Effect of Fe$_3$O$_4$ Magnetic Nanoparticle Concentration on the Signal of Surface Plasmon Resonance (SPR) Spectroscopy

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Abstract. Effect of Fe$_3$O$_4$ magnetic nanoparticle concentration on the signal of surface plasmon resonance (SPR) spectra has been successfully observed. The Fe$_3$O$_4$ nanoparticles with a particle size of about 10.5 ± 0.2 nm were used as active materials to increase the SPR response. X-ray diffraction (XRD) pattern showed that Fe$_3$O$_4$ nanoparticles have a high degree of crystallinity with spinel structure. The SPR system was successfully set up by using a glass prism coupler in a Kretschmann configuration in which gold (Au) thin film was thermally evaporated on the prism base. A green laser of wavelength 543 nm was used as light source. The angular scan in the attenuated total reflection (ATR) spectra showed a dropping intensity. Those things clearly indicated the appearance of SPR coupling phenomenon on the interface of Au thin film. The SPR spectra of fixed Au masses were also performed with same angular positions of dips. The Fe$_3$O$_4$ nanoparticles were deposited on gold thin film as a third layer which was synthesized via co-precipitation method. Hence, it was observed that the variation of Fe$_3$O$_4$ concentration affected the SPR spectra profile. The concentrations of Fe$_3$O$_4$ nanoparticles are 1, 3, 5, 7, 9, and 11 mg/ml which correspond to the angle shift of 0.1^o, 0.3^o, 0.5^o, 0.7^o, 0.9^o, and 1.0^o, respectively. The SPR angle of the dip was shifted to higher value due to change of refractive index of the medium as Fe$_3$O$_4$ nanoparticles concentration increases. Based on this result, we can conclude that the angle shift of SPR increases with increasing concentration of Fe$_3$O$_4$ nanoparticles.

Keywords: attenuated total reflection (ATR), Fe$_3$O$_4$, surface plasmon resonance.

1. Introduction

SPR is a resonant oscillation of conduction electrons at the interface between a negative and positive permittivity material stimulated by incident light. SPR-based biosensor can observe the interaction of biomolecules directly. The utilization of SPR-based biosensor as among others can measure the concentration of biomolecules, the thickness, and kinetic bond for certain biological analytes such as antigen/antibody, ligand/receptor, a protein reaction, and hybridization of DNA [1]. One of the observed responses in SPR-based biosensor is an SPR signal. For example, the trend of SPR signal against material concentration, in this case, is the polyclonal antibodies (PAb). The SPR signal increases with increasing PAb concentration [2]. The increase of SPR signal is observed as a phenomenon that occurs on the SPR system. The SPR phenomenon can be shown by the change in the angle of the SPR or SPR angle shift.

In general, the SPR angle shift occurs due to the difference in optical coating parameters, because of the angle depending on the optical parameter of the SPR system, such as refractive index from both sides of the metal, such as gold [3]. This case is the reason why SPR phenomenon can be used to a variety of biomolecules coated on top of the prism and metal. Given the characteristics of the various biomolecules, each of them that will be detected should then certainly be able to stick to the layer of metal. On the sample preparation process, there are several biomolecules that can be coated on the metal directly, but the obtained response is still low when detected by using SPR-based biosensor. To overcome this problem, SPR system needs an active material to increase the sensitivity, such as dielectric nanoparticles in detecting biomolecules.

One of the dielectric nanoparticles is Fe_3O_4. The Fe_3O_4 nanoparticles have a high dielectric constant that is very useful to enhance the input response. The polymer coated Fe_3O_4 can bind biomolecules by means of their ligand. For this purpose, the concentration of Fe_3O_4 nanoparticles might influence the SPR signal because the angle shift of SPR increases with increasing dielectric medium concentration [4]. Of course, varying the concentration of Fe_3O_4 is an interesting study that needs to be conducted in investigating their relation to the SPR signal. Therefore, this paper is focused on the SPR angle shift changing due to the concentration variation of Fe_3O_4 nanoparticles.

2. Experimental Method

2.1. Preparation of magnetic nanoparticles
Magnetic nanoparticles of Fe_3O_4 were prepared by using co-precipitation method. The stoichiometric amount of 8.109 g $FeCl_3.6H_2O$ (Merck, Germany) was dissolved in 15 ml distilled water, 4.1703 g $FeSO_4.H_2O$ (Merck, Germany) was also dissolved in 15 ml distilled water. Then, the solution was added with dropwise of 24 ml NH_4OH 10% (Merck, Germany) solution and also dissolved in 36 ml distilled water. The reaction was kept under constant stirring at 60˚C for 90 minutes. Precipitated ferrite nanopowders were washed with distilled water for seven times. Finally, the sample was dried in a furnace at 80˚C for 2 hours. The Fe_3O_4 nanoparticles of particle size about 10.5±0.2 nm were used as active materials to increase the SPR response. X-ray diffraction (XRD) pattern showed that Fe_3O_4 nanoparticles have a high degree of crystallinity with spinel structure [5].

