

Fabrication and Characterization study of Surface Plasmon Resonance (SPR) Based on Cu-Nanoparticles Optical Fiber Sensor

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ABSTRACT:

In the present work, we prepared copper nanoparticles suspend in aqueous environments by pulse laser ablation (PLA) of pure copper target in distilled water and then irradiated by (Nd⁺³:YAG) laser light (1064 nm). The peak position of Plasmon resonance absorbance of green colored nanoparticles was noticed at 630 nm . We have implemented the photodeposition technique to deposit Cu- nanoparticles on optical fiber end using laser light and a prepared Cu- nanoparticles suspend in aqueous environments. Using SHG:(Nd⁺³: YAG) (532 NM) pulse laser light and copper nanoparticles suspend in aqueous environments. Surface Plasmon resonance curves of an optical fiber-based sensor were investigated. Effect of laser pulse repetition rate, on structure, and nanoparticles size was studied by analysis of the ultraviolet-visible absorption spectra and AFM analysis of copper nanoparticles .The optical sensor was assembled using a LD light source, a spectrometer and an optical fiber immersed in copper nanoparticles colloidal as a sensor to measure the refractive index of aqueous media. The response and the sensitivity of the optical fiber sensor was investigated .Good agreement was obtained with respect to the resonance peak location and the shape of the curves. Consequently, these results enabled us to predict the ideal functioning conditions of the sensor.

Keywords: Cu- nanoparticles, laser ablation, surface Plasmon resonance (SPR), fiber-optic sensors.

تصنيع ودراسة الخصائص لمتحسس الليف البصري النانوي العامل بمبدأ الرنين السطحي للبلازمون لجسيمات النحاس النانوية

الخلاصة

(LPA) تم في هذا البحث تحضير جسيمات النحاس النانوية بالطور المائي بواسطة تقنية التذرية بالليزر النبضي (للنحاس النقي المغمر في الماء المقطر ، حيث تم تشعيه باستخدام ليزر النيديميوم – ياك بالطول الموجي (1064) نانوميتر. تم ملاحظة أن ذروة موقع الأمتاص الرنيني للبلازمون

لجسيمات النانوية باللون الأخضر عند الطول الموجي (630) نانومتر. تم توظيف تقنية الترسيب الضوئي (الفوتوني) لترسيب طبقة من جسيمات النحاس النانوية على منطقة المتحسس ضمن الليف البصري باستخدام الشعاع الليزري بالطول الموجي (532) نانومتر الناتج عن توليد التوافقية الثانية لليزر النديميوم – ياك لتشيع جسيمات النحاس النانوية المائية المحضرة . تم التحقق تجريبيا من منحنيات اللرنين السطحي للبلازمون لمتحسس الليف البصري المصنع . تم دراسة تأثير معدل التكرار لنبضات الليزر على تركيبية وأبعاد جسيمات النحاس النانوية عن طريق التحليل لطيف الأمتصاصية ضمن مديات الأطوال الموجية فوق البنفسجية – المرئية لعينات المحلول المائي المحضر ، وكذلك من خلال التحليل لقياسات طيف الفلورة الذرية لجسيمات النحاس النانوية . تم تنفيذ منظومة لتقييم أداء المتحسس النانوي باستخدام مصدر باعث ضوئي ومطياف ، حيث تم غمر متحسس الليف البصري المحضر في وسط مائي لقياس معامل إنكساره . إن مقدار الاستجابة والتحسسية لمتحسس الليف البصري تم تحديدها وكانت متوائمة لدرجة كبيرة ومتطابقة مع موقع القمة والشكل مع تلك المثبتة في المنحنيات الموثقة . بالتالي مكننا هذه الدراسة من تحديد مبدأ الأداء و ظروف عمل المتحسس المثالية.

INTRODUCTION

Despite the fact that a unique definition does not exist for nanoparticles, they are usually referred to as particles with a size up to 100 nm. It can be argued that below that size, the physical properties of the material don't just scale down or up, but change. Nanoparticles exhibit completely new or improved properties based on specific characteristics (size, distribution, morphology, phase, etc.), if compared with larger particles of the bulk material they are made of [1]. In addition, interesting optical (light absorbing/filtering) properties can be used for cosmetic applications [2].

