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Evaluation of the third-order optical nonlinearity of Au:SiO_2 nanocomposites in the off-resonant spectral region

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ABSTRACT

The third-order nonlinear optical susceptibility ($\chi^{(3)}$) of Au:SiO_2 nanocomposite films with different Au particle sizes was measured to be on the order of 10^{-10} esu to 10^{-9} esu in the off-resonant spectral region, and the particle size-dependent behavior of $\chi^{(3)}$ was observed. The results were found to deviate substantially from those of the conventional Maxwell-Garnet theory. By adapting the modified invariant imbedding method, which takes into account the effect of interparticle interactions on the nonlinear response, we successfully explain the enhanced third-order nonlinear susceptibility of metal–dielectric nanocomposites at off-resonant wavelengths.

1. Introduction

Metal–dielectric nanocomposites have emerged as promising efficient nonlinear optical (NLO) materials, with their intriguing large and fast optical response stemming from the well-known surface plasmon resonance (SPR) phenomenon [1,2]. Various techniques such as ion implantation [3], melting and heat treatment [4], photoreduction [5], and sputtering [6] have been widely used to prepare high-quality nanocomposites, in which fine particles of metals such as Au, Ag, and Cu are embedded in transparent dielectric matrices. These nanocomposites are known to exhibit quite large third-order nonlinearities ($\chi^{(3)} > 10^{-7}$ esu) near their SPR peaks. They are also known to exhibit size-dependent optical properties, especially in their quantum-size confinement regime. These size-tunable optical properties of nanoparticles are of current interest because they can have a significant impact on the development of nanophotonic devices. For most practical fast photonic applications, however, NLO materials need to possess large $\chi^{(3)}$ values with as low absorption as possible at the wavelengths of interest.

Over the past two decades, the nonlinear optical properties of Au:SiO_2 nanocomposite films, prepared with varying Au particle sizes and volume fraction, have been intensively investigated using degenerate four wave mixing (DFWM) and *z*-scan techniques [3,7,8]. The enhancement of third-order nonlinearity at frequencies close to SPR is mainly attributed to the local field enhancement, which could be predicted by the Maxwell-Garnett (MG) theory, and also to strong interparticle interactions [9]. Most investigations reported up to now, however, have been primarily limited to a spectral range around the SPR wavelength, where the absorption increases rapidly. However, by using single beam *z*-scan method, we showed that the particle size-dependent enhanced nonlinear optical response of the Au:SiO_2 nanocomposite films can also be observed in off-resonant spectral regions near 800 nm [10]. We found that the results deviated substantially from what was expected by the MG theory if we treated our samples as MG media. In the present work, we utilize a relatively new technique, called the invariant embedding method, by considering the samples as homogeneous effective media in order to explain the third-order nonlinear optical response of the Au:SiO_2 nanocomposite at 800 nm and 1250 nm. This numerical calculation takes into account the local field factors inside the metal–dielectric nanocomposites that are analyzed through the dielectric constants, the linear transmittance, and the reflectance. The possible mechanisms for the sign reversal, the magnitude of $\chi^{(3)}$, and the reason for the deviation of the results from the MG theoretical analysis are discussed. Special attention is given to

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verify if the thermal accumulation could modify the optical nonlinearities of Au:SiO_2 samples, by using the thermally managed *z*-scan method [11].

2. Experiment

2.1. Sample preparation

Au:SiO_2 nanocomposite films with different Au particle sizes were deposited on fused silica substrates by alternating sputtering of SiO_2 and Au at room temperature, while the volume fraction of Au was kept constant at 2%. The nominal thicknesses of the Au layers in samples denoted as NC0.2, NC1.0, NC2.0, and NC2.5 were chosen to be 0.2 nm, 1.0 nm, 2.0 nm and 2.5 nm, respectively. To achieve an equal overall film thickness of 1.5 μm for all the samples, different deposition rates were applied by controlling the thickness of the SiO_2 layers. Details of the design parameters for each film and the estimated morphology after the film preparation are listed in Table 1.

Table 1
Design parameters and estimated morphologies of the Au:SiO_2 nanocomposites (NCs).