2.2. Sample Preparation
The Fe_3O_4 powder nanoparticles were dissolved in ethanol for analysis solution to make colloidal nanoparticles. The mixtures were placed in the ultrasonic cleaner about 30-60 minutes to form homogeneous colloids. Six samples of Fe_3O_4 nanoparticles were prepared in this study with a concentration range from 1% to 11% (Table 1). The Fe_3O_4 nanoparticle colloid was deposited on the Prism/Au system by using spray method to form a Fe_3O_4 film.

Table 1. The comparison of Fe_3O_4 powders and ethanol volume.

Sample	Fe_3O_4 powders	Ethanol volume	Colloid concentration
A	5 mg	5 ml	1 mg/ml
B	15 mg	5 ml	3 mg/ml
C	25 mg	5 ml	5 mg/ml
D	35 mg	5 ml	7 mg/ml
E	45 mg	5 ml	9 mg/ml
F	55 mg	5 ml	11 mg/ml

2.3. The observation of Fe_3O_4 nanoparticle concentration effect on the SPR-angle
The SPR phenomenon was observed in the Prism/Air, Prism/Au/Air and Prism/Au/Fe_3O_4 nanoparticles/Air systems by using the method of attenuated total reflection (ATR) in the

Kretschmann configuration by using SPR set up device at Laboratory of Material Physics and Instrumentation, Physics Department of *Universitas Gadjah Mada*, Indonesia (Figure 1). Green laser (with wavelength λ=543 nm) was used here as the light source. The reflectance spectra were observed in range of 30°-80° with duplication to ensure the reliability of measurement. The BK7 type prisms were used in this study. 15 mg Au 99% was evaporated onto the clean prism by using vacuum evaporator. The evaporation was performed at pressure of 2×10^{-3} Pa and electric current of 50 A for 7 minutes, to make Au thin film. This chip was called Prism/Au system. Observation of the Prism/Air system was done to determine the refractive index value of each prism. Based on the value of critical angle (θ_c), by using the Snell's equation, the refractive index of prism (n_p) can be calculated by using equation 1.

$$n_p = \frac{1}{\sin \theta_c}. \tag{1}$$

2.4. Quantitative analysis
The SPR angles against Fe_3O_4 concentration were plotted to built a model of sensor response for the prism/Au/Fe_3O_4/Air system. The model was obtained by using the standard linear curve fitting method facilitated by Igor Pro 6.36 for Windows software.
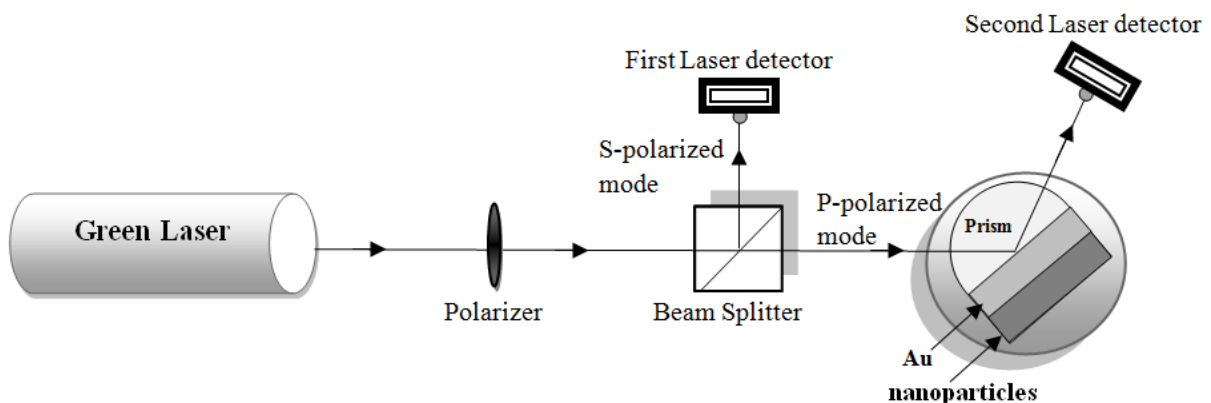