Optical properties are also especially relevant for (SPR) surface plasmon resonance. Metal nanoparticles have been used for high-sensitivity sensors and for enhanced imaging in microscopy of biological samples [3]. Laser ablation in liquid media is a 'top down' approach for the synthesis of nanomaterial's having desired shape, size and chemical composition and surfaces free from chemical contamination, which are essential for further functionalization of nanomaterial's for biological and sensing applications [4].

Optical Excitation of Surface Plasmon's

Plasmon is a quantum or quasiparticle associated with a local collective oscillation of charge density. It is based upon the coupling of Plasmon's (charge density oscillations) excited by light in thin metal films, with waveguide modes in a dielectric layer over coating the metal film [5].

A light wave can couple to a surface plasmon at a metal-dielectric interface if the component of light's wave vector that is parallel to the interface matches the propagation constant of the surface plasmon. As the propagation constant of a surface plasmon at a metal-dielectric interface is larger than the wavenumber of the light wave in the dielectric, surface Plasmon's cannot be excited directly by the light incident onto a smooth metal surface as shown in Figure 1.

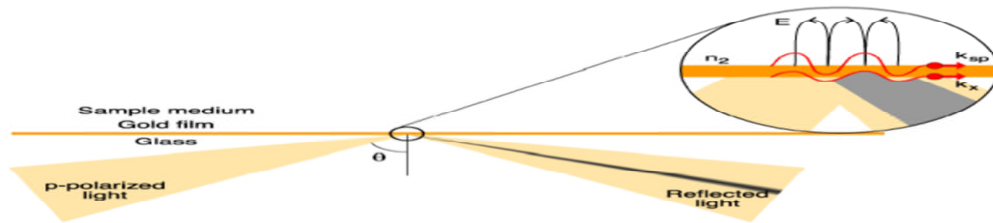


Figure (1) the phenomenon of surface plasmon resonance Occurring at the glass gold interface.

The wave vector of light can be increased to match that of the surface plasmon by the attenuated total reflection or diffraction. This enhancement and subsequently the coupling between light and a surface plasmon are performed in a coupling device (coupler). The most common couplers used in SPR sensors include a prism coupler, and a grating coupler. Surface plasmons can be also excited by a light wave guided such as in an optical fiber. Light propagates in a fiber optics in the form of guided modes. The electromagnetic field of a guided mode is concentrated in the wave guiding layer, and a portion of the field propagates, as an evanescent wave, in the low-refractive index medium surrounding glass layer. When light enters the region of the core containing a metal layer, the evanescent wave excites a surface plasmon at the outer boundary of the metal layer. In the optical phenomenon of Surface Plasmon Resonance, a metal-dielectric interface supports a p-polarized electromagnetic wave, namely the Surface Plasmon Wave (SPW), which propagates along the interface. When the p-polarized light is incident on this metal-dielectric interface in such a way that the propagation constant (and energy) of resultant evanescent wave is equal to that of the SPW, a strong absorption of light takes place as a result of transfer of energy and the output signal demonstrates a sharp dip at a particular wavelength known as resonance wavelength. The so-called resonance condition is given by following expression [6,7]:

$$K_0 n_c \sin \vartheta = K_0 \left(\frac{\epsilon_{mr} n_s^2}{\epsilon_{mr} + n_s^2} \right)^{1/2}; \quad K_0 = \frac{2\pi}{\lambda} \quad \dots (1)$$

The term on the left-hand side is the propagation constant (K_{inc}) of the evanescent wave generated as a result of Attenuated Total Reflection (ATR) of the light incident at an angle θ through a light coupling device (such as prism or optical fiber) of refractive index n_c . The right-hand term is the SPW propagation constant (K_{SP}); with ϵ_{mr} as the real part of the metal dielectric constant (ϵ_{mr}) and n_c as the refractive index of the sensing (dielectric) layer. This matching condition of propagation constants is heavily sensitive to even a slight change in the outer ambience; which makes this technique a powerful tool for sensing of different parameters. In SPR sensors with spectral interrogation, the resonance wavelength (λ_{res}) is determined with reference to the refractive index of the sensing layer (n_s). If the refractive index of the sensing layer is altered by δn_s , the resonance wavelength shifts by $\delta \lambda_{res}$. The sensitivity (S_n) of an SPR sensor with spectral interrogation is defined as:

$$S_n = \frac{\delta \lambda_{res}}{\delta n_s} \left[\frac{nm}{RIU} \right] \quad (2)$$

Experimental part

Copper nanoparticles were prepared by laser ablation of high purity copper (99.89%) target, with (14mm diameter and 0.47 mm thickness) in (10 ml) of distilled water. A pulsed (Nd^{+3} : YAG Model VS301) laser with fundamental wavelength of 1064 nm and pulse width of 10 ns and 6Hz repetition rate was used for ablation nanoparticle from the Cu target as shown in Figure 1a.

