

## Detection of Volatile Organic Compound Gas Using Localized Surface Plasmon Resonance of Gold Nanoparticles

(Pengesanan Gas Sebatian Organik Mudah Meruap Menggunakan Resonans Plasmon Permukaan Tempatan Nanozarah Emas)

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### ABSTRACT

*This paper reports on the detection of several organic vapors using the unique characteristic of localized surface plasmon resonance (LSPR) gold nanoparticles. Gold nanoparticles on quartz substrate were prepared using seed mediated growth method. In a typical process, gold nanoparticles with average size ca. 36 nm were obtained to densely grown on the substrate. Detection of gas was based on the change in the LSPR of the gold nanoparticles film upon the exposure to the gas sample. It was found that gold nanoparticles were sensitive to the presence of volatile organic compound (VOC) gas from the change in the surface plasmon resonance (SPR) intensity. The mechanism for the detection of VOC's gas will be discussed.*

*Keywords: Gold nanoparticles; LSPR; VOC gas*

### ABSTRAK

*Kertas ini melaporkan tentang pengesanan beberapa wap organik menggunakan sifat khas daripada resonans plasma permukaan tempatan (LSPR) nanozarah emas. Nanozarah emas yang difabrikasi pada permukaan substrat kuarza telah disediakan melalui kaedah penumbuhan dengan pengantara benih. Pada proses tipikal, nanozarah emas dengan saiz purata 36 nm telah dihasilkan dan tumbuh dengan padat pada permukaan substrat. Pengesanan gas sebatian organik mudah meruap adalah berdasarkan kepada perubahan LSPR pada filem nanozarah emas apabila didedahkan terhadap sampel gas. Didapati bahawa filem nanozarah emas menunjukkan kepekaan terhadap kehadiran gas sebatian organik mudah meruap melalui perubahan puncak serapan resonans plasmon permukaan (SPR). Mekanisme pengesanan gas sebatian organik mudah meruap akan diperbincangkan.*

*Kata kunci: Gas mudah meruap; LSPR; nanozarah emas*

### INTRODUCTION

Gold nanoparticles have attracted much attention due to their unique optical, electrical and catalyst properties (Zhou et al. 2009). These unique properties of gold nanoparticles were influenced by the effect of quantum confinement of free electron in such a low dimensional structure. Owing to such strong quantum effect, the optical properties of gold nanoparticles represented by surface plasmon resonance (SPR) strongly depend on the size and shapes of the particles (Murray & Barnes 2007).

Recently, gold nanoparticles have been widely used in biosensor application (Zhao et al. 2006) mainly by utilizing the special characteristic of the localized surface plasmon resonance (LSPR). This LSPR was produced via collective oscillation of the conduction electron in gold nanoparticles with the incident photon frequency (Daniel & Astruc 2004; El-Sayed 2001) and exhibits an extremely high sensitivity to the change in the dielectric

of the surrounding medium. This enables the fabrication of sensitive sensor system by simply utilizing the LSPR characteristic change.

This paper reports the study of the plasmonic characteristic (optical response) of the gold nanoparticles ensemble on the surface upon exposed to the vapor samples, such as methanol, ethanol and 2-propanol. The gold nanoparticles was prepared and grown on quartz substrate using our previously reported method for growth of metal and metal oxides, namely seed mediated growth method (Umar et al. 2009; Umar & Oyama 2006a; 2006b; 2005; 2007). We also investigated the optical response of the gold nanoparticles upon exposure to the vapor samples when their sizes were modified. It was found that the optical response increased with the decreasing of the nanoparticle size with typical response and recovery time of 3 s and 4 s, respectively. The present study should find an extensive application in complex gas sensor system, such as electronic nose.

