

Gold cluster coatings enhancing Raman scattering from surfaces: Ink analysis and document identification



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ABSTRACT

Based on the method of laser-ablation in liquids (LAL) with a strategy of bubbling nitrogen through a custom-made chamber, we prepared chemically-pure gold clusters which were found to be metastable for an extensive period of time beyond months. A practical use of discrimination among different surfaces is demonstrated here by applying the gold clusters as surface coatings which result in surface-enhanced Raman scattering (SERS) due to the surface plasmon resonance (SPR). This technique identifies various documents from different printers/copiers and written with different pen-inks. The stable and additive-free gold clusters enable repetitive examinations without impurity interference.

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1. Introduction

Gold nanoparticles (NPs) and clusters are known as one of the most extensively utilized materials in nano scale. Many applications of gold NPs have been demonstrated in recent decades involving diagnostics, therapeutics, catalysis, optical sensing, DNA sequencing and biomarkers, etc. [1,2]. Nano scaled gold has unique optical properties and they support surface-plasmon-resonance (SPR) hence profiting the surface-enhanced Raman spectroscopy (SERS) which has generated a wealth of research activities [3–6]. Recently by applying a monolayer of gold NPs on the sample surfaces, Li et al. [7] revealed a practical use of the SERS spectroscopy allowing for probing biological structures and detecting pesticide residues on fruit surfaces. This technique, just simply sowing gold NPs, is important as it enables application of SERS spectroscopy for *in situ* analysis of any surfaces or materials out of laboratory in help of a portable Raman spectrometer. In order to provide clean Raman signal amplification, it is expected in these applications to employ stable and chemically-pure NPs [8–10].

In general, gold NPs are produced in a liquid by reduction of chloroaurate or chloroauric acid [2,11,12], as well as several advanced and precise methods, such as Brust's method [13], Turkevich's method [14], Perrault's method [15], and Martin's method [16]. Among others, the synthetic procedures for thiolstabilized gold colloids attracted reasonable interest; the thiolate protection can effectively stabilize gold NPs and also lead to preparation of

face-centered cubic and hexagonal closed-packed nano-crystal superlattices of the gold NPs [17–21]. Recently Aslam et al. [22] reported a technique to avoid aggregation of gold NPs via the formation of a gold-amine complex followed by its thermal decomposition which occurs rapidly, so the gold NPs formed in water are protected immediately by the amine molecules. However, it is difficult to eliminate the interference of residue chemicals when applied to critical SERS examinations.

Comparing with the various chemical synthesis procedures, laser ablation in liquids (LAL) is known as an effective physical method to prepare chemically-pure NPs/clusters [23–27]. However, morphology studies show that gold NPs produced by the LAL method vary in size/shape and usually exhibit limited monodispersity and stability. By employing a cationic surfactant (CTAB), researchers have been able to gain an enhanced stability for gold colloids based on the LAL method [28]. However, it remains a challenge to obtain uniform size distribution and expected stability in the case without any stabilizers or surfactants, especially in water. In the present study, we consider an investigation to prepare additive-free gold clusters based on the LAL method by utilizing bubbling-nitrogen through a custom-made chamber. The use of nitrogen flushes out any residual oxygen in the air inside the chamber prior to performing the LAL synthetic method and creates a convective current through the liquid. It has been found that the convective current driven by bubbling nitrogen throughout the entire experimental system promotes uniform particle sizes of the gold colloid, for which we have performed an in-depth analysis on the stability and agglomeration behavior of the as-prepared gold clusters. Further, by applying the additive-free gold clusters

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as surface coatings, the potential of surface identification is examined for printer/copier toners and pen-inks.

2. Experimental

2.1. Preparation of gold clusters

The method used in this work utilizes a specially fabricated stainless steel chamber, seen as Fig. 1. The gold rod (1/4" diameter, 99.99% purity, Research and PVD Materials Corp.) was polished to ensure a smooth surface for ablation and was partially inserted into the chamber through a vacuum feed through (1/4" Ultra-Torr, Swagelok). The chamber was then filled with de-ionized water. Nitrogen gas was used to flush out any remaining air inside the chamber prior to running the experiments, and was also used throughout the experiments to create a convective current through the water in order to promote uniform nanoparticle sizes. Concurrently, the metal rod was rotated at approximately three rotations per minute by a stepper motor (LSG42, Hurst Instrument Motors). The second harmonic of an Nd:YAG laser (532 nm, GCR-150, Quanta Ray) focused through a 30 cm focal length optical lens, at a laser power of 3 W (6-ns pulse length) and a repetition rate of 30 Hz was used to ablate the rod. The duration of each experiment was approximately 2 h. The as-prepared gold clusters were then undertaken characterization via Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) with the microscope operating at 200 kV (JSM-2010 LaB6, JEOL).