We have implemented the photodeposition technique to deposit Cu-nanoparticles on optical fiber end using laser light and a prepared Cu-nanoparticles suspend in aqueous environments. A pulsed (Nd^{+3} : YAG - SHG-Model VS301) emitting at $\lambda = 532 \text{ nm}$ with a pulse width $< 15 \text{ ns}$, and a fiber port collimator (PAF-X-2-A from Thorlabs) for coupling a free space laser into a multi-mode optical fiber (FG105LCA from Thorlabs) were used to perform the photodeposition process (see Figure 1b). The two samples of multi-mode optical fiber (MM) with $60 \mu\text{m}$ core diameter and single mode optical fiber (SM) with $\sim 8.2 \mu\text{m}$ core diameter were prepared by removing the coating, after that, it was cleaved and subsequently placed into the solution. Two of the optical fiber sensor prepared at the first day prepared the solution of colloid Cu NPs and the other sample prepared after a week of prepared the solution of colloid Cu NPs.

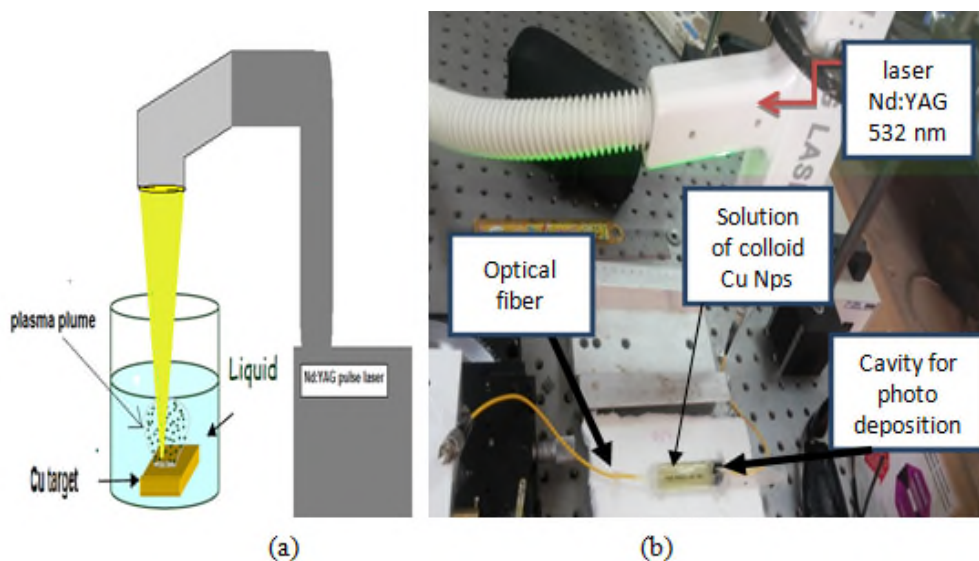


Figure (1) (a) Set up of preparing Cu-nanoparticles (b) Experimental setup for photodepositing by PLA. Cu-nanoparticles on the optical fiber end.

Measurements and Results

The absorption/transmission spectra for prepared Cu-Nanoparticle/ Distilled water fluid were composed by (UV-Vis Spectrophotometer from Thorlabs) at the first day prepared and after a week, as shown in Figure (2a). The best linear relationship was obtained by plotting $(\alpha h\nu)^2$ against $h\nu$, indicating that the optical bandgap of these nanoparticles is due to a direct allowed transition. The bandgap of a synthesized colloidal nanoparticles was determined from the intercept of the straight line at $\alpha = 0$. T_{auc} plot of UV-Visible absorption data of as synthesized colloidal nanoparticles for the

calculation of bandgap energy at the first day prepared was(2.4 eV)as shown in figure (2b).Whileafter a weak of the first day prepared was(2.5 eV) as shown in figure (2c) 2c) that was indicated to an increased in the particle size.

