscopy, and transmission electron microscopic (TEM) studies. The variable size of the particles, obtained in a water methanol system, was employed for SERS measurement. A Raman probe, Rhodamine 6G (Rh 6G), has been found to be suited for the surface modification of the gold particles and it has also been demonstrated that the larger particles show better SERS signal than the corresponding smaller ones.

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# 1. Introduction

The synthesis of metal nanostructures has been an active research area for many decades, because of the importance of these materials in catalysis, photography, electronics, photonics, information storage, optoelectronics, biological labeling, imaging, and sensing [1–8]. Like their semiconductor cousins (e.g., quantum dots), the intrinsic properties of metal nanostructures can be tailored by controlling their size, shape, composition, crystallinity, and structure [9,10]. Novel metal nanocrystallites such as silver and gold provide a more interesting research field due to their close-lying conduction and valence bands in which electrons move freely. Size provides important control over many of the physical and chemical properties of nanoscale materials, including luminescence, conductivity, and catalytic activity. However, the challenge of synthetically controlling the particle size has been met with limited success. To investigate the physical and chemical properties of metal nanoparticles, especially the size-dependent properties, precise control of the particle size is essentially required. Control of the particle size depends on varied parameters like stabilizer, reducing agent, solvent, and concentration of metal ions [11-16]. There are various

preparation techniques such as surfactant-based seed-mediated growth, thermal growth, photoreduction of metal nanoparticles in solution, and template synthesis which control the morphology of the metal nanoparticles [17–24]. On the other hand, few reports on particle size and shape control synthesis of metal nanoparticles in mixed solvent system have been published.

Here for the first time we have reported the role of cosolvent system for the control of the particles size. The main focus of this article is to study the effect of concentration of methanol on the size of the particles in the presence of PVP used as stabilizer. Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) are also used as cosolvents and the sizes of the resulting particles were studied. The particle size and shape of gold have been observed to vary with the used volume ratio of water to cosolvents. Sodium borohydride is used as reducing agent in all the solvent systems. Sodium borohydride is very soluble in water and methanol, reacting slowly to evolve hydrogen which reduces the metal ions in solution [25]. The particles have been characterized by XRD analysis, UV-visible spectroscopy, and transmission electron microscopic (TEM) studies. The influence of the methanol on the morphology of gold has also been investigated. Here, we also report the direct measurement of size-tunable optical properties of the evolved Au nanoparticles. Finally, a Raman probe, Rhodamine 6G (Rh 6G), has been employed for the surface modification of the gold particles. The SERS spectra of Rh 6G on different parti-

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cles sizes have been studied and compared with each other. It has also been demonstrated that the larger particles show better SERS signal than the smaller particles.

# 2. Experimental

## 2.1. Reagents and instruments

All the reagents used were of AR grade. Chloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O) and sodium borohydride and polyvinylpyrrolidone (PVP, MW = 40,000) were purchased from Aldrich. Solvents, viz. methanol, tetrahydrofuran, dimethyl sulfoxide, and dimethylformamide, were purchased from Merck and dried before use. Raman probe Rh 6G was purchased from Aldrich and was used as received.

The absorption spectrum of each solution was recorded in a Spectrascan UV 2600 digital spectrophotometer (Chemito, India) in a 1-cm well-stoppered quartz cuvette and the solvent background was subtracted each time. Electron micrographs of the metal colloids were measured with a Hitachi H-9000NAR transmission electron microscope, operating at 200 kV. The samples were prepared by mounting a drop of the solution on a carbon-coated copper grid and allowing it to dry under vacuum.

SERS spectra were obtained with a Renishaw Raman microscope, equipped with a He–Ne laser excitation source emitting at a wavelength of 633 nm, and a Peltier cooled (-70 °C) charge coupled device (CCD) camera. A Leica microscope was attached and was fitted with three objectives ( $5\times$ ,  $20\times$ ,  $50\times$ ). For these experiments, the  $20\times$  objective was used, giving a spot size on the surface of about 5 mm. Laser power at the sample was 0.08 mW and the data acquisition time was usually 10 s. The holographic grating (1800 grooves/mm) and the slit enabled the spectral resolution of 1 cm<sup>-1</sup>. The Raman band of a silicon wafer at 520 cm<sup>-1</sup> was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than 1 cm<sup>-1</sup>. SERS spectra from different points on the surface were the same, differing only in intensity; the spectrum, which gave the most intense signal, was retained.

