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Hybrid gold-silver nanoparticles synthesis using a nanosecond laser treatment and their use in Raman spectroscopy

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Abstract

Surface-enhanced Raman spectroscopy (SERS) has led to a large number of Raman enhancement studies due to its ability to analyze biomolecules and chemical compounds with remarkable sensitivity. It should be noted that a common problem with SERS substrates prepared chemically is the contamination of surfaces with molecules used to reduce or stabilize nanoparticles. Thus, although SERS substrates can be produced by a variety of methods, there is still a need for the development of SERS substrates with high enhancement factor, excellent reliability, no adsorbed impurities, and good scalability at low cost.
Here, we demonstrate a simple method for the production of SERS substrates using a laser treatment of hybrid gold-silver films. The presented approach does not use complicated procedures such as etching and template creation. The manufacturing process is primarily based on a spinodal wetting process of the molten gold/silver film.

Keywords: Hybrid gold-silver nanoparticles; thin films; SERS;

1. Introduction

In this study, a straightforward approach for producing gold-silver nanoparticles on a glass substrate is presented. It involves the nanosecond laser-induced dewetting of thin bimetallic films. When nanosecond laser pulses with a high enough laser fluence are used to expose a thin bimetallic film, the film melts and

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remains in the molten phase until the equilibrium between electrons and phonons is reached. Due to the slower energy transfer from the electron sub-system, the molten phase can last a long period in noble metals such as gold or silver. Then the temperature fluctuations increase and the thin layer destabilizes. The increase in temperature fluctuations causes the thin layer to spontaneously destabilize and change into a variety of bimetallic nanoparticles. Due to their unique light absorption and scattering, the produced bimetallic nanoparticles have transitional colors between pink and yellow. The various nanoparticle array colors are connected to the various localized surface plasmon resonance wavelengths and widths, which are influenced by the various nanoparticle compositions, morphologies, size dispersion, and distribution. Depending on the thickness and set-up of the thin layers employed, the position of the resonance peak of bimetallic nanoparticles may be varied between 400 and 530 nm, and its width ranges from 40 to 130 nm. The produced nanoparticles have a surface-enhanced Raman spectroscopy (SERS) enhancement factor exceeding 10^5 at an excitation wavelength of 532 nm. The range of excitation wavelengths in SERS may be expanded by utilizing nanoparticles with different chemical compositions. The generated nanoparticles can also be used to improve the efficiency of solar cells due to their wide localized surface plasmon resonance.

2. Results and Discussion

A nanosecond pulsed laser operating at 532 nm wavelength with 75 mW average power, 10 ns pulse duration, and 500 Hz repetition rate was used to generate hybrid gold and silver nanoparticles on a glass substrate from thin gold-silver films, which were prepared using magnetron sputter Quorum Q150T at room temperature in an Ar atmosphere of 10^{-3} bar with a deposition rate of 0.27 nm/s for gold and 0.59 nm/s for silver. At the level of $1/e^2$, the diameter of the Gaussian beam on the surface was around 100 μm. The beam scanning speed was set at 25 mm/s, and the hatch (the space between laser scanning lines) was chosen to be 50 μm. An inVia Raman spectrometer (Renishaw, Wotton-under-Edge, UK) with a thermoelectrically cooled (-70°C) charge-coupled device camera and a 50x/0.50 NA long working distance objective was used to measure the Raman spectra. Diode lasers with average powers of 0.38 mW and 0.45 mW at 532 nm and 633 nm, respectively, served as the excitation sources. The Raman spectra were captured using gratings with 1800 lines/mm (for 532 nm) and 1200 lines/mm (for 633 nm) respectively. The accumulation time was 9 s. The Si-Si vibrational mode at 520.7 cm^{-1} served as the reference point for the Raman wavenumber axis. The samples were submerged for 16 hours in a 1 mM solution of 4-mercaptobenzoic acid (4-MBA) in ethanol. The samples were carefully cleaned with ethanol (96%) before the measurements, and after being purge with nitrogen gas, they were dried at room temperature.

SEM images of nanoparticles produced using the laser-induced dewetting of 12 nm thick silver and 1 nm gold films are shown in Fig. 1(a,b). The morphology and size distribution of nanoparticles depends on the order of silver and gold films. When a silver film is on glass and the gold film is on top of the silver film, the size distribution is narrower compared to the size distribution of nanoparticles obtained from the opposite order of films. The size distribution is determined by the morphology of the untreated films. The size distribution determines the width of localized surface plasmon resonance which can be observed in the extinction spectra given in Fig. 1(c,d). SERS activity of synthesized nanoparticles was assessed by using molecule 4-mercaptobenzoic acid (4-MBA). The measured Raman spectra for the excitation wavelengths (532 and 633 nm) are given in Fig. 1(e,f). The Raman signal intensity at 633 nm is lower compared to the excitation wavelength at 532 nm, because the excitation wavelength at 633 nm is farther away from the plasmon resonance, resulting in a lower enhancement factor for the Raman signal. The same reason leads to the higher Raman signal intensity for nanoparticles obtained from the 1 nm gold film and 12 nm silver film on top as these nanoparticles exhibit broader localized surface plasmon resonance compared to the opposite order.

