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SYNTHESIS OF GOLD NANOPARTICLES DECORATING GRAPHENE FOAM AND ITS APPLICATION TO ELECTROCHEMICAL AND SERS -BASED SENSOR

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Abstract: In this study, Gold nanoparticles (GNPs) were synthesized by electrodeposition technique on the surface of Graphene Foam (GF) by fast scan voltammetry with using Gold (III) chloride trihydrate as the solvent. Then, the synthesized of gold nanoparticles were used in electrochemical sensor and surface-enhanced Raman Spectroscopy (SERS) for detection of sample analyt (200 µlhydrogen peroxide) and (1µMmethylene blue) respectively. The results demonstrate that gold nanoparticles enhanced amplification ofelectrochemical and SERSeffect on graphene foam (GF). The sensitivity of the sensor and size of gold nanoparticles could be controlled by the deposition of time, concentration of reducing agent and applied potential. Therefore, GNPs and GNPs/GF are highly promisingmaterial for electrochemical and SERS substrate for detection of chemical substance in low concentration respectively.

Keywords: gold nanoparticles, graphene foam, electrochemical, SERS, Sensor

I. INTRODUCTION

Gold nanoparticles (Au NPs) have opened up many promising applications in various field due to their unique physical and chemical properties for fabrication of smart sensing devices in biomedical science as bio-diagnostic tools application [1].Wang et al. synthesized gold nanoparticles onto graphene surface and have found that SERS signal of graphene was very large [2].

Recently, there are numerous articles claiming that gold nanoparticles decorated on graphene foam could be greatly enhanced the electrochemical based sensor in comparison with graphene. In addition, it have been arisen both absorption and scattering of electromagnetic due to their size and localized surface Plasmon resonance (LSPR). This enhancement resulting from charge transfer between the graphene to gold nanoparticles. Moreover, localized surface Plasmon resonance which result from hybrid Au/GF have been used to catalyze various chemical reactions [3].

Electrochemical sensors based on graphene foam (GF) as an electrodehas been demonstrated excellent chemical sensing performances with high sensitivity, and highstability [4,5].In addition, GF based gas sensor is able to detect hydrogen peroxide with low concentration [6].

The gas molecule is reacting at the sensing electrode and producing an electrical signal which is proportional to the gas concentration and the current flow between the counter and sensing electrodes. In the other word, Current flows between the cathode and the anode. It can be measured to determine the gas concentration [7, 8].

In electrochemical technique the current vs potential behavior was measured with the voltammetry at an electrode surface. The reduced or oxidized of electro-active chemical species at the electrode was caused by the varied of the potential. The currents was observed during the forward scan which caused by reduction process, and those the oxidation was caused the revers scan. Therefore, the resulting current is dependent on the concentration of the chemical analyte or species. When a molecule absorbed on the sensing device, the conductivity dramatically increased, then, converted into an electrical signal by changing the conductivity of the device.

Molecular Raman spectroscopy on a roughend gold nanoparticles electrode give a significant enhancement of the Raman scattering signals. SERS is able to enhance Raman signal intensity of a molecule magnificent orders of magnitude (10^6-10^{12}) through electromagnetic field enhancements and chemical enhancement due to molecules adsorption on metallic surface. Single molecule detection have been carried out using SERS technique. Electromagnetic enhancement occurs mainly because the excitation of collective oscillation of free electrons shared by the materials in conduction bands and localized Plasmon resonance. Since graphene foam can provide simultaneous sensing enhancement via electromagnetic (EM) and chemical mechanisms, it should be a great platform for electrochemical and SERS based chemical sensors and can detect amount of biochemical analytes or explosives. Thus, EM enhancement of graphene foam with decorated gold nanoparticles will be particularly addressed in this study [10].

According the Kneipp [9],and Srichan [10], when gold nanoparticles onto planer metallic surfaceinfluenced by electromagnetic field, electromagnetic enhancement and surface Plasmon field (E_{sp}) can be expressed as

$$\mathrm{E_{sp}^{Au}} = \mathrm{r}^3 \frac{\varepsilon-\varepsilon_0}{\varepsilon+2\varepsilon_0} \mathrm{E}_0 \left(\frac{1}{\mathrm{r+d}}\right)^3 \quad (1)$$

Where, d is the distance from the analyte to gold nanoparticlessurface,ε and ε_0 are the metallic and vacuum dielectric constant, E_0 and E_{sp}^{Au} are incoming and enhanced electric field, respectively and r is the radius of the metallic nanoparticles.

