Preliminary investigation of the surface activation of disposable screen printed carbon electrodes using synthesized gold nanoparticles

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Abstract
Gold nanoparticles, GNPs, are known to be the most stable metal nanoparticles. They exhibit many unique and interesting physical and optical properties with profound potentials for diverse applications. However, they are highly delimited in terms of size distribution. Different sizes of gold nanoparticles, synthesized through simple laboratory method, were characterized using zetasizer nano series particle size analyzer and ultraviolet-visible spectrophotometer. The synthesized gold nanoparticles were used to modify screen printed carbon electrodes and electrochemical characterization was conducted. The synthesized GNPs sizes range from 42.54-1730.00 nm. The 49.27 nm sized GNPs displayed the highest oxidative peak current in the cyclic voltammogram obtained. All the GNPs modified electrodes gave higher peak over the bare electrode. This implied that the GNP/SPCEs allowed the flow of current or offered least resistance to the flow of current as compared to bare/SPCE. The high peaks indicate successful oxidation process at the anode electrode of the electrochemical process. The present work showcased a simple approach of coating the surface of the disposable SPCEs with GNPs unlike other previously employed pathways. The work also showed that GNPs can successfully be assembled onto the surface of SPCE through simple dipping of the SPCE in the GNPs solution. In addition this approach is cheap, simple and environmentally friendly. The fabricated electrode, GNP/SPCE could be a promising electrode for future detections and determinations.

Keywords: Gold nanoparticles, peak current, Zetasizer, screen printed carbon electrode, spectrophotometry
1 Introduction

A number of studies have been conducted on the preparation, property and developmental utilization of gold nanoparticles (GNPs) which is among the most researched nanomaterials. GNPs have stable physical and optical qualities [1] making them suitable for applications in drug delivery, electronics [2], sensor (biosensor and/or electrochemical sensor) [3] among others. A number of capping and stabilizing agents have been utilized in the synthesis of GNPs. Each approach is determined by the specific area of usage. The production of these interesting nanoparticles is dependent on the amount of sodium citrate and gold salt, pH and temperature [2]. The size and numbers of the particles give rise to the varying architectural structures like rod-, polygon-, starlike and branched GNPs that can be produced from a solution-governed synthetic pathway. Usually, nanomaterials of multiples sizes and shapes are bound to evolve by toiling with the aforementioned factors [4]. The inherent physicochemical properties of GNPs which make them to be utilized in numerous applications are attributed to their non-toxicity, nobility, easy synthetic protocols and stress-free functionalization. Gold cores of 1-150 nm in diameters had been successfully synthesized [5]. GNPs alone and/or GNPs with other nanoparticles of interest are often supported on disposable screen printed electrodes. Screen printed carbon electrodes (SPCEs) are the products of microfabrication screen printing technology involving gradual and controlled deposition of thick film of ink comprising graphite, binder and solvent on unreactive supports like ceramics or plastics. In comparison to the screen printed gold or platinum electrodes, the SPCEs have profited tremendously from the technological breakthrough [6]. They can be electrochemically or chemically activated to enhance their charge transfer traits [7–10]. However, some measures may be employed to modify the surface of the electrodes to obtain better performance. These may include doping with catalysts [11] or surface coating with carbon nanotubes [12–14].

GNPs can be used to decorate the surface of activated MWCNTs in a number of ways. They can be connected to the oxidized nanotube through the use of bifunctional thiols acting as covalent linkages [3]. The connection via hydrophobic and/or hydrogen bonds had also been reported. Acetone can hydrophobically inter play between MWCNTs and GNPs protected with octanethiols. While the alkyl chain on the alkanethiol interact with MWCNTs surface in a non-
aqueous manner, the hydrogen bonds interaction occurred between the carboxylic groups on the MWCNTs and those on the GNPs surface resulting in a rigid nanocomposite [5]. Another approach is pie-stacking using pyrene derivatives and lastly is the electrostatic interaction which is often utilized in layer-by-layer formulations. In this regard ionic polyelectrolytes often links charged GNPs onto oxidized MWCNTs surface. The often used conductive ionic polyelectrolytes include poly(diallyldimethylammonium chloride), PDDA with positive charge and poly(sodium 4-styrenesulfonate), PSS with negative charge. However, charged GNPs can interact solely with activated MWCNTs surface, producing a rather low density binding compared to that involving the ionic polyelectrolytes [15]. The present work employed simple dipping method to observe the binding electrostatic force of attraction between the carbon of SPCE and the GNPs. The present study synthesized GNPs using a modified technique reported elsewhere [16]. The resulting GNPs were subjected to electrochemical and chemical characterization and particle size determination. These methods constitute the preliminary investigation of the activation of SPCEs using various sizes of synthesized GNPs.

