THE EVALUATION OF GOLD NANOPARTICLES EMBEDDED ON POLYVINYL ALCOHOL MATRIX AS OXIDATION CATALYST AND BIOSENSOR

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For my family, but especially for my mom –
thank you for your unconditional love and continuous support
and to Ed and Debo

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PREFACE

This thesis is the result of my work carried out in the Department of Chemistry, Universiti Teknologi Malaysia, between July 2007 to June 2009 under supervision of Assoc. Prof. Dr. Hadi Nur. Parts of my work described in this thesis have been reported in the following publications or presentations:

1. Nur, H., Nasir, S.M. (2008). Gold Nanoparticles Embedded on the Surface of Polyvinyl Alcohol Layer. *Journal of Fundamental Sciences.* 4. 245-252.

2. Nur, H., Nasir, S.M. Gold Nanoparticles Embedded on the Surface of Polymeric Layer as a Biological Sensor. Oral presentation in the Regional *Annual Fundamental Science Seminar 2008 (RAFSS'08).* Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, Skudai, Johor. 27th - 29th May, 2008.

3. Nur, H., Nasir, S.M. Gold Nanoparticles Embedded on the Surface of Polymeric Layer as a Biological Sensor. Poster presentation in the *Minggu Penyelidikan Sains dan Matematik 2007*. Fakulti Sains, Universiti Teknologi Malaysia, Skudai, Johor. 31st December, 2007 – 3rd January, 2008.

ABSTRACT

In this study, a method for synthesizing polyvinyl alcohol (PVA) embedded gold film is presented. This approach takes advantage of the high affinity of thiol molecules towards gold. Gold particles, in the size range of 20 to 180 nm, were first prepared by the conventional Turkevitch method by the reduction of tetrachloroauric acid ($HAuCl_4$) with sodium citrate in water. The Ultraviolet-Visible (UV-Vis) absorption spectra and dark-field microscopy confirmed the presence of a surface plasmon resonance (SPR), attributed to the nanosized gold particles. The resultant gold particles of sizes as low as 27 nm with nearly spherical in shape were achieved as determined by Transmission Electron Microscopy (TEM) and Field Emission Scanning Electron Microscopy (FESEM). In the preparation of PVA embedded gold (PVA-Gold) film, PVA was functionalized with (3-mercaptopropyl) trimethoxysilane (MPTMS) which produced a thiol functionality on the surface. Then, gold particles were chemisorbed onto the surface of partially dried thiol functionalized PVA to produce PVA-Gold composite. The composite materials were characterized using Fourier transform infrared spectroscopy (FTIR), FESEM, TEM and UV-Vis diffuse reflectance (DRUV) spectroscopy. The TEM results showed that the gold particles embedded on the surface of PVA were polydispersed with the average particle size from 30 nm to 150 nm. The catalytic potential of PVA-Gold for oxidation reaction has been investigated in the liquid phase oxidation of styrene with aqueous *tert*-butyl hydroperoxide and the results were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). PVA-Gold were found to be highly active catalyst (95% conversion of styrene) and selective towards the oxidation of styrene to give benzaldehyde (73%) as the main product. Moreover, PVA-Gold also showed a very good regenerability in the repeated oxidation of styrene. The unique optical properties of PVA-Gold were also exploited in the interactions with several amino acids such as L-Arginine (Arg), L-Proline (Pro), L-Tryptophan (Trp) and L-Tyrosine (Tyr). The DRUV demonstrated that the surface plasmon resonance peaks for the amino acid – PVA-Gold conjugates were relatively shifted towards longer wavelength as evidence of a successful functionalization of gold with the amine groups of amino acid. The above findings suggest that PVA-Gold have potential application as heterogeneous oxidation catalyst and can be explored as probes for biosensing application.