2.2. Zeta potential, DLS size distribution and ionic strength measurements

The zeta potential and dynamic light scattering (DLS) measurements were performed using a ZetaPlus Zeta Potential Analyzer (Brookhaven Instruments Corporation, Holtsville, NY). A volume of 1.5 mL of the sample was added to a disposable polystyrene cuvette and the electrode was inserted. The cuvette with sample and electrode was inspected to insure no bubbles or other debris which would interfere with the measurement. The zeta potential was determined by using the ZetaPALS software. For DLS measurements, 2 mL of sample was added to a polystyrene cuvette and no electrode is used. The 90Plus Multi Angle Particle Sizing software on the ZetaPALS instrument measured the particle size. The collection angle for the scattered light for size measurements was 90°.

To estimate ionic strength based on conductivity, a standard curve was constructed to relate the concentration of KCl in solution to the solutions of specific conductivity. A 10⁻² M KCl solution was made in volumetric glassware, and through serial dilutions the fi-

nal solutions ranged from 10⁻² M to 10⁻⁵ M KCl. The specific conductivity was measured using an YSI-3200 Conductivity Meter (YSI Incorporated, Yellow Springs, OH). The specific conductivity of the sample was determined using the conductance measurement from the ZetaPlus instrument and the cell constant for the electrode. To determine the cell constant for the electrode, the conductance of a solution of 10⁻² M KCl solution was measured using the ZetaPlus instrument. The electrode's cell constant was calculated using the ratio of these two values. This cell constant, multiplied by the conductance which was measured by the ZetaPlus, gives the specific conductivity of the sample. The ionic strength of the sample was then calculated using the linear fit of the standard curve and the calculated specific conductivity of the sample.

2.3. Raman measurements and sampling methods

The samples for Raman measurements were prepared by simply dropping the as-prepared gold colloid onto the sample surfaces, dried completely with gold cluster coatings on the ink area. The samples were then kept in vacuum to avoid dust or other contaminate. When running Raman measurements, cut small pieces of the samples (paper) and pasted level off to cover glasses. All Raman experiments were performed on a micro-Raman spectroscope (Renishaw 2000) equipped with a dual laser system. A He-Ne laser (JDS Uniphase) was used with the excitation wavelength at 633 nm. The Raman system was equipped with a holographic notch filter and a CCD detector for high-sensitivity measurements. The laser power was approximately 10 mW with the acquisition time at 10 s for each scan, and the spectral resolution was 3 cm⁻¹. The optical image was captured *in situ* using a 100 × optical microscope.

3. Results and discussion

The as-prepared gold clusters were found to be monodisperse, as shown of a TEM image in Fig. 2a where the particles display spherical structures and mostly have a diameter of ~10 nm. Fig. 2b shows a SAED pattern, while a high resolution TEM image of the crystal lattice is shown in Fig. 2c, which are in agreement with the general crystal data of gold. A statistical analysis based on both ImageJ histogram and DLS measurements again shows that these gold clusters display a size distribution centered at 10-nm and they are metastable for several months, as shown in Fig. 2d.

The size distributions of gold clusters are also associated with the UV-Vis absorption spectra. Fig. 3A shows the corresponding spectra of the gold clusters. The fresh gold colloid displays an absorption peak at 518-nm (curve a) corresponding to an approximate dimension of 10-nm [29,30]. The other curves (b-e) in Fig. 3A refer to spectra obtained at different times after cluster synthesis (i.e., several months), where a decreasing tendency in the absorption intensities and a small red-shift of the absorption peak values (from 518 to 539 nm) were observed with increasing time after the synthesis. Fig. 3B shows a schematic depiction for this process. It is indicated that aggregation/agglomeration of the colloidal clusters begins at about 2 months after preparation, which could be considered as long-term stability comparing with other colloids prepared by LAL although Au NPs prepared by certain chemical methods could also be stable for a long period of time. The obtained gold clusters in this study do not appreciably agglomerate over long periods of time but a gold coating on the container was present upon evaporation of the aqueous solvent. Such findings lead to further analysis on the stability of the gold clusters in aqueous solution.

One of the fundamental differences between the colloid in the current work and interfacial chemistry established in previous

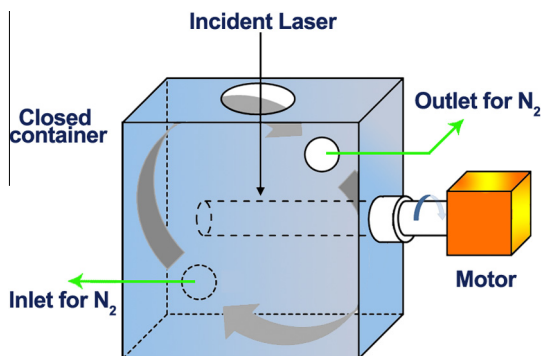


Fig. 1. A sketch of the setup used to prepare the gold clusters by the laser ablation method.

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