2 Materials and Methods

2.1 Reagents

Gold (III) chloride trihydrate (≥99.9%) and sodium citrate dehydrate (≥99%) were purchased from Sigma-Aldrich (St. Louis, USA). Sulphuric acid (95-97%) was procured from Friendemann Schmidt (Parkwood, Australia). Potassium ferric cyanide, K₃Fe(CN)₆ was purchased from Bendosen (Kajan, Selangor, Malaysia) and potassium chloride, KCl (99.5%) was bought from R & M Chemicals (Selangor, Malaysia). Other chemicals are of the qualitative analytical grade. Deionized water from a Millipore Milli-Q purifier was used throughout the experiments. All glass wares, plastic wares and ceramics were washed thoroughly with liquid detergent and properly rinsed with deionized water and oven dried prior to the initiation of the experiments.

2.2 Equipment

Cyclic voltammetry (CV) was performed via a DropSens potentiostat, μStat 8000 electrochemical workstation (Asturias, Spain). A three-electrode system was used for all
electrochemical experiments. Screen-printed carbon electrodes, comprising carbon-based working electrode (4 mm diameter) made of carbon, platinum-based counter electrode and silver-based reference electrode were provided by MIMOS (Bukit Jalil, Selangor, Malaysia). The particle size was measured with Zetasizer Nano 5 system (Malvern Instruments Ltd., Malvern, UK). UV-Visible spectrophotometer (Perkin Elmer, Lambda 35, Massachusetts, USA) was utilized for the routinely quantitative determination of absorbance in the synthesized sample solutions. A digitalized pH meter purchased from Thermo Fisher Scientific (Chicago, IL, USA), was employed in the adjustment of pH values of prepared solutions in the voltammetric experiments. A digital balance used to accurately measure the weight of solids was supplied by A&D Company (Tokyo Japan). Hot plate with stirrer used for heating was obtained from Hwashin Technology Company (Seoul, Korea)

2.3 Preparation of colloidal gold nanoparticles solution

Exactly 0.01% HAuCl$_4$.3H$_2$O was prepared from the solid stock and 1% sodium citrate was equally prepared from the stock. These solutions were used for the production of gold nanoparticles (GNPs) colloidal solution. Synthesis of GNPs was carried out based on the description of Manso et al. [16] with slight modification. Then, 30 ml of HAuCl$_4$.3H$_2$O solution and 0.2 ml of sodium citrate solution were mixed together in a beaker, thoroughly stirred and heated to boiling. The heat source was removed after 10 min, but stirring continued for another 10 min to produce GNPs colloidal solution. The experiment was performed with varying volumes of sodium citrate solution (0.3, 0.4, 0.5 and 0.6 ml) producing different sizes of GNPs solutions. In this study, the prepared GNPs are tagged 30/0.2, 30/0.3, 30/0.4, 30/0.5 and 30/0.6. These ratios implied the constant volume (30 ml) of gold salt solution in combination with the variable volumes of citrate solution.

2.4 Characterization of prepared GNPs colloidal solutions

The prepared GNPs were characterized for size and absorption using Malvern zetasizer nano 5 particles size analyzer and UV-visible spectrophotometry, respectively. The
electrochemical characterization was achieved by coating the surface of the SPCE with various sizes of GNPs. Each bare/SPCE was immersed into the particular GNPs solution for a period of 2 min afterwards the GNPs coated SPCE tagged nGNPs/SPCE was air dried and stored in the desiccator for cyclic volumetric determination. The working electrode of the SPCE was modified with the GNPs.

2.5 Electrochemical characterization of modified SPCEs

The electrolyte employed for determination of effective electroactive surface area (EESA) of modified electrodes, comprised of 1mM K$_3$Fe(CN)$_6$ and 0.1M KCl at variable scan rates. The voltammetric analyzer used for this study comprises of DropSens potentiostat, μStat 8000 electrochemical workstation (Asturias, Spain) attached to a computer system. The instrument was operated at the following conditions for a cyclic voltammetry (CV) method; activating potential -0.6V to +0.6V, scan rate 0.05Vs$^{-1}$, in the presence of 1 mM K$_3$Fe(CN)$_6$/0.1MKCl electrolytic medium at room temperature. The gold nanoparticle SPCE electrodes were prepared by dipping the bare SPCE in respective GNPs colloidal suspension for a time interval of 2 min and then on removal each GNPs coated electrode was air dried. The prepared electrodes for this study are; 0.2GNPs/SPCE, 0.3GNPs/SPCE, 0.4GNPs/SPCE, 0.5GNPs/SPCE and 0.6GNPs/SPCE.

