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Corresponding Author:

* Sanjay.S

Assistant Professor,
Department of Biomedical Engineering,
Bharath University,
Chennai, Tamil Nadu,
India

QR Code AJPTI

*Email Id- sspv44@gmail.com

Surface Tuning Using Gold Nanoparticles and Mixed Thiols

Sanjay.S*

ABSTRACT

SAM's (Self Assembled Monolayer's) are formed by modifying the glass surface at different stages using Silanes, Gold Nanoparticles (Au NPs) and mixture of thiols of different functional groups, chain lengths and proportionate. The synthesized intermediate surfaces and SAM's obtained are characterized for understanding their behavior in terms of physical and chemical heterogeneities. The gold nanoparticles behavior can be observed using the visible spectrum obtained from UV spectro-photometer. The change in chemical heterogeneities are observed by measuring the contact angle using two variant small molecular weight liquids (water and ethylene glycol) on various synthesized intermediate surface.

Key-words: SAM's, silanes, gold nanoparticles, mixed thiols.

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Introduction

Monolayer and multilayers are formed using SAM (Self Assembled Monolayer) technique. SAM's provide the compatibility to control / tune the surface up to molecular scale when surface is modified[1-3]. Nanoparticles today play a key role in the biomedical field and hence attract many researchers of this area. Recently, gold nanoparticles and substrates were used for labeling[4-6], DNA / drug delivery[7-12] and gene regulation[13]. The most preferred material for this purpose is gold nanoparticles, for its tendency to tune the surface properties. For designing the required surface properties from the particles, the commonly used methods are: by surface modification and by particle modification (size, shape and compositions) [14, 15]. The thiols of different functional groups and proportionate provide us the flexibility to choose the surface behavior between hydrophilic and hydrophobic nature[16].

Experimental Section

Chemicals needed

Materials are used as received: Hydrogen Tetraaurochlorate (Sigma Aldrich), Sodium Citrate (Sigma Aldrich), 3-Aminopropyl Triethoxysilane (Sigma Aldrich), 11-Mercapto-1-Undecanol (Sigma Aldrich), 1-Dodecanethiol (Sigma Aldrich), Absolute Ethanol (Merck), Sulphuric acid (Merck), De-ionized water, Glass slides.

Experimental methods

The experimental part is carried out in different stages listed below:

Stage 1: (a) Modification of glass surface
(b) Surface modification using amines
(c) Preparation and deposition of Au NPs on glass surface

Stage 2: Adsorbing Au NP on amine modified surface

Stage 3: Adsorbing thiols of different proportionate on stage 2 modified surfaces

Stage 1: (a) Modification of glass surface

The glass slides are cut into a size of 2 cm^2. The glass slides were washed with a mild detergent followed with absolute ethanol and piranha cleaning (*7% Con. H_2SO_4: 3% H_2O_2*). The piranha cleaned glass slides were washed several times with excess water and dried at 60˚C under nitrogen environment.

(b) Surface modification using amines

All these procedures are performed inside a glove bag under nitrogen environment at 33˚C. A stock solution is made with absolute ethanol as solvent. The Silane of 1×10^{-3}M concentration is added to the stock. Cleaned glass slides are placed inside the stock for 24 hrs. The –OH groups present on the glass surface interacts with the Si-OR groups of silane and forms Si- O-Si~NH_2 bond. The glass slides are finally washed / rinsed with excess water and dried at 60˚ C under nitrogen environment.

(c) Preparation and deposition of Au NPs on glass surface

Gold nanoparticles are prepared by Turkevich process / Citrate reduction method[17]. Depositions of nanoparticles are performed inside a glove bag under nitrogen environment at 33˚ C. The surface modified glass slides are then placed inside the colloidal gold nanoparticles thus obtained for 24 hrs. The glass slides are finally washed / rinsed with excess water and dried at 60˚C under nitrogen environment.

Stage 2: Adsorbing Au NP on amine modified surface

All these procedures are performed inside a glove bag under nitrogen environment at 33˚ C. The amine modified glass slides are then placed inside the colloidal gold nanoparticles thus obtained for 24

hrs. The glass slides are finally washed / rinsed with excess water and dried at 60° C under nitrogen environment.

Stage 3: Adsorbing thiols of different proportionate on stage 2 modified surfaces

All these procedures are performed inside a glove bag under nitrogen environment at 33° C. Mixed SAMs are prepared by mixing any two thiols of different functional groups and chain lengths at various proportionate. A stock solution is made with absolute ethanol as solvent. Mixtures of thiols were prepared in the stock solution with a concentration of 1×10^{-3}M. The Amine and Gold modified glass slides are then placed in the mixed thiols solutions. This method allows us to potentially tune the surface properties. This tuning of surfaces helps in potentially varies the surface behavior in very different extremes (hydrophilic and hydrophobic tuning).

