Awakening to reality

Available online at www.elixirpublishers.com (Elixir International Journal)

Nanotechnology



Self assembling of Gold nanoparticles on modified indium tin oxide substrate

G. Brindha^{1,*}, A.Suganthi², S.Rajendran¹, P.Satyabama³ and Z. Robert Kennedy¹
¹R.V.S. School of Engineering and Technology, Dindigul-624005, India.
²Department of Chemistry, Thiagarajar College, Madurai-625009, India.
³Department of Chemistry, Anna University, Dindigul Campus, Dindigul, India.

ARTICLE INFO

Article history: Received: 1 August 2012; Received in revised form: 31 August 2012; Accepted: 20 September 2012;

Keywords

Synthesis of gold nanoparticles, SAMs of 3mercaptopropyltrimethoxysilane, SAMs of gold nanoparticles.

ABSTRACT

Gold nanoparticles have been synthesized and they have been made to self assemble on indium tin oxide (ITO) coated with 3-mercaptopropyltrimethoxysilane. An aqueous solution of gold chloride was added to tetraoctyl ammonium bromide dissolved in toluene. The mixture was stirred well. Then an aqueous solution of sodiumborohydride was added and the mixture was stirred for 4 hours at room temperature. The organic phase was washed with water in a separating funnel. The solvent was removed by evaporating the solution in vacuum to get a black solid. The black solid was suspended in ethanol and kept under refrigeration overnight. The residue was filtered and washed thoroughly with ethanol. The residue was dried. The gold nanoparticles produced were characterized by Transmission Electron Microscope (TEM). A clean indium titanium oxide electrode was prepared. It was immersed in an aqueous solution containing potassium ferro cyanide and sodium chloride solution in a three electrode cell assembly. Saturated calomel electrode was used as reference electrode. A platinum foil was used as counter electrode. Cyclic voltammogram was recorded in the potential range of -0.1v to 0.5v at a sweep rate of 50mV/s. The experiment was repeated with the ITO electrode coated with 3mercaptopropytrimethoxysilane. It was seen from the cyclic voltammogram that the redox peaks were absent and there was decrease in the current. This suggests the formation of MPTMS monolayer which acts as a barrier. Since the redox probe has to diffuse through the monolayer, the redox current decreased compared to the bare ITO. When ITO electrode modified with MPTMS was immersed in gold nanoparticles self assembled on the monolayer of MPTMS. The gold nanoparticles were attached to the -SH groups of MPMS. When CV was run with this electrode, there was increase in redox current suggesting that the GNPs have assembled on ITO electrode modified with MPTMS. These electrodes may find application in Biosensors.

© 2012 Elixir All rights reserved.

Introduction

Gold nanoparticles (GNPs) have been widely used in modification of various electrodes and fabrication of variety of biosensors. The excellent biological compatibility has also made GNPs good material to immobilize enzymes and to keep the biological activities of enzymes for a longtime. GNPs as a base for the immobilization of enzymes have been used to prepare biosensor like glucose oxidase, NADH, Pyruvate oxidase etc.

For catalytic and electro analytical applications, GNPs must be supported on the electrode such as gold electrode, glassy carbon electrode and carbon nano tubes. Several approaches have been employed to immobilize the GNPs onto the ITO substrate. A general strategy includes self-assembly based on binder molecules such as (amino propyl) siloxane and (mercapto propyl) siloxane which utilizes the binding ability of the silanol group to the ITO glass surface and affinity of the -SH or $-NH_2$ group towards the GNPs. However, the characteristics of GNPs, such as catalytic ability and conductivity are strongly affected by the organic binder molecules.

The synthesis and application of gold nanoparticles are one of the major nanomaterial researches owing to the new discoveries by interdisciplinary works related to self-assembly, nano-catalysis, bio-imaging and molecular electronics.^[1] Gold nanoparticles can play as a core material for the development of novel-type biomedical devices including diagnosis and bio-sensing agents.^[2] Gold nanoparticle substrates have become widely used for surface modification, nanolithography and single molecule studies because of the broad applicability of Self-assembled monolayer (SAM) chemistry.^[3]

The deposition GNPs onto ITO film has been achieved by using a touch-seed mediated growth approach. The attachment of GNP on the ITO surface was observed to have little effect on their surface conductivity and optical absorption characteristics.^[4]

The synthesized GNPs can be coated on a cyclodextrin polymer. Thus the functionalized electrodes were employed for immobilizing horseradish peroxidase (HRP). The enzyme containing electrode was used as a biosensor device. The biosensor showed activity after 40 days of storage at 4^0 C in 50mM sodium phosphate buffer.^[5]

Manesh fabricated a poly (3,4-ethylene dioxy thiophene) – poly (styrene sulphonic acid), PEDOT-PSS. On GNPs the electrocatalytic activity of PEDOT-PSS-Au electrode for the oxidation of NADH. This biosensor showed high sensitivity to



ethanol with rapid detection, good reproducibility and stability. $^{\left[6\right] }$

