Plasmonic Imaging in Thin Layer of PVP Contains Silver Nanowires

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ABSTRACT— Silver nanowires are the favorable material in many applications based on their plasmonic double resonance in the visible region. In this paper, thin films of Poly-vinyl-pyrrolidone (PVP) doped with Silver nanowires (Ag NWs) in different concentrations have been prepared. The plasmonic imaging system using a high numerical aperture objective lens excite the Surface Plasmon in these structures. The hot spot results from reflected light intensity of surface plasmon resonance (SPR) proved that increasing of concentration of Silver nanowires yields to get better hot spot in plasmonic imaging systems by choosing the appropriate wavelength. These obtained results accompanying with third order nonlinear investigations show the ability of samples usage in thermoplasmonic applications.

KEYWORDS: Silver Nanowires, Surface Plasmon Resonance, PVP thin films, Nonlinear Refractive Index, Plasmonic Imaging, and Z-Scan Technique.

I. INTRODUCTION

Plasmonic imaging and collect data from the plasmonic hot spot is one of the main aims in this new born topic [1]. Plasmonic nanostructures proposed as new efficient heat source when illuminated by their correspondence resonance light source [1,2] to use them in nanoscale control of temperature distribution [3], drug delivery [4], cancer photo thermal therapy, photo thermal imaging and many other useful applications. These applications need to the ability of measure the temperature distribution in enough area with high signal-to-noise ratio (SNR).

On the other hand, in these hotspots, the other optical properties like as nonlinear properties is so important due to the self-focusing effect in enhancing the temperature.

In this paper, we want to introduce new excitation method based on large numerical aperture (NA) lens and coupled charge camera to collect the plasmonic imaging from different samples with diverse concentrations of Ag NWs.

Until now, there are a lot of papers which focus on the study the optical properties of Ag NWs in polymer films [5] - [14], but the effect of self-focusing or de focusing onto the plasmonic hot spot by the aid of plasmonic imaging systems remains as an open question.

II. EXPERIMENTAL PROCEDURE

A. *Materials*

The materials used in this work, the silver nanowire (>99%) were purchased from Sigma-Aldrich, its length and width 1um, 100nm respectively. Poly vinyl pyrrolidone (PVP) (Mw=55000 g/mol) was purchased from Merck.

B. *Samples preparations*

The samples investigated in this studying are a mixture of Ag NWs with PVP polymer dissolved in deionized water using a magnetic stirrer. Our samples are prepared by adding the PVP films doped Ag NWs at five different compositional percentages (2%,4%,8%,12%,

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and 16%) and then stirred in an ultrasonic bath for about 15 min, as shown in Fig. 1. This procedure according to the following steps: the first step of samples preparation is solving PVP in deionized water in rate 3mg/ml, the second step mixture the Ag NWs with deionized water in five different concentrations, the third step is mixture the PVP with Ag NWs in rate 50%. The last step is preparing thin films layer by the spin coating method in condition 2000 rpm.

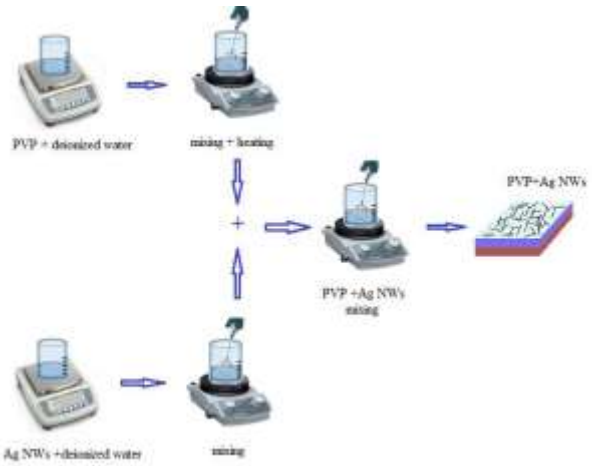

Fig. **1.** Sample preparation steps.

C. *Z scan technique*

The nonlinear refractive index (n_2) of all the samples are measured by z-scan technique. We utilized the closed aperture z-scan technique using a continuous wave Nd:YAG laser at λ =532 nm as the light source. A Gaussian beam of the CW laser with a well-defined vertical polarization and the power of 10 mW. The convex lens with a focal length of 18 cm, was used to focus the laser beam on the sample, the samples were excited at normal incidence geometry for the laser beam. In order to measure transmittance as a function of the sample position, the sample was moved back and forth along the z-axis around the minimum beam waist of the laser during the z-scan measurement. We managed to analyses the distortions of beam wave front associated with distinct effects nonlinear variation of the refractive index, by controlling the diameter of the aperture (S=0.1–0.3). The schematic of the setup for the z-scan experiment, is shown in Fig. 2 [15].