Figure 1. Set-up of SPR instruments

3. Results and Discussion

3.1. Critical angle of prism
Reflectance values are obtained from the comparison between the intensity of the reflected beam against the rays come. On each of the critical angle occurs optimally reflection produced by a prism. Figure 2 shows the ATR curves of Prism/Air system. Based on Figure 2, we know that the critical angles of prism A, B, C, D, E and F are $41.6^o \pm 0.05^o$, $41.6^o \pm 0.05^o$, $41.5^o \pm 0.05^o$, $41.5^o \pm 0.05^o$, $41.8^o \pm 0.05^o$ and $41.4^o \pm 0.05^o$, respectively. The optimum reflection generated by the prism is due to the non-existence of a particle or other material over the surface of the prism that can excite the surface plasmons and causes a decrease in the value of the reflectance or the occurrence of vast rays absorption. We can retrieve the values of the refractive index of prism A, B, C, D, E and F, which are respectively 1.51, 1.51, 1.51, 1.51, 1.50 and 1.51 by using equation (1). Those figures indicate that the difference in refractive index of each prism is not too significant because we use six identical prisms in this study.
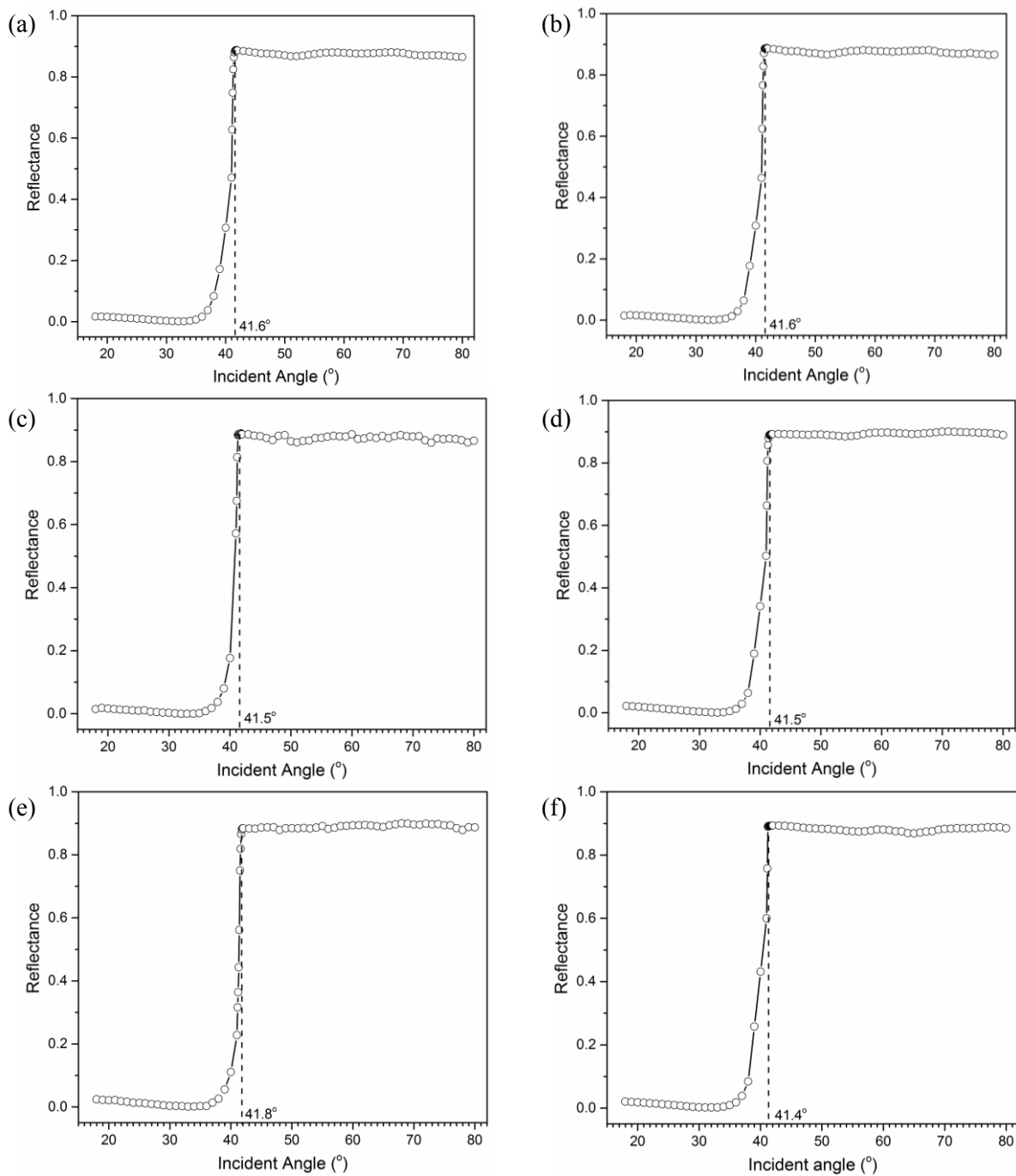
Figure 2. ATR curves of Prism/Air system (a) prism A, (b) prism B, (c) prism C, (d) prism D, (e) prism E and (f) prism F.