## EXPERIMENTAL DETAILS

## MATERIALS

Hydrogen tetrachloroaurate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was purchased from Sigma-Aldrich. Trisodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ ), sodium tetraborohydride ( $\text{NaBH}_4$ ), ascorbic Acid and 0.1 M NaOH solution were purchased from Wako Pure Chemicals Ltd. Cethyltrimethy ammonium bromide (CTAB) was purchased from Amresco. All of the chemical were used as received. The solutions of these chemical were prepared in deionized (DI) water obtained from pure lab UHQ ELGA with resistivity higher than 18 M $\Omega$ d.

## GROWTH OF GOLD NANOPARTICLES ON THE SURFACE

In growing the gold nanoparticles on the surface using the seed mediated growth method, two kind of solution namely seed solution and growth solution were prepared. Seed solution was prepared by adding 0.5 mL of ice-cold of  $\text{NaBH}_4$  0.1 M into the solution that contains 0.5 mL of  $\text{HAuCl}_4$  0.01 M, 0.5 mL of trisodium citrate 0.01 M and 20 mL of deionized water. Using this approach, gold nanoseed that was capped by negative citrate protecting agent with size ca. 3 nm will be obtained. The growth of gold nanoparticles on the surface was carried out by firstly depositing the seed particle onto the substrate surface (quartz) by using electrostatic self assembly technique. Briefly, prior to attaching the seed particle, the substrate was immersed into 5% of poly-L-Lysine solution for 30 min to positively charge the substrate surface. After that, the substrate was immersed into the seed solution. The nanoseed may easily attach onto the substrate surface due to the existence of electrostatic interaction between the positive charged surfaces with the negative charged

nanoparticle. The process was repeated 3 times to obtain high density nanoseed particles on the surface. The nanoseed was then grown up by simply immersing the substrate into a growth solution that contain 20 mL of CTAB 0.1 M, 0.1 mL of ascorbic acid 0.1 M, 0.5 mL of  $\text{HAuCl}_4$  0.01 M and 0.1 mL of NaOH solution 0.1 M. A reddish color on the substrate may be observed within seconds in the growth solution indicating the formation of the gold nanoparticles. After a certain period of growth process, the substrate was removed and then rinsed thoroughly with a copious amount of pure water and finally dried with a stream of nitrogen gas.

The optical absorption spectrum of the sample was investigated using UV-Vis spectrometer (USB-2000 Ocean Optics). The morphology of the gold nanoparticles on the surface, such as shape, size and density, was characterized using atomic force microscopy (AFM).

## OPTICAL RESPONSE STUDY

Figure 1 shows the system set up for investigating the optical response of the gold nanoparticles ensemble (GNE) upon exposed to the vapor samples. The set up consists of one sensor chamber, one light source (LS-1 tungsten halogen lamp), two arm fiber optical probe system and a USB-2000 Ocean Optics spectrometer. The responses were studied by transmitting the light source into one of the arm of the fiber, reaching the gold nanoparticles film at the other end. Then the light source was scattered by the gold nanoparticles and entered the probe that in turn transmitted to the optical analyzer using another arm of the fiber. The scattered light spectra were recorded. The plasmonic characteristic change upon exposed to the vapor samples was considered as the optical response.