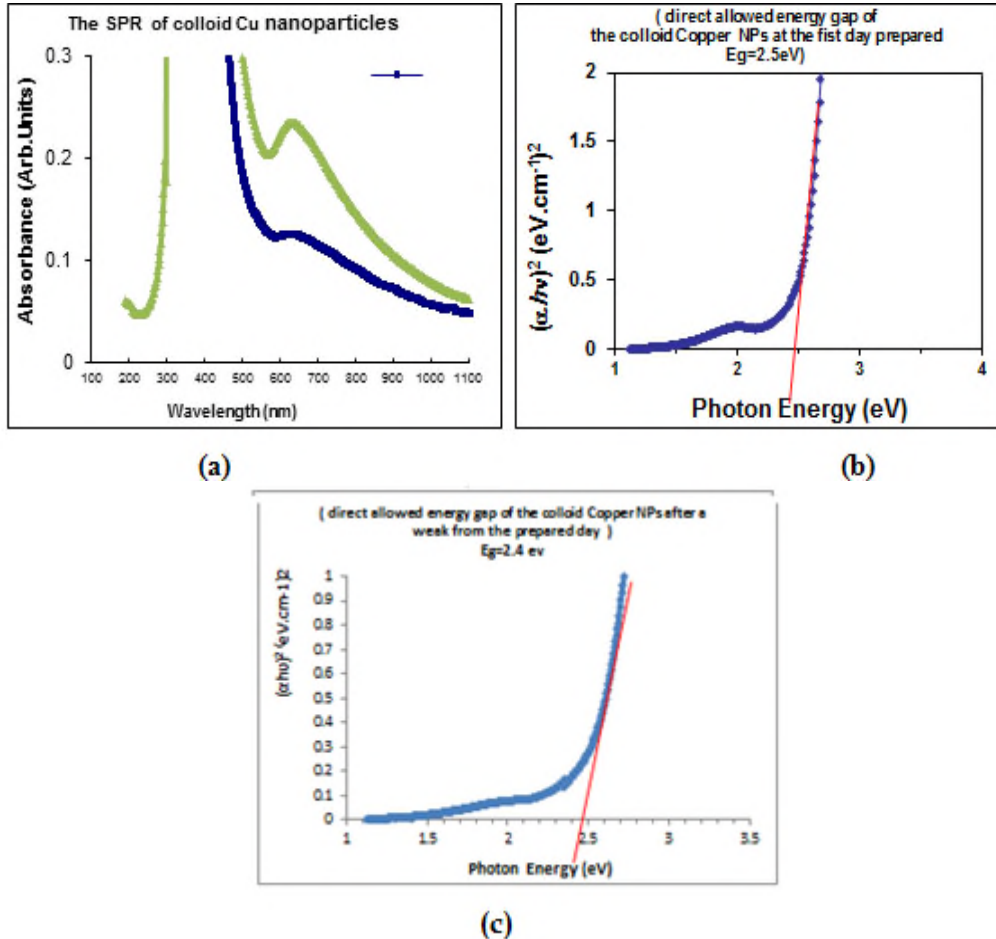


Figure (a) UV-visible absorption spectrum of as synthesized colloidal solutions of nanoparticles by laser ablation of copper in distilled water, (b) T_{auc} plot of UV-Visible absorption data of as synthesized colloidal nanoparticles for calcution of bandgap energy at the first day prepared,(c) T_{auc} plot of UV-Visible absorption data of synthesized colloidal nanoparticles for the calculation of bandgap energy after a weak of the first day prepared.

A Cu- nanoparticle suspended in distilled water was undergone to laser light via optical fiber (approximately 2 min) to obtain a colloidal solution. With laser energy the solution changed its color; this means that the nanoparticles were disagglomeration in process was observed when the laser energy via optical fiber was up of 0.1 μ . After a week the Nano- solution color was changedfrom dark green to the light green as one can see in Figure (3a, b), which was aagglomeration characteristic of the copper colloidal solution.