ABSTRAK

Dalam kajian ini, suatu kaedah bagi mensintesis filem polivinil alkohol (PVA) terpahat emas dilaporkan. Kaedah ini, mempergunakan sifat saling tarik molekul tiol yang kuat terhadap emas. Partikel emas, bersaiz dalam julat 20 nm – 180 nm, pertamanya disediakan menurut kaedah konvensional Turkevitch secara penurunan asid tetrakloroaurik ($HAuCl_4$) dengan natrium sitrat di dalam air. Spektrum serapan ultralembayung-nampak (UV-Vis) dan mikroskopi medan gelap menunjukkan terdapat bukti plasmon resonans permukaan (SPR) yang disebabkan oleh partikel emas bersaiz nano. Partikel emas yang diperolehi bersaiz paling kecil 27 nm dan hampir berbentuk sfera seperti yang diperlihatkan oleh mikroskopi elektron pancaran (TEM) dan mikroskopi elektron pengimbasan pancaran medan (FESEM). Dalam penyediaan filem PVA bertatahkan emas (PVA-Emas), PVA telah difungsikan dengan (3-merkaptopropil) trimetoksisilana (MPTMS) bagi melekatkan kumpulan berfungsi tiol pada permukaannya. Kemudian, partikel emas dijerap kimia pada permukaan separa kering PVA berfungsikan tiol untuk seterusnya menghasilkan komposit PVA-Emas. Bahan komposit tersebut telah dicirikan dengan spektroskopi inframerah transformasi Fourier (FTIR), FESEM, TEM dan spektroskopi pemantulan difusi ultralembayung-nampak (DRUV). Keputusan daripada TEM menunjukkan partikel emas terpahat pada permukaan PVA secara berserakan dengan purata saiz partikel di antara 30 nm hingga 150 nm. Keupayaan emas sebagai mangkin bagi tindak balas pengoksidaan dikaji dalam pengoksidaan stirena dengan *tert*-butil hidroperoksida (TBHP) dalam fasa cecair dan hasil tindak balas tersebut telah dianalisis menggunakan kromatografi gas (GC) dan kromatografi gas-spektrometri jisim (GC-MS). PVA-Emas didapati mangkin yang sangat aktif (95% penukaran stirena) dan selektif terhadap pengoksidaan stirena kepada benzaldehid (73%), sebagai hasil utama. Tambahan lagi, PVA-Emas memperlihatkan kebolehulangan yang sangat baik bagi pengoksidaan stirena. Sifat optik emas yang unik telah dieksploitasikan dalam interaksinya dengan beberapa amino asid seperti L-Arginine (Arg), L-Proline (Pro), L-Tryptophan (Trp) dan L-Tyrosine (Tyr). Spektrum DRUV menunjukkan puncak plasmon resonans permukaan bagi konjugat amino asid-PVA Emas telah beranjak kepada nombor gelombang yang lebih tinggi secara relatif menjadi bukti bahawa emas telah difungsikan dengan kumpulan amina dalam amino asid dengan jayanya. Keputusan kajian menunjukkan bahawa PVA-Emas berpotensi diaplikasikan sebagai mangkin pengoksidaan heterogen dan berguna sebagai prob dalam aplikasi biosensor.

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LIST OF ABBREVIATIONS

% - Percentage
wt %. - Percentage of weight
° - Degree
°C - Degree Celsius
λ_{max} wavelength of maximum absorbance
atm - atmospheric pressure
Au - Aurum (gold)
CCD - Charge coupled device
cm - centimeter
cm^2 - centimeter squared
DNA - Deoxyribonucleic acid
E° Electrode potential
FESEM - Field emission scanning electron microscopy
FTIR - Fourier transform infrared
FTIR-ATR - Fourier transform infrared – attenuated total reflectance
g - Gram
GC - Gas chromatography
GC-MS - Gas chromatography with mass spectrometry
$HAuCl_4$ - Hydrogen tetrachloroaurate
HCl - Hydrochloric acid
HNO_3 - Nitric Acid
L - Liter
M - Molar
mL - milliliter

μL	-	microliter
μm	-	micrometer
mm	-	millimeter
MPTMS	-	(3-mercaptopropyl) trimethoxysilane
nm	-	Nanometer
NA	-	Numerical Aperture
SO_2	-	Sulfur dioxide
SPR	-	Surface plasmon resonance
TBHP	-	*tert*-butyl hydroperoxide
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet-visible
UV-Vis DR	-	Ultraviolet-visible diffuse reflectance spectroscopy