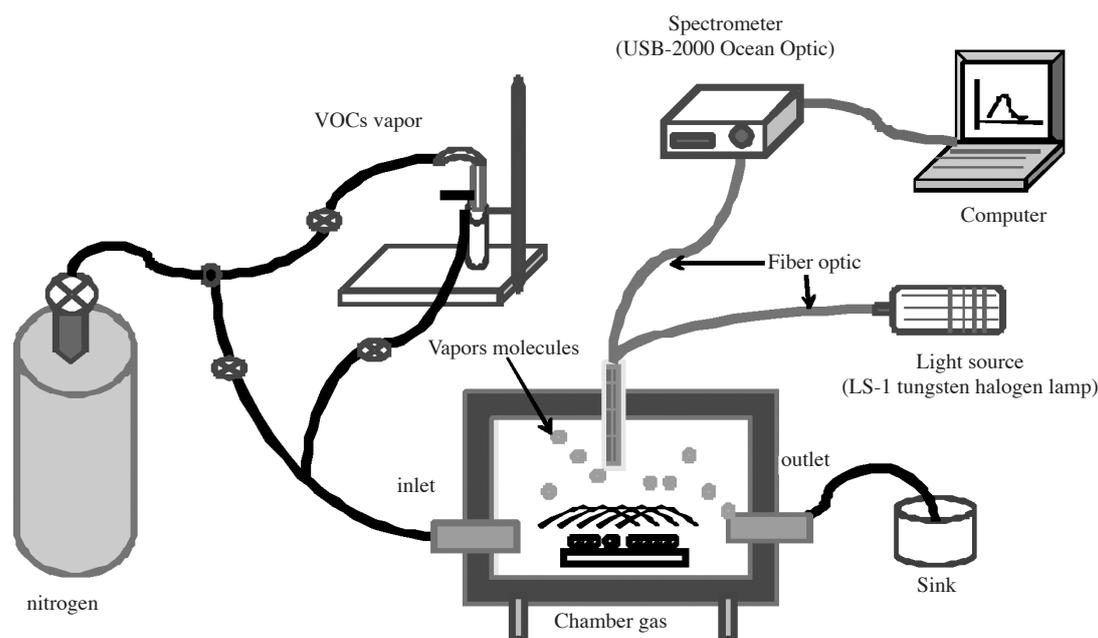


FIGURE 1. Gas sensing system setup

## RESULTS AND DISCUSSION

## GOLD NANOPARTICLES GROWTH

Gold nanoparticles have been directly grown up on the substrate surface using the present approach. The visible optical absorption spectroscopy has been used to confirm the formation of the gold nanoparticles on the surface. Figure 2 shows the visible absorption spectrum of the as prepared gold nanoparticles that was grown up for 2 hours in the growth solution. It was observed that single absorption band was emerged in the spectrum without the presence of other peaks. The centre absorption peak was found to be 530 nm. This peak can be directly associated with the transverse surface plasmon resonance of gold nanoparticles. Since, only single absorption band appeared in the spectrum, it can be confirmed that spherical gold nanoparticles might be obtained.

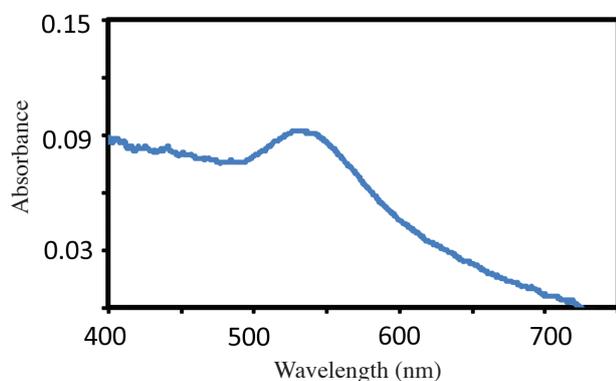


FIGURE 2. Optical absorption spectrum of the gold nanoparticles ensemble on the substrate prepared using the seed mediated growth method with 2 h growth time. Single SPR band centering at 530 nm was appeared on the spectrum

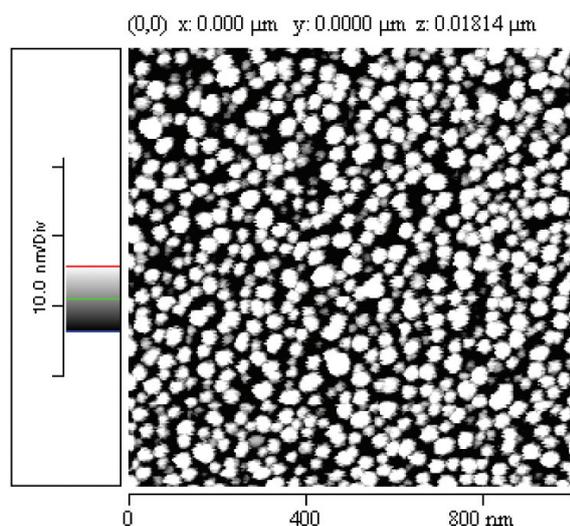


FIGURE 3. A typical atomic force microscopy image of the spherical gold nanoparticles ensemble on the substrate