3.2. Effect of Fe_3O_4 concentration on the SPR-angle

Figure 3 shows the ATR curves of Prism/Au/Air systems and Prism/Au/Fe_3O_4 nanoparticles/Air systems at different concentration. Curves of prism/Au are different because the difference of Au thickness result deposited on the prism. Based on Figure 3, it was observed that the variation of Fe_3O_4 concentration affects the SPR spectra profile. The dip of SPR angle shifts to higher value due to change of refractive index of medium as Fe_3O_4 nanoparticle concentration increases [4]. The

concentrations of Fe_3O_4 nanoparticles are 1, 3, 5, 7, 9, and 11 mg/ml which correspond to the angle shifts of 0.1^o, 0.3^o, 0.5^o, 0.7^o, 0.9^o and 1.0^o, respectively.
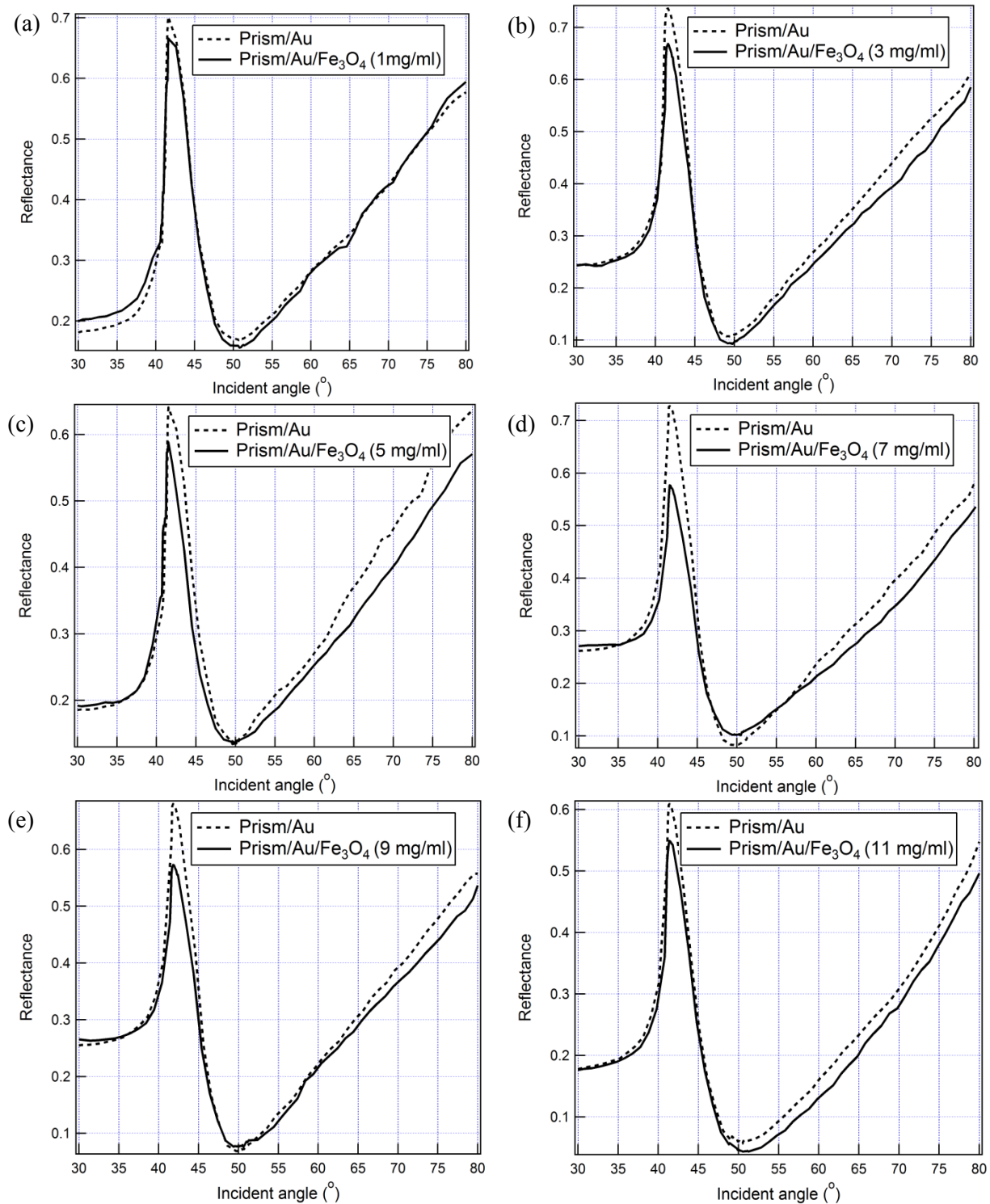
Figure 3. ATR curves of Prism/Au/Fe_3O_4 nanoparticles/Air systems at concentration of (a) 1, (b) 3, (c) 5, (d) 7, (e) 9, and (f) 11 mg/ml.