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Nanoparticles can be defined as particles with at least one of their three-dimensional sizes in the range of 1 – 100 nm. Recent intense interest in nanoparticles stems from the fact that nanoparticles exhibit unique properties compared to their bulk counterparts. Many of these properties including physical, chemical, optical, electrical and magnetic can be controlled by relatively simple tuning of their sizes, shapes, compositions, protecting ligands and interparticle distance. To date, the most widely studied nanoparticles have been those of metals, semiconductors and magnetic materials due to the potential applications of these materials in optoelectronics, catalysis, reprography, and other areas [1]. However, among these metallic particles, gold nanoparticles stand out in particular due to their associated strong surface plasmon resonance (SPR). Surface plasmon was found to be dependent not only on the size of the gold nanoparticles but on their shape as well [2]. The SPR absorption and other unique properties resulting from the small gold particle size can be exploited in a wide range of sensing applications such as bioimaging [3-5], chemical and biological sensing [6, 7] and colorimetric assays for DNA detection [8, 9].

It was demonstrated that gold nanoparticles could readily bind thiol, amine, cyanide and diphenylphosphine functional groups [10-13]. Amino acids, which is a constituent of proteins, are considered as suitable agents in the biofunctionalization of gold nanoparticles due to the presence of different functional groups, such as –SH and $–NH_2$, with affinity for gold. Generally, amino acids can be adsorbed on the gold particle surface during the formation of particles, using amino acid itself as a reducing agent [14-16], or in the latter stage, by ligand exchange reactions or binding on the former adsorbed stabilizing molecules [17]. Most applications of gold nanoparticles as sensors are based on detecting the shifts in the SPR peak, due to either the change in the local dielectric constant of the nanoparticles resulting from adsorbed biomolecules or due to biomolecule induced agglomeration of the nanoparticles [18].

Gold in the bulk is chemically inert and has often been regarded to be poorly active as a catalyst. However, when the dimension of gold is reduced below ~10 nm, it turns out to be surprisingly active for many reactions such as CO oxidation, especially at low temperatures as first discovered by Haruta [19]. The catalytic activity of both heterogeneous and homogeneous gold based catalyst is now well established in different processes: selective or complete oxidation, hydrochlorination, and hydrogenation reactions [20]. All of these applications show the special reactivity of gold compared with platinum group metals and this may be explained in terms of the electronic states (+1, +3) and the high electrode potential of gold ($E^o = +1.69$ V).

Nanoparticles have a tendency to aggregate and are difficult to recover from reactions due to their small size. Therefore, in order to overcome these difficulties, it is necessary to immobilize the gold nanoparticles onto a matrix material such as polymers because the immobilized nanoparticles are more stable. The principle advantages of the method are that the resulting materials are easily prepared in a single-step procedure and the possibility to control the thickness of the polymeric layer. These materials also possess the processing and handling advantages of bulk materials. Other benefits of immobilizing nanoparticles in polymeric matrices include increased stability, improved processability, recyclability, and solubility in a variety of organic solvents. Among polymers, polyvinyl alcohol (PVA) is a commercially important water soluble polymer which is known to be a good stabilizer of noble metal particles. PVA is also the most important material for the dehydration of organic mixtures owing to its good chemical stability, film forming ability and high hydrophilicity [21]. Other polymers commonly used for the stabilization of gold nanoparticles are poly(1-vinylpyrrolidone) and poly(ethylene glycol) [22]. In the case of heterogeneous catalysis, the catalytic properties of gold were shown to depend strongly on the support, the preparation method, and particularly the size of the gold particles [23, 24].

1.2 Problem Statement

Gold nanoparticles hold a particular interest to those in the biological sciences because they are on the same size scale as biological macromolecules, proteins and nucleic acids. The interactions between biomolecules and nanomaterials have formed the basis for a number of applications including detection, biosensing, cellular and *in*-situ hybridisation labelling, cell tagging and sorting, point-of-care diagnostics, kinetic and binding studies, imaging enhancers, and even as potential therapeutic agents.

Recently, it has been reported that the scattering property of gold nanoparticle could be harnessed in a living cell to make cancer detection easier [25, 26]. What makes the approach so promising is that the method was simple, employing only inexpensive microscope and white light. However, the method used was not practical because in the above method, the gold nanoparticles were in solution form such that it could not be recovered and reused. In this research, we investigated the feasibility of immobilizing gold nanoparticles (and also their conjugates) in polymer film without degradation of their SPR properties.