The solution electrical conductivity of the solution was measured by Unitech type U131C digital conductivity meter (USA) with a solute concentration of about  $10^{-4}$  M. XRD was done in a PW1710 diffractometer, a Philips, Holland, instrument using a CuK $\alpha$  source with wavelength 0.154045 nm. The XRD data were analyzed using JCPDS software. Fifty microliters of each nanoparticle solution was dropped on a glass slide and dried to make a thin layer.

#### 2.2. Synthetic procedure of PVP-protected Au nanoparticles

A 2.5 mM aqueous solution of PVP was prepared by dissolving 1 g of PVP in 10 mL distilled water. The solution was sonicated and finally filtered through ultrafiltration membrane (30k molecular weight cutoff) to get rid off tiny undissolved particles, which might create a nucleation center. Appropriate amounts of water and cosolvent were mixed together and 1 mL of 2.5 mM previously prepared aqueous solution of PVP was added to it. The mixture was stirred on a magnetic stirrer and 100  $\mu$ L, 10 mM HAuCl<sub>4</sub> was introduced. Finally, the entire mixture was treated with freshly prepared aqueous solution of NaBH<sub>4</sub> (200  $\mu$ L, 10 mM) to reduce the Au(III) to Au(0). The v/v ratio of water to cosolvent was altered in order to investigate the effect of volume ratio of the solvent system on the particle size. Methanol to water (v/v) ratio was varied from 1:4, 1:1 to 4:1, keeping the stabilizer concentration fixed throughout the experiment.



Fig. 1. UV-visible absorption spectra for the evolution of gold nanoparticles in methanol-water system with time. Conditions:  $[HAuCl_4] = 0.5 \text{ mM}$ , [PVP] = 0.25 mM,  $[NaBH_4] = 0.2 \text{ mM}$ .

#### 2.3. SERS measurements

The as-synthesized particles were centrifuged and washed with alcohol and finally dispersed in water for SERS studies. The threedimensional assemblies of gold nanoparticles were easily obtained on gold surface by addition of 100  $\mu$ L of NaCl (1 M) to 1 mL of colloidal gold (0.1 mM) solution. To the gold assemblies 100  $\mu$ L of 10  $\mu$ M dye was added so that the final concentration of dye solution in the experiment became 1  $\mu$ M and the resulting solution was incubated for 5 h.

# 3. Results and discussion

#### 3.1. Evolution of gold nanoparticles in methanol water system

Fig. 1 shows the absorption spectral features for the evolution of gold nanoparticles in the methanol–water system 1:4. The mixture of PVP, methanol, and water shows no characteristic absorption maximum in the range of 250–700 nm. The  $AuCl_4^-$  ions in the methanol–water 1:4 exhibit an absorption peak at 290 nm that can be attributed to the metal-to-ligand charge transfer (LMCT) band of  $AuCl_4^-$  complexes [26].

On addition of NaBH<sub>4</sub> to the reaction mixture, the yellow color of the solution disappears and the peak at 520 nm gradually appears which corresponds to the plasmon band of gold nanoparticles. For lower proportion of methanol it takes 30 min to complete the reaction whereas for methanol water system 4:1 the absorbance becomes constant after 15 min. Here, the rate of formation of gold particles decreases with the increase in the concentration of water.

#### 3.2. Characterization of the gold nanoparticles

#### 3.2.1. UV–visible spectroscopy

The absorption spectral profile for the gold nanoparticles in methanol–water system is shown in Fig. 2a. The absorption maxima in methanol–water mixture appear at 520, 513, and 508 nm for a variation of methanol to water ratio 1:4, 1:1, and 4:1, respectively. The position of absorption maxima shifts toward red, which authenticates the increase in particle size [27]. It is reported previously that a change in solvent system changes the refractive index of the medium. A solvent with higher refractive index shifts the surface plasmon band of Au nanoparticles to a higher wavelength [28]. Papavassiliou reported that the color of the coinage metal sols, viz. Cu, Ag, and Au, is quite sensitive to the change of refractive index of the solvent [29]. In contrast, Hostetler et al.

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