Sample	Nominal thickness (nm)		Mean diameter of Au (nm)	Number of layers		Volume fraction (%)		Film thickness (nm)
	Au	SiO_2		Au	SiO_2	Au	SiO_2	
NC0.2	0.2	19.54	1.08	75	76			
NC1.0	1.0	92.81	2.00	15	16			
NC2.0	2.0	165	3.03	8	9	2	98	1500
NC2.5	2.5	212.14	3.23	6	7			

The plan-view TEM images of four separate SiO_2/Au/SiO_2 films (see Fig. 1), which were grown on carbon-coated Cu grids, were recorded for verifying the size of the embedded Au particle. The deposition procedure for similar Au:SiO_2 nanocomposite films is described in detail elsewhere [12,13]. The linear optical absorption spectra and the refractive indices were estimated by employing a spectrophotometer and a variable angle spectroscopic ellipsometer (VASE, Woollam), respectively.

2.2. Conventional/thermally managed z-scan

The *z*-scan technique [14] was used to determine the nonlinear refractive indices (n_2) and nonlinear absorption coefficients (β) of the Au:SiO_2 nanocomposites. A Ti:sapphire oscillator and an optical parametric oscillator (OPO) were used as the excitation sources. The Ti:Sa laser (Chameleon, Coherent Inc.) operates at 80 MHz and delivers 150 fs pulses at 800 nm, and the synchronously-pumped OPO (Mira OPO, Coherent Inc.) delivers 200 fs pulses at 1250 nm with the same repetition rate as that of the Ti:sapphire oscillator. The output pulses from the oscillator were focused on the sample by a lens with a focal length of 5 cm. The sample was translated around the focal point and the transmission changes were recorded in both the closed-aperture (CA) and open-aperture (OA) *z*-scan geometries. The beam waist at the focal point was measured by the knife-edge method. To improve the signal-to-noise ratio, the pulses were modulated by using a chopper, and the transmitted signal was measured by a photodetector that was connected to a lock-in amplifier (SR850, SRS). Subsequently, the measured signal was corrected by the reference signal from the same source, which was detected by a separate photodetector in front of the focusing lens.

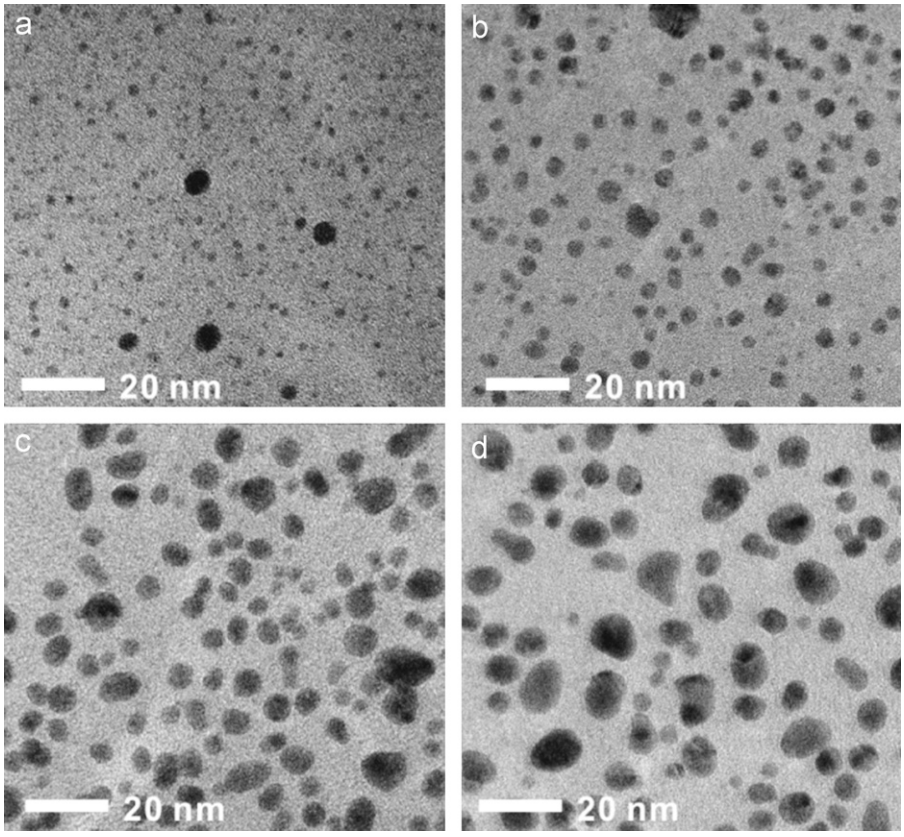

Fig. 1. Top-view TEM images of the SiO_2/Au/SiO_2 nanocomposite films with Au mean diameters of (a) 1.08 nm, (b) 2.00 nm, (c) 3.03 nm, and (d) 3.23 nm.