

## Laser-Induced Light Absorption in 2D Silver Nanoparticle Array

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Nanocomposite comprising planar array of silver nanoparticles in polymer matrix was submitted to Ar laser irradiation at the wavelength of 488 nm. The extinction spectra of the array were measured as a function of the irradiation power density. Two collective surface plasmon modes, namely T and P, associated with particle dipoles parallel and perpendicular to the plane of the layer were identified. The extinction bands of T and P modes exhibit blue spectral shift with the increase of radiation power. P mode band broadens when laser power increases. The observed effects are explained by heating of the nanocomposite by the intense laser radiation.

**Keywords:** Localized Surface Plasmon Resonance, Silver Nanoparticles, Nanostructures, Extinction Spectra.

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### 1. INTRODUCTION

The unique optical properties of noble metal nanoparticles are governed by the excitation of free electrons oscillations. Since oscillations are localized within the surface of a nanoparticle they termed localized surface plasmon resonance (LSPR). The resonant frequency depends on the nature of the metal, size, and shape of a nanoparticle as well as on dielectric environment. Localization and resonant character of free electrons oscillations results in the enhancement of both electric and magnetic fields in the nanoparticle vicinity. This enhancement gives rise to various surface-enhanced techniques including well known SERS, SEIRA, and some nonlinear optical effects. Noble metal nanoparticles and their ensembles have a great potential in various areas of applications such as sensors, optoelectronics, photovoltaics, and metamaterials.

It was established earlier that arranging of Ag nanoparticles into closely spaced 2D arrays leads to the strong electrodynamic coupling between LSPR associated with individual nanoparticles. As a result the collective plasmon mode emerges in the array upon light excitation. This mode manifests itself as a narrow band in the extinction spectra and is an eigenmode of the entire array. The control over the optical response of 2D metal nanoparticle array can be achieved through the variation of the size of nanoparticles and distance between them. Temperature is another issue, which is important for many practical applications of metal nanoparticle structures such as thermally assisted magnetic recording, thermal cancer treatment, catalysis, and computer chips. In particular, increasing of the temperature results in the red shift and broadening of plasmon resonance associated with individual metal nanoparticle or non-interacting ones [1].

In present work, we have experimentally studied

changes in the extinction spectra of 2D array of Ag nanoparticles embedded into polymer matrix under the influence of intense laser radiation. The observed changes may have thermal origin.

### 2. EXPERIMENTAL

#### 2.1 Materials and Sample Preparation

Ag<sub>2</sub>O (99.99%) was purchased from Alfa Aesar. Hydrogen gas (99.9999%) was purchased from National Welders. Glycidyl methacrylate (GMA) from Aldrich was polymerized radically to give poly(glycidyl methacrylate) (PGMA), number average molecular weight ( $M_n$ ) = 176000 g/mole. Carboxyl-group-terminated poly(2-vinyl pyridine), P2VP-COOH ( $M_n$ =40600 g/mol), was obtained from Polymer Source, Inc. Chloroform (Aldrich) was used for preparing 2% PGMA and 2% P2VP solutions.

Silver nanoparticles with an average diameter of 115 nm were synthesized via hydrogen reduction of supersaturated silver oxide aqueous solution. Random planar arrays with closely spaced Ag nanoparticles were prepared by self-assembling of the particles onto chemically modified glass substrates [2]. The arrays exhibit no long-range order in the arrangement of the particles. The distance between adjacent nanoparticles in the array is 100–300 nm. Prior to self-assembling the slides were cleaned in freshly prepared 1:3 mixture of 30% H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> (piranha solution) and dried under a stream of nitrogen gas. After drying, the slides with Ag nanoparticle layer was covered with a 150–160 nm poly(glycidyl methacrylate) (PGMA) layer, so the entire array was encapsulated into the polymer. Polymer films were characterized by both ellipsometry and AFM techniques. Particles' size was determined employing scanning electron microscopy.