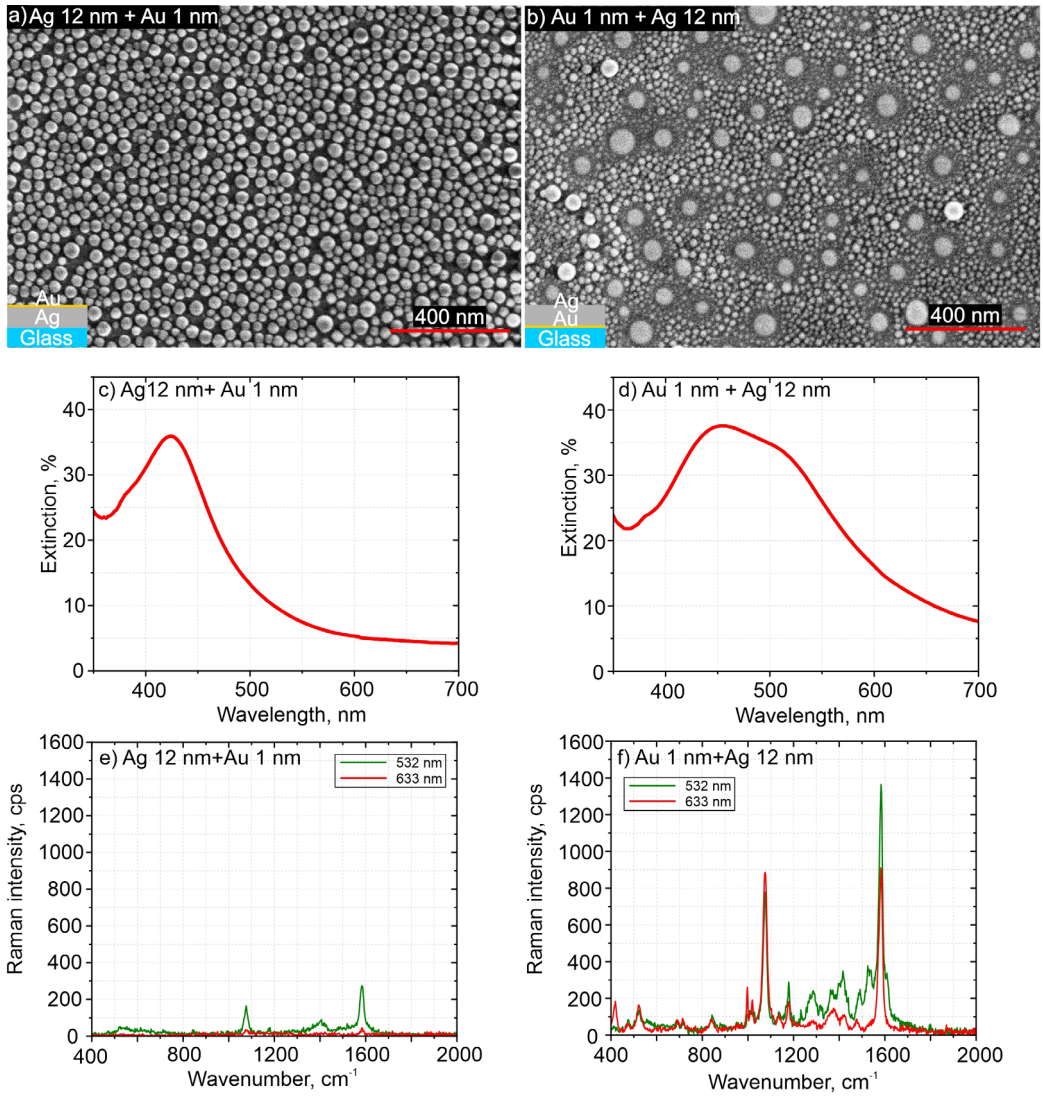

Fig. 1. (a, b) AgAu nanoparticles obtained from 12 nm silver and 1 nm gold films, which are coated in a different order on the glass substrate; (c, d) extinction spectra of the nanoparticles shown on top; (e, f) Raman spectra of 4-MBA using the same nanoparticles.

3. Conclusions

In this work, bimetallic thin films were thermally heated using a nanosecond pulsed laser to produce hybrid gold-silver nanoparticles. The experimental results show that the primary layer of hybrid thin films affects the size and size dispersion of the obtained bimetallic nanoparticles. The nanoparticles obtained from the bimetallic layer containing the primary silver layer have a lower size dispersion. The order of silver and gold layers affects the width of the localized surface plasmon resonance. The wider resonances are obtained when the primary layer is gold. The larger wideness of the localized surface plasmon resonance may be the main reason of the higher Raman signal enhancement.

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