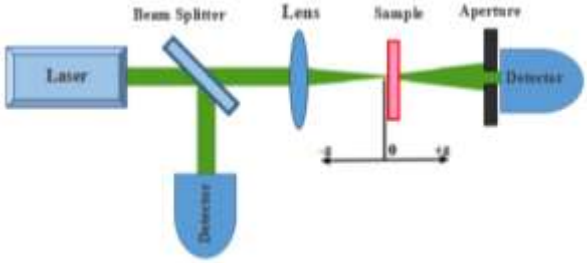

Fig. **2.** Schematic diagram of the experimental setup for closed aperture z-scan technique.

D. *Surface Plasmon Polariton (SPP) Excitation*

A high numerical aperture objective lens can be used to excitation surface plasmon-polariton (SPP). In this work, a high numerical aperture objective lens (10x, NA=1.25) used for SPPs excitation, as shown in Fig. 3(a), objective lens through the oil layer (oil-immersion) is in contact with the sample, and the input laser beam is focused onto the sample by the objective lens. High NA satisfies the dispersion condition between SPPs and incident laser. The propagation constant of the excited SPPs of the Ag NWs is given by

$$k_{sp}(\omega) = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1(\omega)\varepsilon_2(\omega)}{\varepsilon_1(\omega)+\varepsilon_2(\omega)}} \qquad (1)$$

where ω is angular frequency, c is the light speed in vacuum, and $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the relative permittivity of the Ag NWs and PVP, respectively [16]-[18].

The schematic array of our plasmonic imaging system is shown in Fig. 3(b). According to this figure, the laser beam is divided into two equal parts by a beam splitter. Then, the sample is illuminated by the objective lens, and the reflected light of the sample is received by it.

Finally, the image of the sample will be collected by the lens onto the CCD camera.

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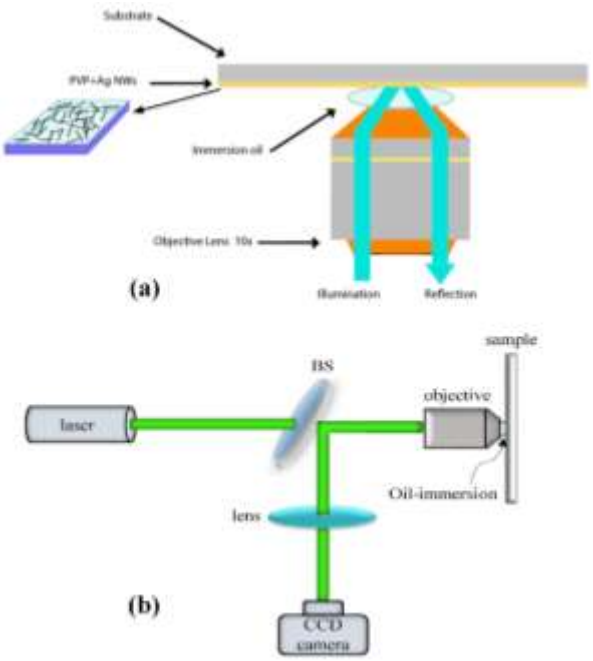

Fig. **3.** (a) SPPs excitation by a high NA objective lens, (b) schematic array of the plasmonic imaging system.

III. RESULTS AND DISCUSSION

The UV-VIS absorption spectra of the samples used in this work are shown in Fig. 4. We can clearly observe the absorption spectrum changes accordingly to their Ag NWs ratio. In addition, the absorption spectrum of this sample indicates that the intensity peak becomes stronger as Ag NWs quantity increases. Moreover, the absorption spectra of the samples containing three distinct peaks at wavelengths of 285nm indicates absorption PVP polymer, as well two peaks at 300nm and 330nm indicates absorption Ag NWs.

Measurements of the nonlinear refractive index of samples revealed by using the z-scan technique. The scan started from a distance near the focus until out of focus.

A nonlinear refractive index has been observed, the peak-valley pattern of the normalized transmittance curve configuration indicates the positive sign in which the peak comes after the transmittance valley for all the samples, as are shown in Fig. 5 and the linear absorption coefficient, the difference between T in peak and valley and n_2 are summarized in the Table 1.