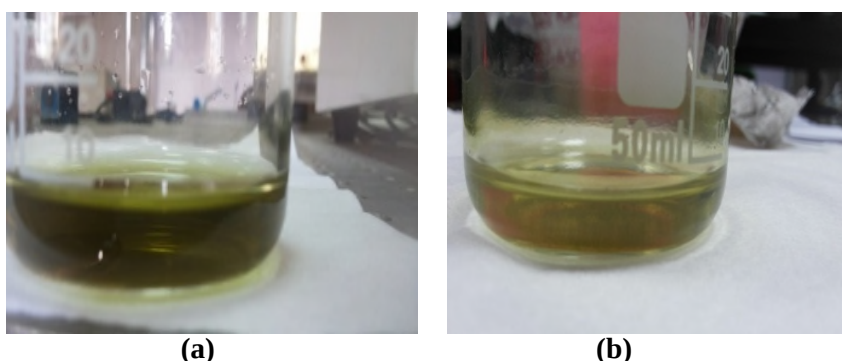
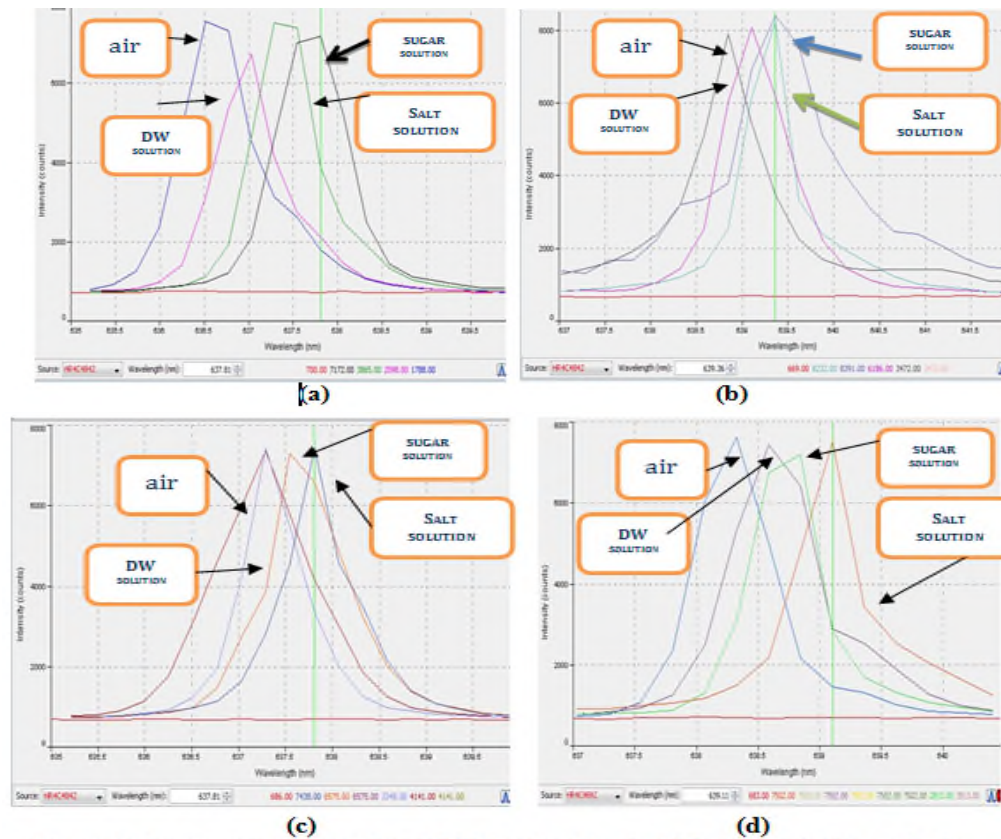


Figure (3) photograph of Cu- nanoparticles solution (a) at the first day prepared (b)) after a weak of the prepared day.

The results of two prepared Sensor samples response based on LSPR localized when it was in air ($n = 1.00$), deionized water ($n = 1.33$), sugar solution ($n = 1.35$), and salt solution ($n \sim 1.45$) are shown in Figure(4a, b.)for sample 1(SMF splice with MMF at the first day prepared the Cu NPs solution and after a weak respectively). From above Normalized absorption spectrum as a function of refractive index changes, it can be seen that, there is a change about (0.52 nm,0.78nm,,1.3nm) in the LSPR peak wavelength position when the sensor was changed from air to (deionized water, sugar solution, and salt solution) respectively . This position of the peak was moved to red region when the refractive index of the aqueous medium is increased. While Figure (4c, d.) show the same sensor responsebehaviorfor (SMF splice with SMF at the first day prepared the Cu NPs solution and after a weak respectively).Salt solution has a strong absorption in the ultraviolet region that LSPR spectrum shape in this region has a high value. The peak position of absorbance spectrum shown in Table 1, the shift of peak position to the IR region is due to index of the medium around the nanoparticles. This may be attributed to the change in the polarization properties of the metal nanoparticles , which affect both the absorption and scattering cross – section and small change in the local refractive index may occur , which is responsible for a change in the shift .While the two sample prepared after a weak of prepared the solution of colloid Cu NPs the peak position of absorbance spectrum in the same case as example in air case shows shift in position to IR region than the sample prepared in fist day prepared the solution of colloid Cu NPs.This is due to the agglomeration of nanoparticles that affect the sensibility of variation refractive index as in figure 5.



