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Enhancement of optical nonlinearity in binary metal–nanoparticle arrays

Weitian Wang *, Zhenhong Dai, Yuming Sun, Yuanping Sun

Institute of Opto-Electronic Information Science and Technology, Yantai University, Yantai 264005, PR China

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ABSTRACT

Periodic binary metal–nanoparticle arrays, comprising of Au and Fe, were fabricated on quartz substrates using nanosphere lithography and pulsed laser deposition technique. The dimension of the obtained triangular Au(Fe) particles was about 80 nm which was defined by the single-layer masks prepared by self-assembly of polystyrene nanospheres with radius $R = 100$ nm. The structural characterization of the particle arrays was investigated by atomic force microscopy. In the optical absorption spectra, the metal–nanoparticle arrays show a strong absorption peak of ~550 nm due to the surface plasmon resonance of metal particles. The nonlinear optical properties of the nanoparticle arrays were determined using a single beam *z*-scan method at a wavelength of 532 nm with laser duration of 55 ps. By adding Fe, the resonant absorption of Au particles was quenched, and the figure of merit $\chi^{(3)}/\alpha$ (with $\chi^{(3)}$ being the third-order nonlinear susceptibility, α being the absorption coefficient) was obviously increased. The obtained maximum $\chi^{(3)}/\alpha$ is about 6.15×10^{-12} esu cm. The results show that periodic Au + Fe nanoparticle arrays exhibit a large nonlinear optical property with fast response.

1. Introduction

Nanocomposites comprising of metallic nanoparticles have attracted much attention because of their interesting nonlinear optical properties which have opened many possibilities for their use in various technological applications, such as phase conjugation, optical switching and light frequency converter. The idea is that the third-order optical nonlinearity of a low dimensional material with delocalized electrons can be enhanced because of the giant amplification of the local electric field near and inside the metal particles at the surface plasmon resonance [1].

Unfortunately, many studies show that the enhancement of third-order nonlinear susceptibility, $\chi^{(3)}$, is always accompanied by an increase in absorption coefficient α [2]. In practical applications, a large $\chi^{(3)}$ is insufficient as the strong absorption causes great damage. Therefore, the more important parameter for practical use is the figure of merit (FOM), defined as $\chi^{(3)}/\alpha$. Some researchers suggested that the FOM of a nonlinear material with geometric anisotropic structure can be enhanced greatly [3]. We previously presented an approach based on materials architecture for eliminating the resonant absorption and increasing the optical nonlinearity in the nanometer-sized metal-dielectric composites [4]. However, the metal particles were randomly distributed and the shape was disordered. As is known, the third-order susceptibility of the composite material is related to that of its constituents and sensitive to the metal particle distributions [3,5]. The physical properties of nanoparticles with periodic or ordered arrangement are different from those of unorganized particles.

In this paper, we report the fabrication and nonlinearities of periodic binary metal–nanoparticle arrays deposited on quartz substrates using nanosphere lithography (NSL). The particles consisted of two kinds of metal, Fe and Au, which were used to decrease α and increase $\chi^{(3)}$ simultaneously, therefore, the FOM $\chi^{(3)}/\alpha$ was enhanced. The dimension of the obtained triangular Au(Fe) particles was about 80 nm which was defined by the size of the polymer nanospheres on the masks. Atomic force microscopy (AFM) was used to characterize the structure and metal distribution. The optical nonlinearity was investigated with *z*-scan technique [6,7] in order to determine both the real and imaginary parts of the third-order susceptibility.

2. Experimental details

The periodic metal nanoparticle arrays were fabricated using nanosphere lithography (NSL), an inexpensive, simple and high throughout nanofabrication technique [8]. The NSL structure begins with the self-assembly of size-monodisperse polystyrene nanospheres of radium $R = 100$ nm to form a two-dimensional colloidal crystal deposition mask on the fused quartz substrates which was cleaned with acetone and alcohol beforehand. Fig. 1(a) schematically shows a single layer of nanospheres with chosen radius R on substrates. When

* Corresponding author.
E-mail address: wtwang@ytu.edu.cn (W. Wang).

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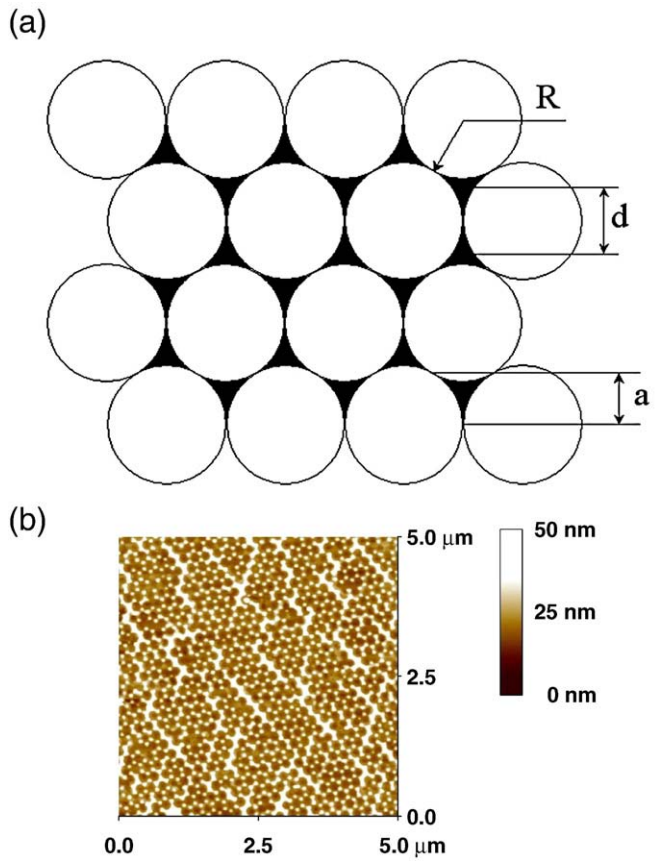