When incident field (E_0) resonates with the surface-induced field (E_{sp}^{Au}), the incident wave and the surface Plasmon reinforce each other to from a large enhancement of(E_M). The enhancement of field intensity results in the increase of Raman scattering signals.

A field enhancement factor EF for a molecule at a distance d from the surface of the sphere, is defined as the ratio between

the fields at the position of the molecule(E_M) and the incident field as describes fellow:

$$EF = \frac{E_M(\nu)}{E_0(\nu)} \approx \frac{\varepsilon(\nu)-\varepsilon_0}{\varepsilon(\nu)+2\varepsilon_0}\left(\frac{1}{r+d}\right)^3 \quad (2)$$

Total electromagnetic enhancement for SERS process can be expressed as

$$G(\nu_s) = \left|A(\nu_L)\right|^2 \left|A(\nu_s)\right|^2 \approx \left|\frac{\varepsilon(\nu_L)-\varepsilon_0}{\varepsilon(\nu_L)+2\varepsilon_0}\right|^2 \left|\frac{\varepsilon(\nu_s)-\varepsilon_0}{\varepsilon(\nu_s)+2\varepsilon_0}\right|^2 \left(\frac{r}{r+d}\right)^{12} \quad (3)$$

Where $A(\nu_L)$and$A(\nu_s)$ are the electromagnetic enhancement factors of the incident light(ν_L) and the Raman Stokes scattering at frequency(ν_s). Theenhancement is highest when surface Plasmon are in resonance with both the incident and Raman-scattering field. From the equation, the field enhancement is related to the forth order of the frequency/resonance dielectric terms; and the decay is strongly related to the distance d from the Raman-active molecule to the metallic surface. Therefore, the closer the molecule to the metallic surface, the higher enhancement. Due to high surface area and enhanced optical scattering of graphene foam, it should be useful for electrochemical and SERS based chemical sensor.In this work, gold nanoparticles were synthesized by electrodeposition technique on the surface of Graphene Foam (GF) by fast scan voltammetry with using Gold (III) chloride trihydrate as the solvent at room temperatureby reduction of reaction between trisodium citrate ($Na_3C_6H_5O_7.2H_2O$) and tetrachloroauric acid or Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$) [11]. The size and size distribution of nanoparticles are dependent on concentration of gold salt, trisodium citrate, applied potential and vary time. Thus, graphene foam decorated with gold nanoparticles have been reported to be highly-sensitivity substrate for both SERS and electrochemical sensing.

II. RESULTS AND DISCUSSION

To obtain the most effective electrochemical and surface enhanced Raman scattering based sensor, different sizes of gold nanoparticles were prepared by altering the ratio of $HAuCl_4$and the reducing agent [12].To produce large gold nanoparticles, less sodium citrate should be added in varying amount of auric acid. An immediate color change from pale yellow to deep red occurred within 10 minutes. The solutions were kept at the boiling point for 15 minutes to assure the completion of the reaction and finally allowed to cool at room temperature.

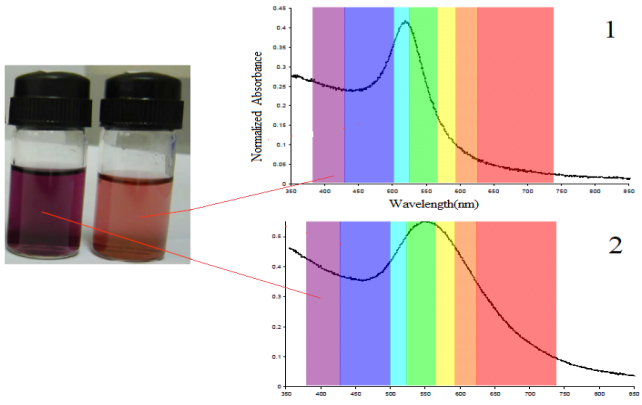

Figure 1. UV-Vis absorption spectrum of gold nanoparticles.