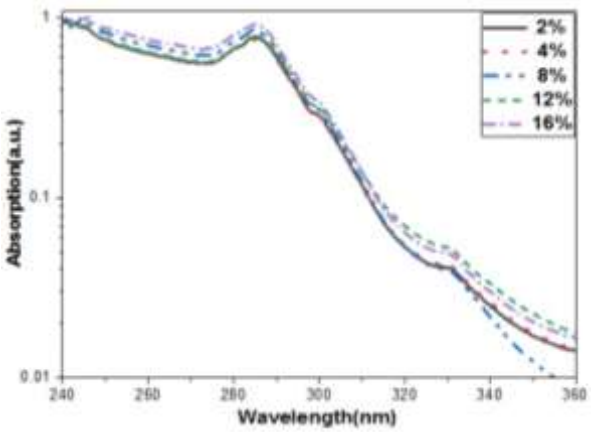

Fig. **4.** Absorption spectra of different samples by concentrations set to 2, 4, 6, 8 and 16 percent.

These parameters show that the nonlinear refractive index of the PVP films is increased when the Ag NWs ratio increases. Results are explained that n_2 parameter of the PVP films can be controlled by adding different ratios for Ag NWs to polymer.

Table **1.** The linear and nonlinear optical parameters for all the samples

Compositional percentages of the samples	Linear absorption coefficient α (cm^{-1})	ΔT_{P-V}	$\Delta \emptyset_0$	n_2 (cm^2/watt)
2%	0.24	0.0078	0.019	1.89×10^{-11}
4%	0.14	0.0105	0.026	2.54×10^{-11}
8%	0.23	0.014	0.034	3.40×10^{-11}
12%	0.20	0.0258	0.064	6.27×10^{-11}
16%	0.28	0.0879	0.216	21.10×10^{-11}

In the next step, we investigate the plasmonic hot spot of the samples to get the sense about the dependence of the nonlinearity and hot spots.

The hot spot images for our five samples are shown in Fig. 6. One can see the excited SPPs by two different wavelengths, 532nm in the left column and 405nm in the right column. Figure 6. approves that the blue wavelength (405nm) can excite the SPPs better than the green wavelength (532nm) that is because we have Ag NWs and this material have a good absorption in blue range. In addition, increasing of Ag NWs concentration yield to enhance the hotspots width, because the increasing of SPPs due to increasing in the internal electric field. This fact can be

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approved in Tables 2 and 3, as we list properties of hotspot like hotspot width at 14% of full intensity and at half width as 50%.

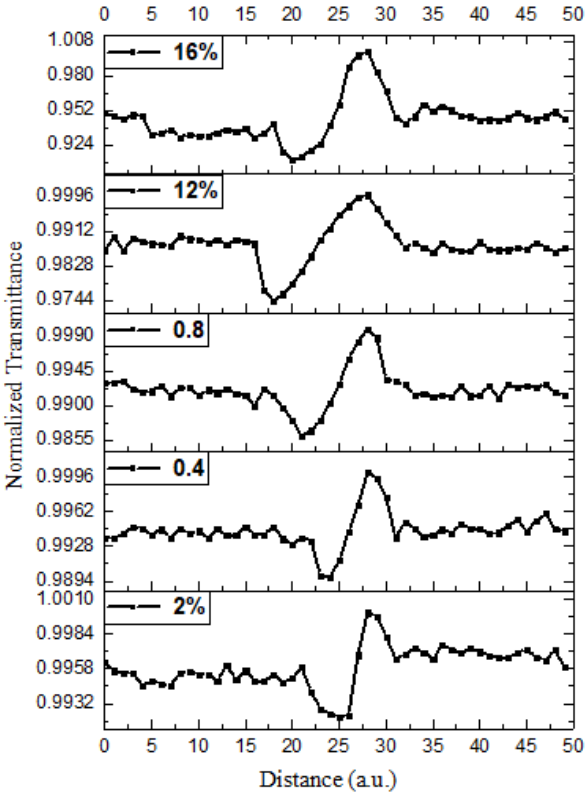
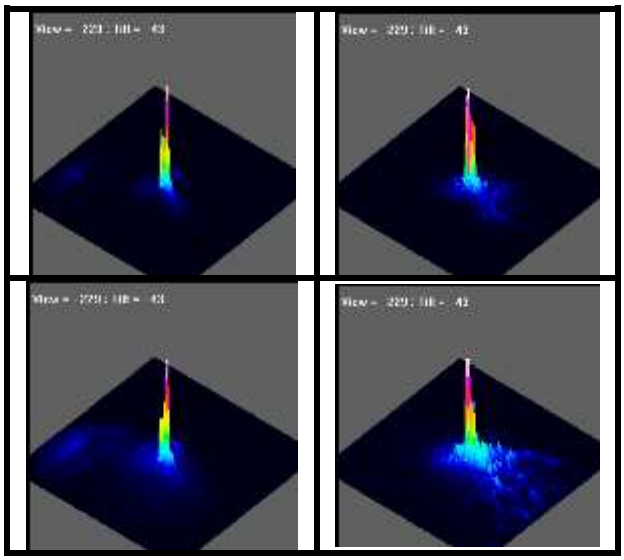


Fig. **5.** Transmittance with closed aperture z-scan for all samples.