The catalysis by metal nanoparticles is one of the most important and attractive research owing to an increase in exposed surface area and to a possibility of finding novel properties generated by quantum size effect [27]. The use of homogeneous gold catalyst could be unfavourable in practical applications as the separation and reuse of the catalyst after reaction would be problematic. Most studies on gold catalysts have been focused on gold oxide supports as these catalytic systems are mostly used for gas-phase oxidation. However, as recently reported, gold catalysts also represent a useful alternative to platinum group metals systems for liquid phase oxidation [28]. In this case, the presence of a solvent such as water dramatically affects the interaction between the reagent and the catalytically active materials. In particular, gold on polymer shows superior selectivity and is much less affected by poisoning, when compared with classical palladium and platinum catalysts. As poisoning represents one of the major drawbacks limiting industrial application in liquid phase oxidation involving oxygen as the oxidant, the advantage of using a gold catalyst may not be of only academic interest but could also have industrial potential. As a consequence, there is a growing need for a general procedure to prepare gold catalysts with high dispersion, regardless of the polymer support used.

Despite a large number of methods reported to immobilize gold nanoparticle in polymer film, it is still desirous to develop a simple and effective synthesis of such nanoparticles with better size control and uniform particle distribution. Nevertheless, the difficult handling of these extremely fine particles has posed a strong limitation to their use. Most metal nanoparticles are very unstable. They can aggregate because of the high surface free energy and readily oxidized-contaminated by air, moisture, sulfur dioxide (SO_2) and so on. Therefore, the embedding of gold nanoparticles in a polymer surface represents a valid solution to the manipulation and stabilization problems. Furthermore, polymer embedding represents a straightforward but effective way to use the mesoscopic properties of metal nanoparticles.

Previous studies reported that the immobilization of gold nanoparticles on polymeric surfaces or substrates involved the immersion of the functionalized surface such as thiol functionalized polymer in gold solutions [20] followed by drying. However, this method is not practical as the gold nanoparticles attached to the surface may be easily detached since they are only linked to the functionalized polymeric surface via chemisorption so that the particle-to-surface contact area is too small to allow a strong attachment. Our approach is different compared to the previous study as the gold nanoparticles are annealed on the surface of partially dried functionalized (3-mercaptopropyl) trimethoxysilane (MPTMS) polymeric layer. Thus, the gold nanoparticles are not only linked to the functional groups on the polymer surface but are actually embedded in the polymer layer which enhanced the particle-to-surface contact area between gold nanoparticles and PVA film, making it more difficult for the detachment of the gold nanoparticles as presented schematically in Figure 1.1.