3 Results and Discussion

The size distribution of GNPs is shown in Figure 1. The DLS plot shows a bimodal distribution for 30/0.2 GNP (Figure 1A) with peaks at 10 and 90 nm respectively, a unimodal distribution for 30/0.3 GNP (Figure 1B) with peak around 1000 nm, a quadrimodal distribution for 30/0.4 (Figure 1C) with peaks estimated around 5, 60, 700 and 7000 nm respectively, a trimodal distribution for 30/0.5 GNP (Figure 1D) with peaks approximated around 2, 8 and 90 nm respectively and a bimodal distribution for 30/0.6 GNP (Figure 1E) with peaks at 50 and 100 nm respectively. The genesis of these peaks is difficult to explain and may be attributed to the intricacy of the design of the DLS method [19].
Figure 1. Particle size distribution (PSD) of GNPs with different sizes (A), (B), (C), (D), (E) from Zetasizer nano series using DLS technique and picture of the 5 synthesized GNPs dispersions (F).

Also, the multiple peaks may arise from other species present with GNPs, since single peak and a somewhat narrow distribution is expected for a pure gold solution. These outcomes show similarity to those reported elsewhere [19] where gold sizes were measured in the presence and absence of plasma. Table 1 is the extrapolation of the intensity versus particle size diameter of Figure 1. The modal size of 30/0.3GNP is the highest (1281 nm), while the least modal value (1.294 nm) is jointly shared between 30/0.4 and 30/0.5 GNPs. The mean volume range of the all the GNPs approximate to 0.1 - 22.0 with the exception of 30/0.3GNP. However, among all the modal sizes, size 30/0.2 GNP (7.531 nm) corresponded to the reported value in the literature [18]. DLS is an approach that makes use of particulate assembly in the determination of particle size distribution [19]. The z-average of the synthesized GNPs over the diameter range of particle sizes are displayed in Table 1. The 30/0.2 GNPs also satisfied both conditions of average size (49 nm) being within the nanoscale region and acceptable polydispersity index (46%). This choice is also in agreement with previous findings [20] which posited that polydispersity index should not be above 50% for a monodisperse medium.

Figure 2 shows the GNPs particle size distribution with the mean volume obtained from the zetasizer nano series analyzer. Four out of the five GNPs are within the diameter less than or
equal to 20 nm (Figure 2A). The odd of the synthesized GNPs is 30/0.3 which is apparently
displayed as curve e (Figure 2B). However, the 30/0.3 GNPs is represented as curve a (Figure
2C) with size ranging from 500-2500 nm. This value is well outside the nanoscale range of 1-
100 nm. The reason for this anomaly may be attributed to particle agglomeration during the
preparation of the colloidal gold nanoparticle solution.

**Figure 2.** A plot of Mean volume (%) against diameter (nm) for PSD of synthesized GNPs,
curve a, 30/0.5; curve b, 30/0.4; curve c, 30/0.6, curve d, 30/0.2(A) and curve e, 30/0.3(B), curve
a, 30/0.3 (C)

**Table 1.** Particle size distribution of synthesized GNPs from Zetasizer Nano series using DLS
technique

| Parameters                        | 30/0.2 GNPs | 30/0.3 GNPs | 30/0.4 GNPs | 30/0.5 GNPs | 30/0.6 GNPs |
|-----------------------------------|-------------|-------------|-------------|-------------|-------------|
| Z-average (nm) (x & α)            | 49.27± 0.245| 1730± 1.013 | 43.35± 0.585| 42.54± 0.170| 46.95± 0.050|
| Polydispersity index (x & α)      | 0.457± 0.003| 0.419± 0.083| 1.00± 0.000 | 0.560± 0.003| 0.538± 0.005|
| Diameter range (nm)               | 4.187-164.2 | 712.4-6439.0| 0.8332-7.531| 0.8332-8.721| 7.531-396.1 |
| Mean volume range (%)             | 0.100-18.50 | 0.300-23.40 | 0.100-17.20 | 0.100-22.10 | 0.100-14.90 |
| Modal size (nm)                   | 7.531       | 1281        | 1.294       | 1.294       | 13.54       |

NB: x = mean, α = standard deviation

The UV-visible absorption spectra of synthesized GNPs are shown in Figure 3. The
absorbance peaks of GNPs appear at wavelength range approximating 520-530nm, depending on
the size of GNPs. The wavelength is a measure of the size of nanoparticles. As displayed in Figure 3, the peaks of the absorption spectra shifted towards the short wavelength side and the full breadth at mid peak of the spectra decreased with soaring volume of sodium citrate from 0.2 to 0.6 ml. This is a realization that citrate solution is a determinant of the size of GNPs. The faster the capping of the GNPs by citrate molecules, the smaller the ensuing nanoparticles. Similar results have been reported in the literature [21].