Accordance with the peak value. In these tables, the width of hotspot in X direction not equal or close to the Y direction this is because the polariton of Ag NWs.



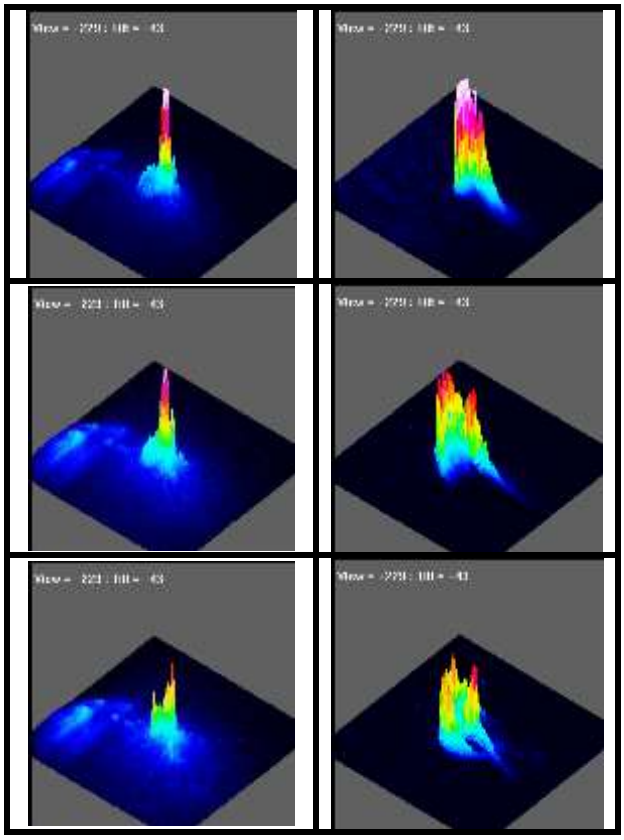


Fig. **6.** Hot spot for five different concentrations (from top to bottom) samples, left images for green excitation, right images for blue excitation.

The logic trend can be seen below half intensity of spots in X and also Y directions by enhancement in the Ag NWs concentrations. We can note the behavior of peaks values; it almost decreases when the concentration on Ag NWs increasing in our samples that is occurs because increasing in SPPs dispersion. Another fact which appears from this figures is not logic trend in the intensity at 50% that is logic because non symmetric distribution of NWs in the coating processes.

Table **2.** Hotspots properties for five different samples excited by 532nm

Samples	width of hotspot at X direction (μm)		width of hotspot at Y direction (μm)		Peak value %
	at 14%	at 50%	at 14%	at 50%	
Sample 1	127.7	54.4	168	99.9	92.6
Sample 2	166	76.6	114.7	57.1	91.8
Sample 3	200.3	51.5	358.6	124.2	91
Sample 4	349.7	53	424	145	90
Sample 5	403.2	199	1047	228.4	64.2

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Table **3.** Hotspots properties for five different samples excited by 405nm

Samples	width of hotspot at X direction (μm)		width of hotspot at Y direction (μm)		Peak value %
	At 14%	At 50%	At 14%	At 50%	
Sample 1	140.1	93	189	41.5	97.7
Sample 2	244.8	40.6	249.5	99.3	100
Sample 3	260	80	534	207.7	100
Sample 4	413.7	33	752	615.8	77.8
Sample 5	405.3	334.7	590	403.1	67.9

IV. CONCLUSION

In summary, the nonlinear responses of Ag NWs in PVP mixtures are determined. We studied the effect of PVP of the nonlinear refractive index of Ag NWs, using z-scan technique. In addition, we used high numerical aperture objective lens to excite the SPPs on Ag NWs. In the closed aperture, a strong variation of n2 can be observed when the pure Ag NWs were dispersed in PVP in order 10^{-11} cm2/ watt.

The results that we have from this work proved the peak value of hot spot will be decreases when the concentration of Ag NWs increasing. This decreasing occurs by increment in dispersion of polaritons. Furthermore, the excitation of SPPs by blue laser is better than the excitation by green because the absorbance of Ag NWs near the blue range. Such results suggest that PVP doped with Ag NWs can be a good candidate for such a dielectric medium and it can be useful for gain enhancement applications.

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