Figure 4 shows the relationship between the Fe_3O_4 concentration and SPR angle shift. The model in this section uses the SPR angle changes in determining the SPR response against the concentration variations of Fe_3O_4 nanoparticles. Based on the linear fitting model by using Igor Pro software for Window, the angle shift versus Fe_3O_4 concentration clearly shows a straight line relationship.
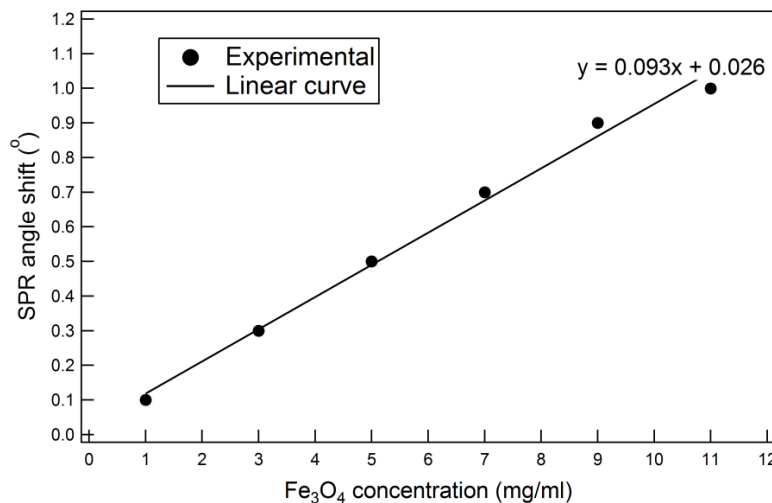

Figure 4. Curve for the angle shift of SPR versus variation of Fe_3O_4 nanoparticle concentration.

The equation of sensor response model is

$$\Delta\theta_{SPR} = 0.093c + 0.026 \qquad (2)$$

where $\Delta\theta_{SPR}$ is a change of SPR dip angle and c is Fe_3O_4 concentration. Based on equation (2), the sensitivity of the sensor is $0.093^o \pm 0.004^o$ to any change in the 1 mg/ml concentration of Fe_3O_4 nanoparticles. Based on Figure 4, the concentration of the Fe_3O_4 nanoparticles causes shifting in the SPR angle dip toward a greater value where both are linear in the range of 1-11 mg/ml concentration of Fe_3O_4 nanoparticles.The angle shift of SPR increases with increasing Fe_3O_4 concentration [4]. The SPR angle shifts due to the change of refractive index in each layer with different concentration. Indirectly, changes in the refractive index of Fe_3O_4 nanoparticle layers will cause a change in absorbance of such layers. The changing of concentration and absorbance of Fe_3O_4 nanoparticles change reflectance value. The absorbance value of the effect on the value of extinction coefficient signifies that the Fe_3O_4 nanoparticles can absorb light passing through it. The lower value of extinction coefficient which represents the imaginary part of the refractive index indicates that concentration of material decreases [6]. This phenomenon causes the refractive index is getting smaller.

4. Conclusion
Fe_3O_4 nanoparticles have been successfully synthesized through co-precipitation method and deposited on the Prism/Au system. The SPR angle of dip was shifted to higher value due to change of refractive index of the medium as Fe_3O_4 nanoparticle concentration increases. Based on this result, we can conclude that angle shift of SPR increases with increasing concentration of Fe_3O_4 nanoparticles.

5. References
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