GNPs were synthesized as SAM and this SAM was used for the immobilization for horseradish peroxidase (HRP). This modified electrode was used for H_2O_2 oxidation.^[7]

Ordered structure of nanoparticles can be obtained either by the self-organization of particles capped with alkyl chains or assembly on modified substrates.^[8] In either case, an intermediating ligand plays an important role for the ordered packing density. Several research groups have evaluated the effect of mono-functional ligands (such as alkyl or aromatic),^[9] thiols (or dithiols), alkylamines,^[10] ammonium salts,^[11] and alkyl silanes^[12] on the self assembly of nanoparticles. The primary amine groups in alkyl chains, which is well known to interact with gold ions and the corresponding reduced metal, is expected to exhibit a significant effect on the self assembly of GNPs.^[13] William et al. reported an incomplete coverage of gold colloids (ranged in 25-120 nm) on indium tin oxide (ITO) surface, i.e., GNPs were deposited as a discontinuous layer with a large gap among the adjacent particles.^[14]

In the present work, initially synthesized GNPs are selfassembled on pretreated ITO plates. The resulting GNPs selfassembled ITO plates are used as electrode for electrochemical applications.

Materials and methods

Materials

Very pure chemicals were used in the present study.

Gold nanoparticles synthesis

Synthesis of 2nm Gold Nanoparticles

About 50mg (1mmol) of HAuCl₄·3H₂O was dissolved in of 7.5mL water and about 104.13mg (1.5)tetraoctylammoniumbromide (TOAB) was dissolved in 15mL toluene. The above two solution were mixed and stirred vigorously. After decoloration of the aqueous phase, about 0.016ml (1mmol) of pentane thiol was added to the two phase solution and stirred for 30 minutes. Then 0.1114g (0.02944mmol) of sodiumborohydride (NaBH₄) in 5mL water was added to the flask under vigorous stirring. The reaction mixture was stirred approximately 3 to 4 hours at room temperature. The organic phase was washed with water using separating funnel. The solvent was removed by evaporating in a vacuum to give black solid solution. Then, the resulting black solid was suspended in ethanol and kept under refrigeration for over-night. The suspended residue was filtered and washed thoroughly with ethanol twice. Finally, the residue was dried and confirmed as nanoparticle by characterization using absorbance and (transmission electron microscope) TEM.

Electrode preparation

Working electrode

Initially an indium tin oxide (ITO) pieces were cleaned ultrasonically using acetone and water for each 10 minutes. After that the pieces were immersed in 5mL of piranha solution $(H_2O_2+NH_3+H_2O)$ in the ratio of 1:3:4 for about 1 hour. The conducting side of cleaned ITO plate was connected with copper rod then covered by Parafilm and Teflon. Before that the copper rod was polished using emery sheet. This copper rod connected ITO plate was used as a working electrode and was washed with distilled water 3 times.

Reference electrode

Calomel electrode was used as a reference electrode. The ground mixture of mercury and mercurous chloride was filled up in a glass tube. 1M KCl was used as an electrolyte.

Counter electrode

A platinum foil was used as auxiliary electrode. *Standardization of working electrode*

The working electrode was standardized using 1mM of potassium ferro cyanide K4[Fe(CN)6] redox species in 0.1M sodium chloride (NaCl) acts as an electrolyte. This is made upto 25 ml. This solution was taken in a cell. -0.1v to 0.5v potential range was applied for cyclic voltammetry (CV) characterization. 50m v/s scan rate was applied. The potential difference of the redox couple peak shows the reversibility and clean surface. This is used as a working electrode for further procedure.

Preparation and Electrode fabrication by SAM: (3-mercapto propyltrimethoxysilane)

1mL of 3-mercapto propyltrimethoxysilane was dissolved in 10 mL toluene. The ITO plates were washed with toluene and then dipped in to the above mercaptosilane solution for about 12 hours. Afterwards the mercaptosilane coated ITO plates were taken out and washed with toluene.

Thus treated ITO plate was used as a working electrode. This working electrode is placed in a cell containing reference electrode and counter electrode. To the cell about 15mL of 0.1M NaCl and 1mM K₄[Fe(CN)₆] mixture was added and the resulting solution was used as an electrolyte. Potential scan ranging from of -0.1v to 0.5v at 50 mV/s is used for CV characterization.

Electrode fabrication by GNPs SAM:

The synthesized GNP was diluted in 5mL toluene. 1mL of this solution was taken and dissolved in 10 ml of toluene. Mercaptosilane coated ITO plates were then immersed in the above solution for over night.

The next day this ITO was again cleaned using toluene and made as an electrode. This electrode was washed with distilled water and placed in a electrochemical cell having reference and working electrode. 15mL of 0.1M NaCl+1mM K₄[Fe(CN)₆] mixture was used as an electrolyte. Potential scan ranging from of -0.1v to 0.5v at 50 mV/s is used for CV characterization. **Results and discussion**

Characterization of gold nanoparticles (GNPs):

The formation of GNPs was confirmed by electron diffraction images (Fig 1).