However, when the particles size increased, the absorption peak shifts to longer wavelength. In addition, the width of absorption spectra is related to the size distribution range. Because of surface Plasmon resonance and show heavy absorption of visible light at 520 nm. Therefore, gold nanoparticles show a single absorption peak in the visible range between 510 – 550 nm. The typical SPR peak of AuNPs measured by UV-Vis absorption spectroscopy isdemonstrated in Fig.1.

Figure 2 shows the comparison of Au nanoparticles decorated onto graphene foam with electrodepositing process with two different sputtering times of 20 s and 40 s. As seen with increasing sputtering time the average particle size was increased butthe average particle distance decreased due to particle aggregation.

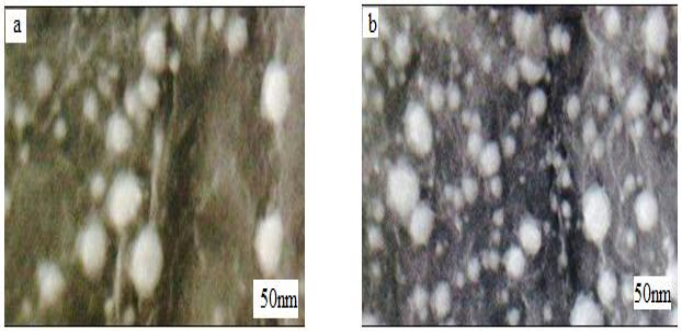

Figure 2. SEM image of AuNPs/GF substrates deposited with Au sputtering timesof (a) 20 s and (b) 40 s.

We add the 200 μl of H_2O_2 then characterized with cyclic voltammetry and Graphenefoam was used as sensor modified electrode. As seen in figure 3, the H_2O_2 is sensitive to surface chemistry of Graphene foam modified electrode. The cyclic voltammetry (CV) was used to characterize the electron transfer behavior in Graphene foam at H_2O_2. However, this figure shows the enhanced electrochemical response of H_2O_2 at Graphene foam modified electrode.

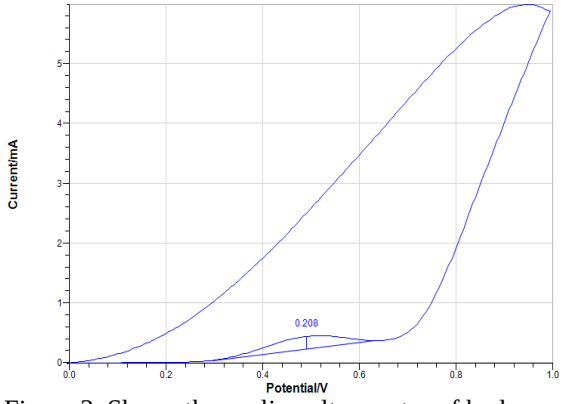

Figure 3. Shows the cyclic voltammetry of hydrogen peroxide at scan rate in 50 mV/s.

Here, as seen in figure 4. The GNPs decorated onto Graphene foam modified electrode showed good electro-catalytic activity toward hydrogen peroxide, it means that the electrode can be served as a new bio-sensing which made it ideally to construct oxidase-based biosensors. In addition, the AuNPs/GF has large specific surface area which adsorbs much more hydrogen peroxide than GF modified electrode.

One can see that the AuNPs were sensitive toward hydrogen peroxide than Graphene foam. Due to current response it can result that large amount of hydrogen peroxide are adsorbed onto the gold nanoparticles decorated onto Graphene foam surfaces.

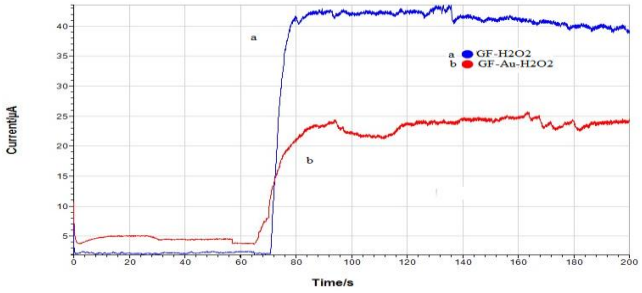

Figure 4.shows the comparison gold nanoparticels synthesised on Graphene foam (red color) and the Graphene foam (blue color) modefied electrodes in hydrogen peroxide.
We dropped the methylene blue (MB) onto a substrate surface (AuNPs-Graphene foam) then analyzed with surface-enhanced Raman spectroscopy. On the other hand, SERS indicate that the methylene blue was observed on gold nanoparticles-Graphene foam. The figure 5 is indicating the SERS spectra of $1\mu M\ MB$on Graphene Foam substrate compared with AuNPs/GF. It is seen that the AuNPs/GF substrate exhibits higher MB peak amplitude than the Graphene Foam substrate.