Results and Discussions

U-V Spectra

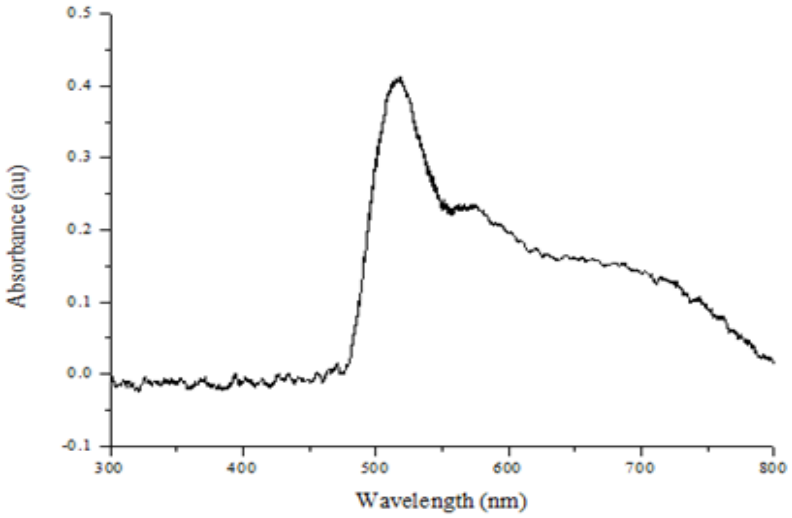

Fig 1: *U-V absorption spectrum of Gold nanoparticles*

UV-Visible spectrum is obtained from Ocean Optics Spectrophotometer. The spectra thus obtained prove the formation of gold colloids as gold nanoparticles exhibit an absorption peak due to SPR (Surface Plasmon Resonance). The SPR results from the collective excitation of conduction electrons in a metal[18]. Fig 1 shows the UV spectra of the gold colloids. The plasmon peak is obtained at 530 nm. The size of the gold nanoparticles is constantly maintained at 20 nm as any variation in the size results in shift in the wavelength[19].

Contact angle measurement

Contact angle measurements are obtained from goniometer. Two different liquids (water and ethylene glycol) are used for measuring the contact angle. The surface wettability and contact angle values are obtained for different chemicals with varying compositions. Surface wettability is an important factor for better understanding of the surface properties. Any variation in the wettability, alters the surface energy and contact angle values. Table 1 shows the contact angle values at various stages.

Table 1: *Contact angle values at different stages.*

Different Stages	SAMs	Contact Angle (degree)	
		Water	Ethylene glycol
Stage 1	Cleaned glass slides	14±1	8±1
	Gold on glass slides	67±1	47±1
	Amine (APTES) on glass slides	49±1	36±1
Stage 2	Gold on amine modified glass	71±1	59±1
Stage 3	Mixed thiols of [100% (-OH) :0% ($-CH_3$)] on stage 2 modified surface	69±1	55±1
	Mixed thiols of [75% (-OH) :25% ($-CH_3$)] on stage 2 modified surface	79±1	66±1
	Mixed thiols of [50% (-OH) :50% ($-CH_3$)] on stage 2 modified surface	91±1	78±1
	Mixed thiols of [25% (-OH) :75% ($-CH_3$)] on stage 2 modified surface	110±1	95±1
	Mixed thiols of [0% (-OH) :100% ($-CH_3$)] on stage 2 modified surface	126±1	110±1

The contact angles of the surfaces are analyzed in three stages. From table 1, the following observations are made: Stage 1 shows the contact angle values of "Amine (APTES) on glass slides" is less than "Gold on glass slides". This is due to the arrangement of Au NPs on the surface. Stage 2 shows the contact angle value of the "Gold on amine modified glass" is higher than the "Gold on glass slides". This is due to the complete adsorption of gold nanoparticles on amine surface and presence of gold on amine surface increases the Hydrophobicity. Stage 3 shows that, very less contact angle is obtained when "Mixed thiols of [100% (-OH):0% ($-CH_3$)]" is adsorbed on stage 2 modified surface. This is due to presence of terminal -OH group at the stage 2 modified surfaces. When the proportionate of $-CH_3$ functional group is increased, a high contact angle is obtained due to presence of pure hydrocarbon moieties at it.

Conclusion

The modification of glass slides at different stages using Silanes, Gold Nanoparticles (Au NPs) and mixture of thiols of different functional groups, chain lengths and proportionate, two observations are made: the gold nanoparticles here provide better binding between amines and thiols and the mixed thiols of different functional groups and proportionate along with gold nanoparticles as interface helped in tuning the surface hydrophobicity.

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