![Figure 3. UV-visible absorption spectra of synthesized spherical GNPs](image)

The cyclic voltammograms of GNPs modified screen-printed carbon electrodes and bare SPC electrodes are shown in Figure 4. All the voltammograms exhibited excellent reversible redox process, GNPs modified and bare electrode alike. This justifies the establishment of equilibrium at the electrode surface involving the redox couple Fe$^{3+}$/Fe$^{2+}$ from the ferric cyanide electrolyte. However, the anodic oxidative peak current ($I_{pa}$) for each modified electrode slightly differs, approximately, with 0.2GNPs/SPCE providing the highest peak current of 10.2 µA and 0.4GNPs/SPCE giving the least amount of 9.1 µA (Figure 4).
Figure 4. Cyclic voltammograms of overlay forms of all the voltammograms for all the different sizes of GNP/SPCE in comparison with the bare/SPCE in 1mM K$_3$Fe(CN)$_6$/0.1MKCl at a scan rate of 0.05V/s.

The oxidative peak current of each of the GNP/SPCE is higher than that of the bare/SPCE (Figure 4). The high value of $I_{pa}$ recorded from the modified electrodes may be due to the catalytic property of GNP which enhances rapid electron transfer at the surface of SPC electrodes. The 30/0.2GPN/SPCE gives the highest oxidative peak current, while 30/0.4GNP/SPCE gives the least oxidative peak current. The electrochemical study outcome also supported previous findings regarding the 30/0.2GNP. Thus 30/0.2 sized gold nanoparticles may be utilized in the future development of the new electrode.

The effective electro-active surface area (EESA) for both bare and modified electrodes is also evaluated with the aid of Randles-Sevick equation [22, 23].

$$i_p = (2.69 \times 10^5)n^{3/2}A_{eff}D^{1/2}Cv^{1/2}$$

(1)

Where $n$ is the number of electron(s) participating in the redox process, $A$ is the effective electro-active surface area (cm$^2$), $D$ is the diffusion coefficient of the molecules in the solution (cm$^2$ s$^{-1}$), $C$ is the molar concentration of [Fe(CN)$_6$]$^{3+}$ and $v$ is the scan rate (Vs$^{-1}$).
The effective electro-active surface area of each of the electrode can be obtained by substituting the value of the respective slope in the plot of $I_p$ vs $v^{1/2}$ (Figure 5) and other constants for the ferrocyanide electrolyte, $Fe^{3+}/Fe^{2+}$ redox couple such as $n=1$, $D=7.6 \times 10^{-6}$, $C=1x10^{-3}$ into the equation

$$A_{eff} = \frac{\text{slope}}{2.69 \times 10^5 n^{3/2} D^{1/2} C} \quad (2)$$

The calculated effective electro-active surface area ($A_{eff}$) for the bare/SPCE is $0.01163327 \text{ cm}^2$. There was an increase in $A_{eff}$ to $0.055007407 \text{ cm}^2$ when bare/SPCE was modified with colloidal solution of GNPs films. The $A_{eff}$ of GNPs/SPCE is approximately 4.7 folds greater than bare/SPCE. These results suggest that the surface modification of bare/SPCE using GNPs provided much more effective surface areas than the bare/SPCE. The increase in the EESA of the GNPs modified SPCE may lead to corresponding increase in oxidative peak current as earlier discussed, suggesting rapid rate of electron transfer at the surface of modified electrode over the bare electrode.

**Figure 5.** A plot of peak current (A) versus square root of scan rate (vs$^{-1}$) for bare/SPCE (A) and GNPs/SPCE (B)
4 Conclusion

Various sizes of gold nanoparticles were successfully prepared through simple laboratory techniques. Physicochemical and electrochemical characterizations of the prepared GNPs were carried out via basic instrumental means. Enlargement of effective surface area of modified electrode over bare electrode was also confirmed. All the modified electrodes produced higher oxidative peak current over bare electrodes confirming the relevance of surface active agents on SPCE. The present findings may be the much needed harbinger for the future development of sensitive, selective, cheap and environmentally friendly electrodes for all kinds of pertinent detections and determinations.

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