To further confirm the formation and the morphology of gold nanoparticles, we carried out the atomic force microscopy imaging on the surface. The result is shown in Figure 3. From the image, it can be clearly seen that high-density gold nanoparticles have been successfully grown up on the surface. The morphology of the nanoparticle was found to be spherical. It was also found that the gold nanoparticles indicated a uniform size and shape. Based on the surface profile analysis experiment, we found that the average size of the nanoparticles was ca. 36 nm. Although high-density gold nanoparticles was found on the surface, to our surprise, the nanoparticle did not agglomerate but formed unique inter-particle space with distance ca. 30 nm. This condition may be potentially due to the diffusion of gaseous molecules during the detection of gas. Hence, high-sensitivity gas sensor system can be obtained.

## SURFACE PLASMON RESONANCE GAS SENSING

Gas sensing performance of the as prepared GNE to several organic vapor samples, such as methanol, ethanol, 2-propanol, have been evaluated. The result is shown in Figure 4. In the figure, the optical absorbance profile of the GNE obtained while exposed to a flow of nitrogen gas is shown in curve a. When nitrogen gas containing a certain organic vapor sample, namely methanol here,

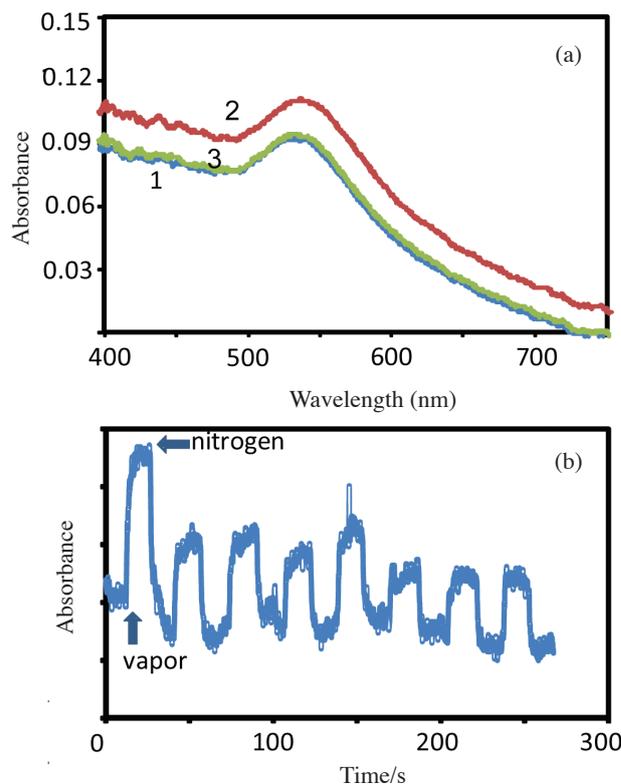


FIGURE 4. (a) Plasmonic characteristic of spherical gold nanoparticles ensemble under nitrogen (curve 1), methanol (curve 2) and recovery (curve 3) and (b) its corresponding plasmonic characteristic change upon gas flow in and out recorded at absorption peak

flowed into the gas chamber, the optical absorbance of the GNE independent of the wavelength drastically increased (curve 2), reflecting a successful interaction between the vapor molecule and the gold nanoparticles. In spite of a high increase in the absorbance, the absorption spectrum might return to its initial condition when vapor was taken out of the gas chamber (curve 3). It indicates that the vapor molecule might simply bind to the gold nanoparticles surface, probably, via a weak physical adsorption process such as Van Der Waals interaction. Hence, it becomes easily removable when a flow of nitrogen was purged into the sensing chamber.