Fig.1. Electron diffraction image of gold nanoparticles

The samples for TEM were prepared by dissolving the nanoparticles in toluene and the dispersion was drop coated on carbon coated Cu grid. The transmission electron micrograph (TEM) of GNPs is shown in Fig 2.



Fig.2. Transmission electron microscope (TEM) of GNPs The TEM of GNPs showing lattice fringes is shown in Fig 3.



Fig.3. TEM of GNPs showing lattice fringes

The size of GNPs was in the range of 3 to 5 nm. There is no particle aggregation (Figs 2 and 3) which confirm the stability of prepared nanoparticles.

Cyclic voltammogram:

Indium tin oxide electrode was used as the working electrode. Saturated calomel electrode was used as reference electrode. Platinum foil was used as counter electrolyte. The working electrode was immersed in the solution containing potassium ferrocyanide and sodium chloride solution. The potential range was from -0.1V to 0.5V at a sweep rate of 50 mV/s scan rate.

The cyclic voltammogram of blank ITO electrode, siloxane thiol (SAM) coated ITO electrode and gold NPs on SAM electrode are shown in Fig 4.





It is observed that when blank (bare) ITO is used, the cyclic voltammogram shows the redox behaviour of ferro/ferri cyanide (Fig 4). The cyclic voltammogram obtained when siloxane thiol SAM modified electrode was used as working electrode, reveals the absence of potassium ferro/ferri cyanide redox peak and decrease in the current when compared to bare ITO electrode. This confirm the formation of MPTMS monolayer on the ITO monolayer. The monolayer acts as a barrier. Since the redox probe has to diffuse through the monolayer, the redox current decreases compared to bare ITO. When ITO electrode containing SAMs of silane was immersed in gold nanoparticles

solution in toluene, GNPs were attached on the SAMs of MPTMS; the –SH group bonded with GNPs. When this modified electrode was used as working electrode, the cyclic voltammogram showed an increase in redox current for potassium ferro/ferri system suggesting that the GNPs are assembled on ITO.

Conclusions

• Gold nanoparticles have been synthesized and characterized by TEM and electron diffraction image.

• When Indium tin oxide electrode is immersed in 3mercaptopropyltrimeethoxy silane (MPTMS), MPTMS self assembling monolayers are formed on ITO.

• When this electrode was immersed in a toluene solution of GNPs, GNPs are attached onto the SAMs of MPTMS, through the –SH group.

• Such modified electrodes can be used as biosensors.

Scope for future work

The GNPs modified electrode may be treated with P-Aminothiophenol (p-ATP), 2-Mercapto-5-nitrobenzothiazole(MBT), 2-Mercaptobenzimidazole(MBI) for biosensors like Glucose oxidase(Gox), Pyruvate oxidase(Pox). The electrode having self-assembled GNPs may be washed with ethanol and dipped in 5mL ethanol solution containing about 10mM p-ATP. After 10 hour electrode dipping it can be washed with ethanol and CV can be run in 0.1MNaCl+1mM K4[Fe(CN)6] mixture with potential sweep ranging from -0.1v to 0.5v at 50mV/s. This electrode may be used for Gox as well as Pox sensors. Similarly the above procedure may be followed for the fabrication of MBT and MBI and it could be tried for biosensors.

Acknowledgement

The authors are thankful to their respective managements for their help and encouragement.

References

1. Brust, M.; Schiffrin, D. J.; Bethell, D.; Kiely, C. J. Adv. Mater. 1995, 7, 795.

2. Rosi, N. L.; Mirkin, C. A. Chem. Rev. 2005, 105, 1547.

3. Liu, G.; Xu, S.; Qian, Y. Acc. Chem. Res. 2000, 33, 457-466.

4. Akrajas ali umar, Growth of goldnanoparticles by touch seed mediated technique, Journal of crystal growth and design, vol-399, pp 599-607, 2004.

5. Conrado Camacho, Enzyme biosensor for H2O2 detection, Journal of Biosensor ana Bioelectronics, vol-24, pp 2028-2033, 2009.

6. K.M.Manesh, Biosensors and bioelectrochemistry, Journal of chemical biology, vol-10, pp 1032-1038, 2008.

7. Fengxian gao, Immobilization of HRP on GNPs, Journal of Biochemical and Biophysical methods, vol-70, pp 407-413, 2007.

8. Moleller, M.; Spatz, J.P.; Roescher, A. Adv. Mater: 1996, 8, 337.

9. Kim, B.; Tripp, S.L.; Wei, A.J. Am. Chem. Soc. 2001, 123, 7955.

10. Leff, D. V.; Brandt, L.; Heath, J. R. Langmuir 1996, 12, 4723.

11. Yamamoto, M.; Nakamoto, M.J. Mater. Chem. 2003, 13, 2064.

12. Prasad, B. L. V.; Stovea, S. I.; Sorensen, C.M.; Klabunde, K. J. Chem. Mater. 2003, 15, 935.

13. Kuo, P. L.; Chem, C. C.; Jao, M. W. J. Phys. Chem. B 2005, 109, 9445.

14. Doron, A.; Katz, E.; Willner, I. Langmuir 1995, 11, 1313.