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Self-assembled 3-dimensional arrays of Au@SiO_2 core-shell nanoparticles for enhanced optical nonlinearities

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Abstract

Homogeneous SiO_2 coated Au nanoparticles were prepared and assembled into densely-packed 3-dimensional arrays by a simple ''one-step'' route based on the layer-by-layer self-assembly (LBL) technique. Every layer of films exhibited densely packed 2-dimensional arrays of Au@SiO_2 composite nanoparticles and the film thickness was controllable through the number of deposition cycles. These multilayer films exhibited high effective packing density of composite nanoparticles (0.57). Those arrays also exhibited enhanced third-order optical nonlinear responses and ultra-fast response times. The third-order nonlinear optical susceptibility of the seven layer arrays was estimated to be 1.7×10^{-9} esu at 532 nm and the response time was as fast as several picoseconds. The enhancement of the optical nonlinearity was calculated according to the electrostatic approximation by solution of Laplace's equation under the boundary conditions appropriate to the model of core-shell nanoparticles, and mainly attributed to localized electric-field effects.

Keywords: Self-assembly; Gold; Atomic force microscopy; Surface structure, morphology, roughness and topography; Nonlinear optical methods

1. Introduction

Nanoscale architectures of composite nanoparticles have attracted tremendous interest because of their potential applications in nanoelectronics devices, catalysis, molecular recognition, nonlinear optical devices [1,2]. Especially, these composite nanoparticles with core-shell structure (CSNs) often exhibit improved physical and chemical properties over their single-component counterparts, making them attractive from both scientific and technological viewpoints [3]. Those CSNs can simultaneously provide scaffolds for devices and

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serve as building blocks for the creation of extended 2- and 3-dimensional ordered arrays [4]. The self-assembly of CSNs into super-structure, thin films or 3D ''artificial solids'' offers an exciting pathway for the construction of materials with designer-specified optical, electrical and catalytic properties [5,6]. Xia et al. [7] have prepared Au@SiO_2 core-shell colloids (with average diameter of hundreds of nanometers) with long-range ordered arrangement and explored the potential use of these core-shell colloids as building blocks to fabricate functional optical devices such as photonic crystals and plasmonic waveguides. Liz-Marzán et al. [8] have synthesized Face Centered Cubic (fcc) opals with a suitable lattice constant to yield photonic band gap effects in the visible waveband based on silica-coated gold particles and studied their optical properties through transmission and specular reflectance measurements. Moreover, the metal-semiconductor core-shell composite nanoparticles could exhibit strongly enhanced nonlinear response by several orders of magnitude higher than their single-component based on the theoretical calculations by Neeves et al. [9] and related reports [10]. However, the optical nonlinear properties of these Au@SiO_2 core-shell nanoparticles or films are seldom reported.

Materials with large third-order optical nonlinearity and ultra-fast response time are essential for light-controlled phase and refractive index modulation for future applications in various fields such as optical telecommunications, optical data storage, optical computing and information processing [11]. It is well known that metal nanocrystallites embedded in transparent matrix exhibit novel linear and nonlinear optical properties due to local field enhancement near the surface plasmon resonance (SPR) of the metal. The metal particles' shape, dielectric environment, interparticle distance and interaction are the most important parameters determining the surface plasmon frequency and the optical nonlinear properties [12]. A significant challenge for enhancing the optical nonlinear response in materials is achieving high particle filling factor and preserving monodispersity of metal nanoparticles in the process of incorporation particles into host matrices. Here, we applied a simple route based on LBL method to self-assemble the densely-packed 3-dimensional ordered arrays of homogeneous SiO_2 coated gold nanoparticles. The inorganic SiO_2 shell layer could be used to keep gold nanoparticles monodisperse and control the interparticle spacing and interactions. Furthermore, the densely-packed 3-dimensional ordered structure of Au@SiO_2 was also helpful to increase the volume fraction of gold nanoparticles. Finally, the enhanced optical nonlinear response of these arrays was reported. The enhanced mechanism was also investigated according to the electrostatic approximation by solution of Laplace's equation under the boundary conditions appropriate to the model of core-shell nanoparticles, and mainly attributed to localized electric-field effects. The present paper also provides experimental evidence for Neeve's theory [9] about core-shell structures for the enhancement of nonlinear-optical susceptibility.

Materials composed of 2-dimensional (2D) and 3-dimensional (3D) ensembles of nanoparticles have been prepared previously, by infiltration of nanoparticles [13,14], electroless deposition [15], or electrochemical deposition [16] and layer-by-layer self-assembly (LBL) technology [17]. Especially LBL technology is used frequently for particle assembly, and preparation of composite films containing a very diverse range of materials because of the simplicity and versatility of the technique. The LBL technique has many advantages such as that the coating process is independent of the substrate size and topology. Liz-Marzán et al. [18] reported that silica coated gold nanoparticles were prepared using silane coupling agent firstly, and deposited on glass slides by the LBL method. But for their samples, only clusters of two or more particles were randomly distributed over the substrate in the first deposition cycle, and the substrate surface was completely covered with randomly packed composite nanoparticles until an additional fourth deposition cycle. To overcome this problem, we presented one different and simple ''one-step'' route combined with LBL technique to prepare Au@SiO_2 core-shell composite nanoparticle films with periodical 3D superstructure ''artificial solids''. In this study, the