We further observed such unique change in the optical absorption properties of the GNE upon exposed to the gas sample by recording the absorbance value at the absorption peak during the gas flow in and out. The result is shown in Figure 5. It was found that the optical absorption of the nanoparticle ensemble may be regularly fluctuated upon exposed in and out to the vapor samples. The maximum time required for reaching the saturated value on the absorbance change (response time) was considered to be very fast, namely 3 s. Meanwhile, the time to reach the initial condition upon removing (recovery time) the gas sample from the chamber was calculated to be 4 s. Based on these experimental results, it can be concluded that GNE were very sensitive to the presence of vapor samples by showing a very fast responsive time. The optical response of the gold nanoparticles was also very stable by showing a gradual fluctuation in the response upon gas flowing in and out the sensing chamber.

The optical response of the GNE toward other vapor samples, namely, ethanol and 2-propanol, were also studied. Figure 5 shows the response time of the GNE to the presence of three vapor samples. It was found that the gold nanoparticle were very sensitive to all vapor samples by exhibiting a high change in the absorbance during the vapor exposure. However, based on the experimental result, it can be seen that the highest sensing response was shown by the methanol vapor while, the next was for the ethanol and 2-propanol, respectively. The response time of GNE was found to be 3, 5 and 6 s for methanol, ethanol and 2-propanol, respectively. Meanwhile, their corresponding recovery time was 4, 10 and 13 s, respectively. From the figure, as has been obtained for methanol vapor, the optical response of the GNE to all of the vapor samples was very stable as the presence of gradual change in the response and the recovery profile

As has been mentioned earlier, the change in the absorption profiles of the GNE upon exposure to the gas samples could be directly associated with the successful interaction between gold nanoparticle and the vapor molecules. Although the exact mechanism of the interaction between gas and gold nanoparticle is not yet clear at this moment, we predict that it could be the result of the modification of the dielectricity of the surrounding medium upon gas presence. Another mechanism could be due to a successful adsorption of vapor molecules on the

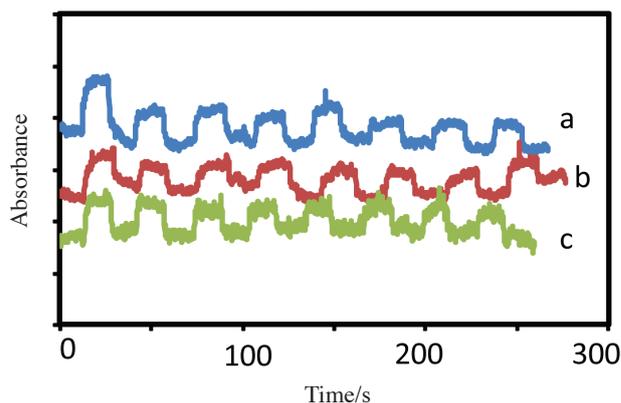


FIGURE 5. Optical response characteristic of spherical GNE to three different vapor samples measured at the peak of plasmonic band (a) methanol, (b) ethanol and (c) 2-propanol

gold nanoparticle surface that in turn modifies the dipole-dipole oscillations strength of the GNE. Hence, changes in the optical absorption profile. The investigation on the exact mechanism that plays behind such process is in progress.

## CONCLUSION

The optical responses of the GNE to several vapors samples have been studied. It was found that the plasmonic characteristic of the GNE was very sensitive to the presence of the vapor samples. The GNE also showed a cross-sensitivity characteristic by showing a different sensitivity to the vapor samples, which on the highest was found for methanol and followed by ethanol and 2-propanol, respectively. Since optical properties strongly depend on shape, the sensitivity and selectivity may be further enhanced by preparing the GNE with certain morphology, such as nanorod, nanoplate or nanocube. The effort to prepared gold nanoparticles with variety of shape is in progress.

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