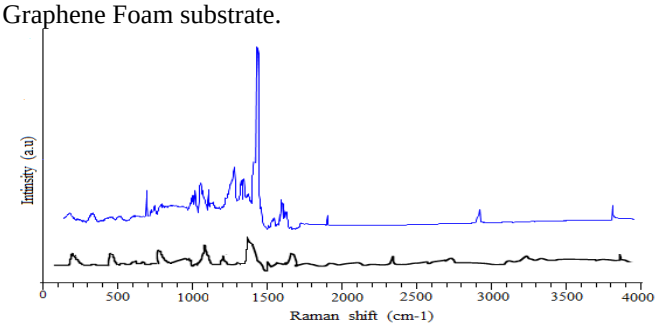

Figure 5. Comparison of SERS intensity of $1\mu M\ MB$on different SERS including Graphene Foam (black color) and AuNPs/GF (blue color).

Figure 6 shows Raman spectra of $1\mu M\ MB$ on AuNPs/GF decorated with varying sputtering time from 20s to 40 s. it shows that changing the particle diameter has a large effect on the enhancement of signal as seen that 50nm particle give significantly larger enhancement than either 30nm and 100 nm particles.

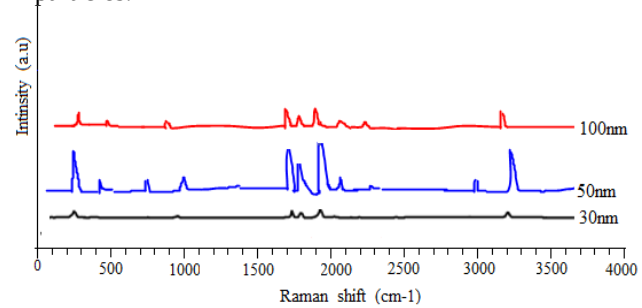

Figure 6. SERS spectra of $1\mu M\ MB$ using AuNPs/GF substrate prepared with various sputtering times including 20s, 30 s and 40 s in different size (30nm, 50nm and 100nm) respecrivly.

From overal results, gold nanoparticles decorated onto graphen foam has shown high sensitivity in electrochemical based sensor and high SERS enhancement factor and excellent MB detection sensitivity. Moreover, the average Au particle size of 50 nm which produced with 30 s sputtering time has optimal sensitivity for detiction of MB in low concentrtion.

In conclusion, gold nanoparticles decorated onto graphene foam have been developed as a SERS substrate and electrochemical bio sensor and applied for detection of hydrogen peroxide and MB respectivly. The effect of Au nanoparticles size have been sudied with different sputterning time. Results show that the sputterning time of 30 s which produced the average size of 50 nm exhibits much SERS enhancement factor and have optimal senstitivity for detection of MB with low concentrtion.

Methods

Material preparation and characterization. In order to synthesis of gold nanoparticles through the citrate reduction for preparing gold nanoparticles we added 25mM sodium citrate ($Na_3C_6H_52H_2O$) into the 3mM ($Au(III)Cl_3$) which results auric acid or Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$). Here, we added the 2mM of ($HAuCl_4.3H_2O$) into clean glass then the solution was break up with used electrical current through electrodeposition to reduce the Au(III) into neutral Au atoms and coating onto Graphene Foam. After turn on the PalmSens (controlled-potential source) the reaction would start and the current was generated which allowing forming the gold nanoparticles on Graphene foam. Au (III) ions are reduced and thus deposited onto the Graphene foam surface. In this study, the synthesized of gold nanoparticles decorated on Graphene foam have been done by electrodepositing process. The electrodepositing was performed using amperometric under different potential at room temperature for variant times. Here, we have investigated gold nanoparticles deposition with small applied potential and short deposition times.

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