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## 2.2 Optical measurements

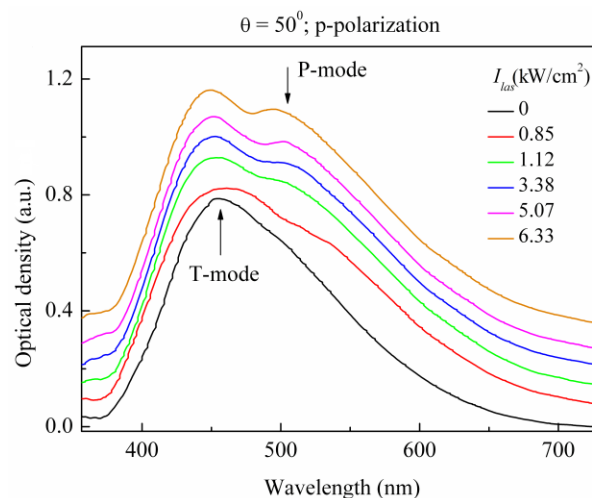
The extinction spectra of 2D Ag nanoparticle array were measured using double-grating spectrometer DFS-12 equipped with a tungsten-halogen incandescent lamp as a light source within the spectral range of 320–800 nm. The measurements were performed at two different angles of incidence  $\theta=0^\circ$  and  $\theta=50^\circ$ . The light beam was polarized linearly with polarization angle parallel to the plane of incidence (p-polarization) and perpendicular to the plane of incidence, which corresponds to s-polarization. The polarization angle is measured between the electric vector of light  $\mathbf{E}$  and the plane of incidence containing incident, reflected, transmitted light beams, and the normal to the sample surface. Focused CW Ar laser radiation at  $\lambda=488$  nm was used to heat up the nanoparticles. Laser beam was directed against probing beam outgoing from the monochromator (Fig. 1). The angle of incidence was varied by rotating the sample around the axis orthogonal to the light beam.

## 3. RESULTS AND DISCUSSION

Our earlier studies revealed the emerging of two types of collective LSPR modes in the planar monolayer of closely spaced Ag nanoparticles [2, 3]. Those are tangential (in the plane of the array) T mode and normal P mode, which is orthogonal to the plane of the array. Those modes appear as distinct bands in the extinction spectra measured at oblique angles of incidence at different polarizations of the incident beam. For s-polarization the electric vector of the incident light beam is parallel to the layer plane, thus exciting tangential mode only. The electric vector of a p-polarized beam contains both parallel and perpendicular components leading to the excitation of both P and T modes. The contribution of P and T modes into the spectra depends on the angle of incidence. Indeed, there is no difference between s- and p-polarized light at normal incidence. As the angle of incidence increases, the normal component for p-polarized light also increases while the tangential component for s-polarized light remains the same.

Fig. 2 depicts the extinction spectra of 2D Ag nanoparticle array submitted to CW Ar laser irradiation at the angle of incidence  $\theta=50^\circ$  for p-polarization. One can clearly see the increase of total absorption with increasing of laser radiation power density. Also, the band associated with P mode becomes more prominent with the increase of irradiation power density. Both P and T bands were

approximated as Lorentzian functions, normalized integral intensity of those bands is presented in Fig. 3.

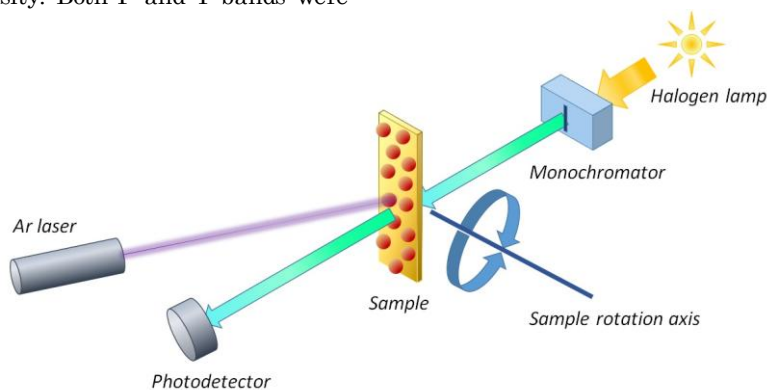


**Fig. 2** – Polarized extinction spectra of 2D Ag nanoparticle array embedded in PGMA matrix as a function of Ar laser irradiation power. The angle of incidence  $\theta=50^\circ$ .

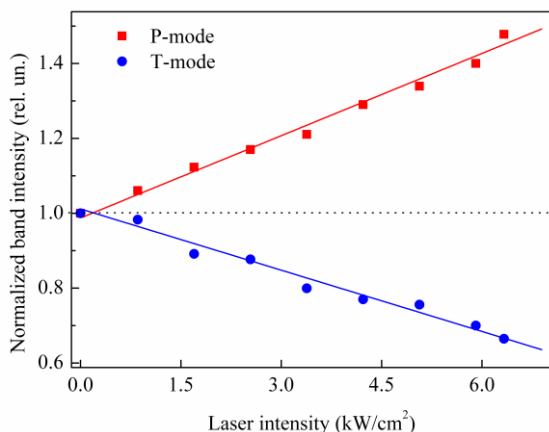
Detailed studies of the extinction spectra revealed broadening of the collective LSPR band and its slight shift towards the short wavelengths spectral range. Dependence of those parameters for P and T modes upon laser radiation power density is presented in Figs. 4 and 5.