Figure(4) Sensor response based on LSPR localized in air, DW, sugar solution and salt solution. (a,b) for SMF splice with MMF at the first day prepared the Cu NPs solution and after a week respectively ,(c,d) for SMF splice with SMF at the first day prepared the Cu NPs solution and after a week respectively.

Table (1) Shows the peak position of the LD laser light and cases test for optical fiber sensor beads on SPR of Cu NPs

Type of sample	Cases test	Peak position (nm)	Type of sample	Cases test	Peak position (nm)
SMF splice with MMF At first day	Air	636.51	SMF splice with MMF after a week	Air	638.85
	DW	637.03		DW	639.11
	Sugar solution	637.29		Sugar solution	639.36
	Salt solution	637.81		Salt solution	639.36
SMF splice with SMF At first day	Air	637.29	SMF splice with SMF After a week	Air	638.33
	DW	637.29		DW	638.59
	Sugar solution	637.55		Sugar solution	638.85
	Salt solution	637.81		Salt solution	639.11

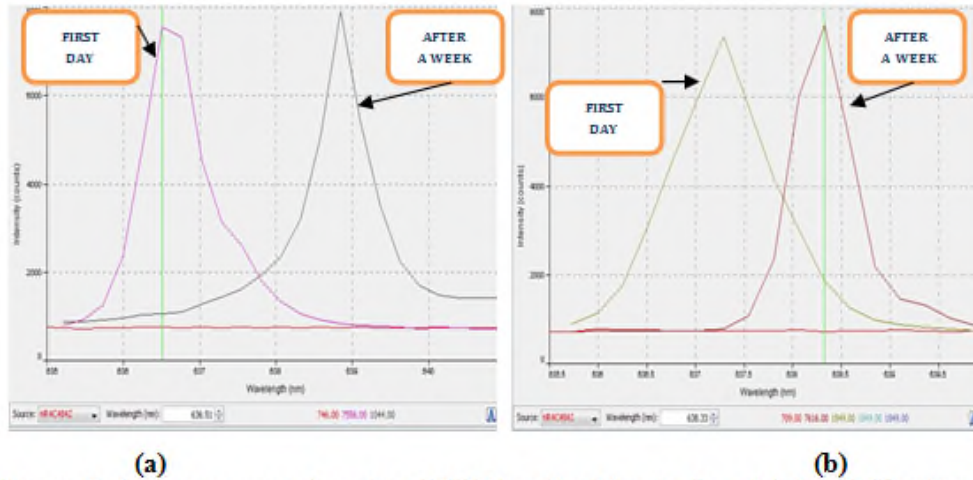


Figure 5. Sensor response based on LSPR localized in air. Case (a) for SMF splice with MMF at the first day prepared the Cu NPs solution and and after a week respectively, (c,d) for SMF splice with SMF at the first day prepared the Cu NPs solution and after a week respectively]

The sensitivity S of a LSPR sensor expressed in nanometers per refractive index unit (nm/RIU) is defined as the change in the LSPR peak wavelength maximum per unit change in the refractive index of the medium and it can be calculated by [8] :

$$S = \Delta\lambda / \Delta n$$

Figure. 6 summaries the peak LSPR wavelength changes of the sensor with the change of refractive index, in which a linear curve can be fitted to the data. Therefore, it is possible to determinate the refractive index of an unknown aqueous media knowing the peak LSPR wavelength and using the Equation of the straight line that arises from the data (Figure 6). Finally, from Equation 6 we can calculate the sensor sensitivity $S = 67.6$ nm/RIU.