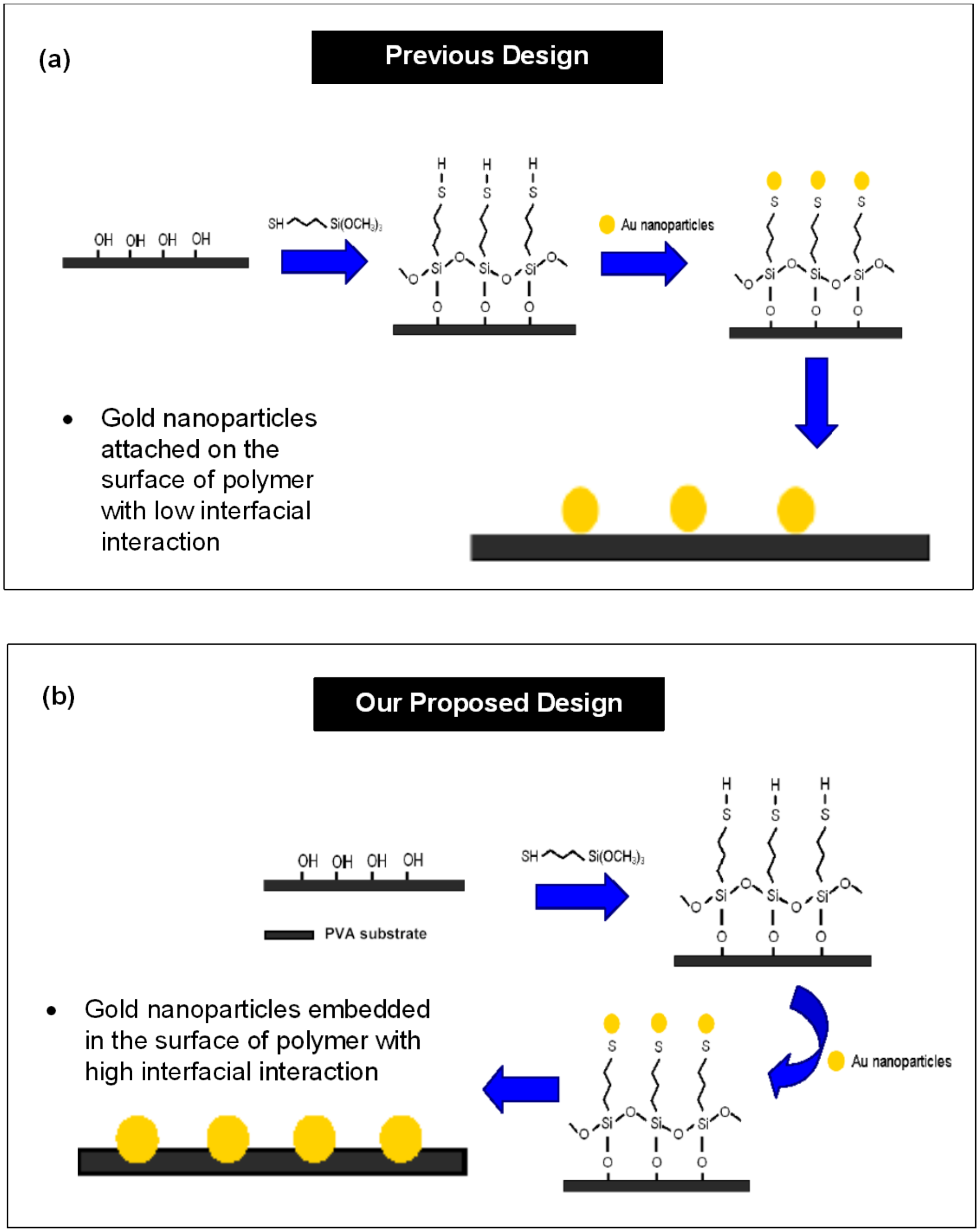

Figure 1.1: Schematic representation of the proposed gold nanoparticles embedded in the surface of polymer: (a) gold nanoparticles attached on the surface of the polymer layer by chemisorption, (b) gold nanoparticles embedded in the polymer layer by attachment of nanoparticles on the surface of partially dried functionalized polymeric layer.

1.3 Research Objectives

The objectives of the study are:

(1) To synthesize gold nanoparticles using the Turkevitch method via the reduction of $HAuCl_4$ with sodium citrate in water.

(2) To incorporate gold nanoparticles on the surface of functionalized PVA.

(3) To investigate the catalytic activity of the gold nanoparticles embedded on PVA for liquid phase oxidation of styrene.

(4) To investigate the structural and morphological properties of the gold nanoparticles embedded on PVA in the interactions with amino acids.

1.4 Scope of Study

In this research, the gold nanoparticles will be synthesized by the reduction of Au (III) ions with citrate in water, a process pioneered by Turkevitch [30] in 1951 and later refined by Frens [31]. In this method, citrate serves as both reducing agent and an anionic stabilizer. It yields uniform and almost spherical particles with diameters ranging from a few to approximately 150 nm. The size of the resulting colloidal gold nanoparticles, whose surfaces are negatively charged with citrate, is controlled by the molar ratio of $HAuCl_4$ / sodium citrate (the lower the ratio, the smaller the particle size). The produced gold nanoparticles will be studied on its surface morphology and physical properties especially related to its SPR absorption and scattering properties.

Then, the stable incorporation of gold nanoparticles on the surface of polymeric layer, such as PVA, will be achieved by using MPTMS as a linker molecule which has the ability to react with the functional groups of the polymeric layer [32]. The catalytic activity of gold nanoparticles embedded on PVA (PVA-Gold) was investigated for the oxidation of styrene and the biosensing capability of PVA-Gold were studied on the interactions with various amino acids.