Fig. 1. (a) Schematic picture of single-layer nanosphere masks with chosen radius *R*. (b) Typical 5×5 μm^2 2D AFM image of metal–nanoparticle arrays.

the nanospheres assembled compactly, periodic array composed of threefold hole (black) was formed. The interparticle spacing *d* and the in-plane particle dimension *a* defined in Fig. 1(a) are given by

$$d = \frac{2}{3}\sqrt{3}R \tag{1}$$

and

$$a = \frac{1}{2}\sqrt{3}R, \tag{2}$$

respectively.

Once the nanophere masks were dry, the substrates were mounted into a pulsed laser deposition system. Gold or iron targets were ablated using a Lambda Physic KeF excimer laser (248 nm, 20 ns full width at half maximum, 4 Hz repetition rate) and deposited onto the mask-coated substrates, and the ratio of Au to Fe was controlled by adjusting the relative area proportion on the target, which was mounted on a rotating holder, 40 mm from the substrates. The typical energy density was about 2.5 J/cm^2. During the deposition process, the deposition chamber was vacuumed to a pressure of 5×10^{-3} Pa and the substrates were maintained at room temperature. Five samples, namely Sample 0–4, were prepared in our experiment. Sample 0 was grown with a pure Au target, while Sample 4 with Fe target, and other three samples were produced with an Au/Fe two-material physical assembly as target. The concentrations of Au and Fe in the samples were detected by X-ray photoelectron spectroscopy (XPS) which was carried out under vacuum of 1.33×10^{-8}Pa using MgKα *x*-radiation. The atomic ratio (at.%) of Fe/(Fe + Au) were determined to be 19%, 41%, and 68% for Sample 1, Sample 2, and Sample 3, respectively. The thickness of the deposited metal films was about 80–100 nm, controlled by the deposition time. After deposition of metals, the polystyrene nanospheres were completely removed from the substrates by dissolving them in chloroform with the aid of ultrasonication for 1–3 min. With the mask liftoff, the metal-nanoparticle arrays with well-ordered planar structures were obtained.

The microstructure of the metal-nanoparticle arrays was investigated by AFM (Digital Instrument Nanoscope IIIa) in contact mode with a NPS-type Si_3N_4 tip. The linear optical absorption measurements were made at room temperature in air from 330 to 800 nm using a SpectraPro-500i spectrophotometer (Acton Research Corporation). The nonlinear optical properties of the periodic metal-nanoparticle arrays were investigated using *z*-scan technique. In our measurements, a Q-switched Nd:YAG laser with frequency doubled at 532 nm and characterized by pulse duration of 55 ps at a repetition rate of 1 Hz was employed as the light source. The laser beam was focused on the sample with a 120 mm focal length lens leading to a measured beam waist of 30 mm and pulse energy of 4.6 mJ at focus. A weak reference beam was used to monitor energy fluctuation. The *z*-scan experimental details were reported previously [9].

3. Results and discussion

With controlling the humidity and temperature carefully, we formed a homogenous dense nanosphere monolayer with area larger than 1 cm^2 by drop coating a little amount of polystyrene nanosphere solution onto cleaned quartz substrates which were polished on both sides (0.5 mm in thickness). Fig. 1(b) gives 5×5 μm^2 images of metal-nanoparticle arrays generated from the polystyrene nanosphere mask. The AFM image exhibits a hexagonal patterned 2D periodic nanoparticle arrays consisting of homogenous triangular-shaped metal nanoparticles. The in-plane width of the particles is about 80 nm and the interparticle spacing is estimated to be 110 nm, which is in agreement with the Eqs. (1) and (2). As the polystyrene nanospheres were obtained from a commercial source, the impurity or slight vibrations from surroundings during preparation could induce some defects in nanosphere monolayer mask. As a result, the strip-shaped defects can be seen clearly in the metal–nanoparticle arrays. However, the cubic optical nonlinearity of a material with delocalized electrons can be enhanced by artificially confining the electrons in regions smaller than their natural length in the bulk [1]. This means the dominating contributions to the enhancement of third-order optical nonlinearity of the arrays are from the hexagonal patterned nanometer-sized metal particles. The effects of the defects can be neglected since the size is as long as several microns.

Fig. 2 shows the optical absorption spectra of the samples as a function of photon energy. A strong absorption peak due to the

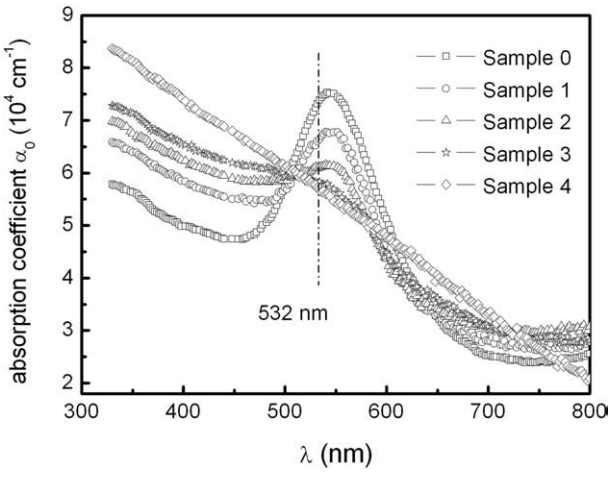

Fig. 2. The optical absorption properties of the prepared samples.