The most plausible reason of the observed phenomena is heating of the sample by the intense laser radiation. Moreover, one should expect higher values of the temperature for metal nanoparticles rather than for transparent polymer matrix. While the former absorb laser light directly, the latter heats up due to thermal flow from the nanoparticles to matrix.

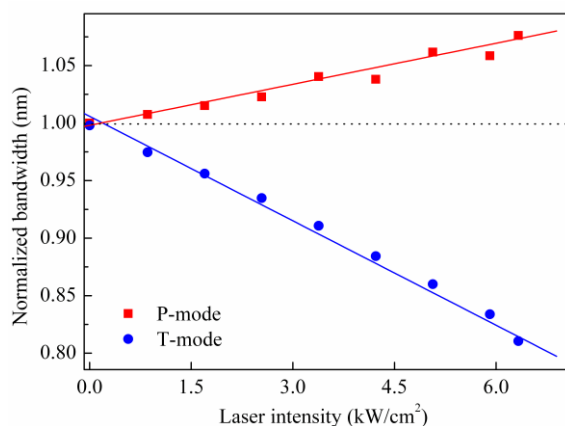
Several processes take place when the sample temperature increases, namely surface damping, electrons spill-out, and dielectric environment effects. Finally, metal nanoparticles undergo significant thermal expansion. The latter effect results in the decrease of free electron density within a nanoparticle, thus lowering its resonant plasmon frequency. At the same time, the electron–phonon scattering rate increases with the temperature rise. That immediately leads to the increase of damping constant and to the broadening of LSPR band. Note that the bandwidth P and T modes behaves



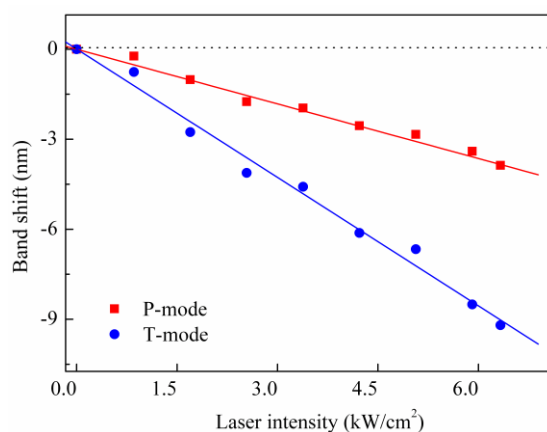
**Fig. 1** – Experimental set-up and arrangement.



**Fig. 3** – Intensity of P and T plasmon bands as a function of laser irradiation power. The spectra are normalized on the spectrum of non-irradiated sample.



**Fig. 4** – Normalized bandwidth of P and T bands. The bands were approximated as Lorentzian function.



**Fig. 5** – Spectral shift of P and T bands as a function of laser irradiation power.

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different with respect to the radiation power (Fig. 4). The bandwidth of P mode increases with increasing of laser power according to the above considerations, while T mode becomes narrower. The intensity of T mode goes down as the irradiation power increases.

Let us discuss some unexpected blue shift of plasmon P and T modes with the increase of irradiation power (i.e. temperature). First of all, host matrix expands with the temperature increase, so the distance between nanoparticles in the array becomes larger, thus weakening coupling between them. It is well known that dielectric properties of the surrounding strongly affect resonant frequency of metal nanoparticles. In particular, red shift of plasmon resonance is observed with the increase of the refractive index of the medium and vice versa, plasmon frequency increases when lowering the refractive index. Unlike glass, PGMA exhibits negative thermo-optic coefficient  $dn/dt$  [4]. Synergetic action of those two factors, enlarging of the distance between nanoparticles and lowering of the refractive index of PGMA matrix, outweighs the effect thermal expansion of a nanoparticle and results in observed blue shift of the plasmon bands.

## 4. CONCLUSIONS

It was found experimentally that the extinction spectra of metal-dielectric composite consisting of dense 2D silver nanoparticle array embedded into polymer matrix are affected by intense CW Ar laser radiation at 488 nm. Two distinct bands associated with collective plasmon modes are observed in the spectra. The tangential T mode corresponds to charge oscillations within a nanoparticle parallel to the plane of the nanoparticle array, while normal P mode corresponds to dipoles normal to the plane of the nanoparticle layer. The bandwidth of P mode broadens with the increase of irradiation power. Broadening of the band is a result of the increase of electron-phonon scattering rate caused by heating of the sample under intense laser radiation. The intensity and bandwidth of T band decreases due to enlarging of the distance between nanoparticles in the array after thermal expansion of PGMA matrix. Blue shift of both P and T bands can be explained by synergetic action of host matrix expansion and lowering its refractive index with the temperature rise.

Our experimental findings are of great importance for applications in opto-electronic and photonic devices.

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