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ORIGINAL RESEARCH

Size-dependent optical properties of Au nanorods

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Abstract In the fast evolving field of nanoscience and nanotechnology, where size and shape are crucial in deciding the optoelectronic properties of nanomaterials, the understanding of size and shape dependent behavior is of direct relevance to device applications. Present study reports the synthesis of Au nanorods with well controlled aspect ratios, and the influence of the aspect ratio on the surface enhanced Raman scattering (SERS) activity using crystal violet (CV) as the probe molecule. The influence of pH and the concentrations of reducing agent and Ag ions in controlling the aspect ratio of gold nanorods are also investigated. The structural and optical properties of the synthesized samples have been characterized by transmission electron microscopy (TEM) and UV–visible absorption spectroscopy. The nonlinear optical (NLO) transmission of the Au nanorods investigated using the open aperture Z-scan technique revealed the absorption saturation followed by an optical limiting behavior, which may find potential applications in optoelectronic nanodevices.

1. Introduction

Anisotropic metallic nanoparticles like rods have recently attracted a lot of attention due to their distinctive optical properties which lead to device applications such as nanoprobes, plasmonic waveguides and optical limiters. When excited by electromagnetic radiation nanorods give rise to longitudinal and transverse surface plasmon absorption peaks corresponding to the collective oscillation of the quasi-free electrons along the long and short axes respectively. The transverse plasmon resonance is almost insensitive to the morphology of nanorod, i.e., the spectral location of the longitudinal surface plasmon resonance (LSPR) can be easily tuned from green to NIR by modifying the nanorod aspect ratio [1]. On the basis of these properties, noble metal nanorods are considered to be good candidates for different applications such as nanoparticle mediated hyperthermal cancer therapy, optical data storage, and surface enhanced Raman scattering (SERS) [2]. Since its discovery SERS has served as a valuable tool in analytical chemistry in the

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characterization of compounds owing to the wealth of structural information it can provide. It is a powerful spectroscopic technique capable of non-destructive and highly sensitive characterization down to single molecule levels.

The SERS phenomenon is often described in terms of the electromagnetic as well as chemical enhancement mechanisms. By the electromagnetic mechanism, when the wavelength of incident light is close to the surface plasmon resonance, molecules adsorbed or in close proximity to the surface experience an exceptionally large electromagnetic field, resulting in Raman signal enhancement. The magnitude of electromagnetic enhancement is highly dependent on the plasmon absorption of the SERS substrate [3,4]. On the other hand chemical enhancement depends on the nature of the molecule, and results from an increased molecular polarizability by the formation of a charge transfer complex between the metal surface and the adsorbed molecule. The electronic transitions of many charge transfer complexes are in the visible region, which leads to a resonance Raman enhancement. The enhancement factors for different molecules can be different on identical SERS substrates.

In general SERS requires the use of rough surfaces of conductive materials or metal colloids, and therefore, spheroidal or rod shaped Ag and Au nanoparticles are of significant interest as SERS substrates. The fact that for rods the LSPR can be tuned is often exploited to increase the contribution of electromagnetic enhancement mechanism. The most common SERS substrates are metal particles dispersed in a colloidal suspension, rough surfaces of electrodes, and metal island films. The presence of nanostructured metal surfaces is essential for obtaining an efficient coupling between the incident radiation and the plasmon resonance bands of the substrate, whose wavelengths depend on the size and shape of the metal nanoparticles. In addition, SERS provides the possibility to acquire information specifically from the surface of materials. This trace analytical capability at the nanoscale can be used, for example, to track the migration of molecules inside cells and to design integrated cellular probes [5–8]. Single molecule detection has been reported [9] with enhancement factors as large as 10^{14}. Since the introduction of the SERS phenomenon on roughened Ag electrodes, much attention has been given to SERS on colloidal substrates of either Au or Ag to maximize the Raman signals [10–13].

Murphy and coworkers [13] have studied the aspect ratio dependence on SERS using Au and Ag nanorods and observed an enhancement in activity upon the coupling of the localized surface plasmon of Au nanorods. El-Sayed and coworkers [14] have investigated and compared the SERS property of Au nanorods and Au nanospheres under the off-surface plasmon resonance condition, and concluded that Au nanorods have a stronger activity. This is attributed to the partial excitation of the LSPR band and the contribution of the chemical effect between the strong binding of the adsorbate and the {110} facets of the Au nanorods.

In the present investigation the synthesis of Au nanorods of different aspect ratios by a seed mediated technique is reported. The influence of various parameters like the silver ion concentration, seed concentration, ascorbic acid concentration and pH of the growth solution on the aspect ratio of the Au nanorods is discussed. Au nanorods grown under optimum conditions has been then tested for Raman enhancement using crystal violet (CV) as probing molecule, and the influence of aspect ratio on the enhancement factor is investigated. The prepared nanoparticles exhibit efficient SERS properties, and their SERS activities are found to be highly dependent on the aspect ratio. Investigations of the nonlinear transmission of Au nanorods in an aqueous suspension has been carried out using open aperture Z-scan employing 7 ns laser pulses at 532 nm, and the results are discussed in detail.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$, 99.99%), silver nitrate ($AgNO_3$, 99.99%), sodium borohydride ($NaBH_4$, 99.99%) and crystal violet (CV, 99.9%) were purchased from Sigma Aldrich. Cetyltrimethylammonium bromide (CTAB, 99%) and ascorbic acid (98%) were obtained from Alfa Aesar. Deionized water was used throughout the experiments.

2.2. Instrumentation

UV–visible absorption spectra were recorded using Jasco V-550 UV–vis spectrophotometer with the samples in 1 cm optical path quartz cuvette. The shape and size of the particles were obtained using FEI TECNAI 30 G^2 S-TWIN transmission electron microscope. The SERS spectra were collected with a Renishaw invia microRaman spectroscopy system with a 785 nm laser as excitation source. The laser beam was focused on the samples through a 20X objective and the Raman signals were collected through the same objective in the back scattering geometry. The laser power used was 50 mW and the acquisition time was 30 s. The nonlinear transmission properties were investigated using the open aperture Z-scan method. Here the sample is moved a certain distance through the focal region of a focused laser beam, and the sample transmission is measured at small intervals of position. We used a stepper motor controlled linear translation stage to move the sample (taken in a 1 mm glass cuvette) through the beam in precise steps. The transmission of the sample at each point was measured by means of two pyroelectric energy probes (RjP7620, Laser Probe Inc.). The second harmonic output (532 nm) of a Q-switched Nd:YAG laser (Minilite, Continuum) was used for excitation. The nominal pulse width of the laser was 5 ns. The pulses were fired in the single shot mode, allowing about 1 s between successive pulses to avoid accumulative thermal effects in the sample. The experiment was automated using a program written in LabView.

2.3. Preparation of Au nanorods

Gold nanorods were prepared by a seed-mediated growth method with slight modifications [15]. Briefly, seeds are prepared by reducing 10 mL of an aqueous solution containing 0.25 mM gold tetrachloride ($HAuCl_4$) in 0.1 M cetyltrimethylammonium bromide (CTAB), adding 0.6 mL of 0.01 M sodium borohydride ($NaBH_4$). After 2 h, 10 μL of the seed solution is added to 10 mL of a growth solution consisting of 0.5 mM $HAuCl_4$ and 0.08 mM silver nitrate in 0.1 M CTAB mixed with 0.0788 M ascorbic acid. The solution was gently mixed for 1 min and then left undisturbed for 24 h to complete rod growth. The prepared Au nanorods were separated from