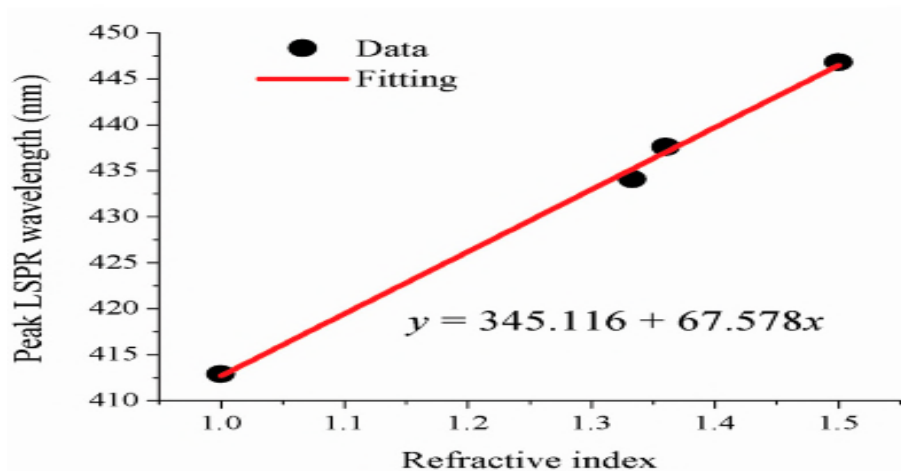


Figure (6) LSPR peak wavelength as a function of the refractive index.

An image of copper nanoparticles samples obtained via a scanning electron microscope SEM& FEM is shown in Figure 7 (a,b). The inset is a magnification that shows copper nanoparticles agglomerated and disagglomerated whose sizes are less than 100 nm.

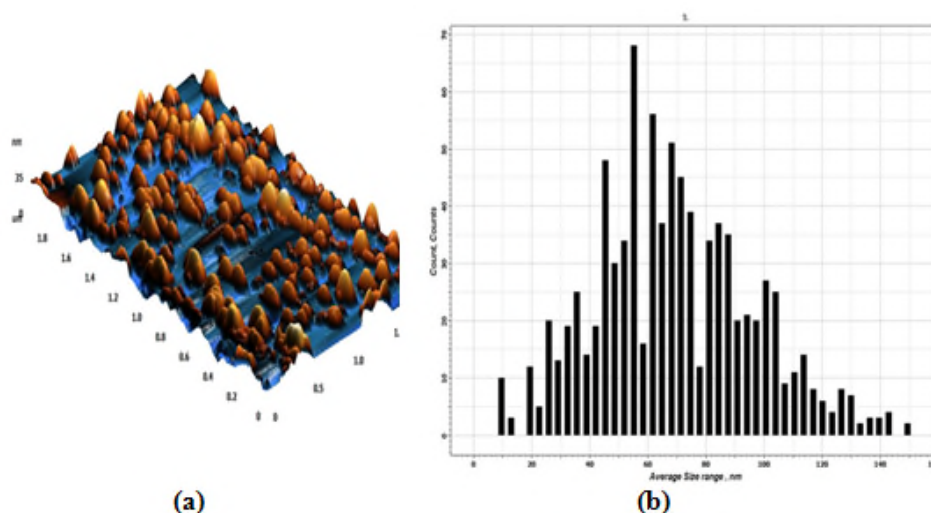


Figure (7) Image of copper nanoparticles samples obtained with (a) SEM and (b)FEM.

CONCLUSIONS

The absorbance spectrum of the solution was determined at different stages of the synthesis process. The plasmon resonance absorbance of green colored nano colloids was noticed at 631 nm. The particle size and their distribution, of the freshly prepared system and after storing for 24 hours in atmospheric condition, were examined by the color change and according to related literatures shows that the maximum size of the particle was increased during storage for 24 hours. We have then implemented and characterized an optical fiber sensor based on LSPR phenomenon using prepared Copper nanoparticles using a novel technique known as photodeposition to immobilize the Copper nanoparticles on the optical fiber end in less than 20 min. The response of this sensor is such that the LSPR peak wavelength shifts linearly to longer wavelengths as the refractive index increase, showing a sensitivity of about 67.6 nm/RIU. Our conclusion that is possible to increase the sensibility by optimizing the photodeposition process to prevent the formation of nanoparticles agglomerated. This optical sensor can be used for determining the quality in different fluids considering their refractive index.

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