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Nanografting of polymer brushes on gold substrate by RAFT-RIGP†

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Abstract: Optical sensors based on surface plasmon resonance (SPR) have made great strides in the detection of various chemical and biological analytes. A surface plasmon is a bound, non-radiative evanescent wave generated as resonant electrons on a metal-dielectric surface absorb energy from an incident light. As analytes bind to a functionalized metal substrate, the refractometric response generated can be used for quantitation with great selectivity, sensitivity, and capacity for label-free real-time analysis. Polymer nanobrushes are ideal recognition elements because of their greater surface area and their wide range of functional versatility. Here, we introduce a simple "grafting-from" method to covalently attach nanometer-thick polymer chains on a gold surface. Nanografting on gold-coated BK-7 glass was performed in two steps: (1) self-assembly of organosulfur compounds; and (2) RAFT-mediated radiation-induced graft polymerization (RAFT-RIGP) of polyglycidyl methacrylate (PGMA). Surface modification was monitored and verified using FTIR and SPR. Layer-by-layer thickness calculated based on Winspall 3.02 simulation fitted with experimental SPR curves showed successful self-assembly of 1-dodecanethiol (DDT) monolayer with thickness measuring 1.4 nm. These alkane chains of DDT served as the graft initiation sites for RAFT-RIGP. Nanografting was controlled by adjusting the absorbed dose in the presence of chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid. The molecular weight of grafted polymers measuring 2.8 and 4.3 kDa, corresponded to a thickness increase of 3.6 and 7.9 nm respectively. These stable nanografted gold substrates may be further functionalized for sensing applications.

Keywords: surface plasmon resonance; nanografting, radiation-induced graft polymerization; reversible addition fragmentation chain transfer polymerization; optical sensors

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1. Introduction

Surface plasmon resonance (SPR) sensor technology for the detection of chemical and biological substances has been receiving growing interest from the scientific community. It has been increasingly employed, not only in gas sensing, but also in many other important applications in food safety, biology, and medical diagnostics [1]. The overall performance of an SPR sensor is affected by the characteristics of the surface functionalization. The most commonly used approach is through covalent attachment of the receptor molecules/functional groups on the metallic film supporting the propagation of charge density waves [2]. Covalent immobilization strategies include chemical reactions such as amine, aldehyde or thiol coupling on previously formed functional self-assembled monolayers on gold surfaces. The use of polymers to modify the gold layer is also an alternative. This can be done through surface-initiated polymerization or grafting-from approach based on the immobilization or production of initiator on the surface of the sensor substrate, which can be accomplished chemically or through the use of ionizing radiation. Radiation processing is a unique tool for synthesis of nanosized polymers of various types and offers a promising alternative to conventional synthetic methods because (a) it is environmentally friendly due to the fact that it consumes less energy, (b) creates less waste, and (c) uses a lesser amount of chemicals.

Ionizing radiation can be used to initiate polymerization from solid surfaces in a process known as radiation-induced graft polymerization (RIGP). RIGP generally proceeds via a free radical polymerization process. The challenge in this process is the occurrence of irreversible termination of propagating polymer chains and chain transfer reactions that can result in a loss of control over chain length (i.e. thickness of polymer film) and chain structure together with broadening of the molecular weight distribution [3–5]. These drawbacks have led to the research area of controlled free-radical polymerization (CRP), which can be utilized to control the polymer architecture and to reduce polydispersity. One such type of CRP is reversible-addition fragmentation chain transfer (RAFT), which has been found to be compatible with ionizing radiation as the mode of initiation. In the work of Barsbay et al. [6], they demonstrated RAFT-mediated radiation induced grafting (RAFT-RIGP) of poly(acrylic acid) (PAA) into the nanochannel walls of track-etched poly(vinylidene difluoride) (PVDF) membranes, achieving good chain length control and corresponding graft polymer nano-thickness. These features can be easily manipulated by adjusting the ratio of added RAFT agent to monomer and monomer conversion via absorbed dose [7–10]. In light of these findings, RAFT-RIGP was identified as a viable synthesis technique in the development of SPR sensors with well-defined surface characteristics. This will involve a two-step process as shown in Figure 1: (a) formation of a self-assembled layer; and (b) RAFT-RIGP from the SAM layer.

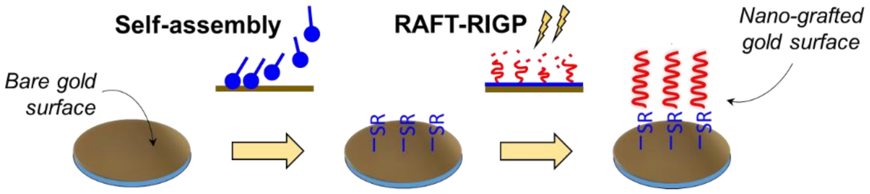


Figure 1. General synthesis scheme for the surface functionalization of gold surfaces

2. Materials and Methods

2.1. Formation of self-assembled monolayer (SAM)

Bare BK-7 gold-coated glass disc from KEI International was immersed in a solution containing 2 mM 1-dodecanethiol (DDT, Sigma Aldrich) in absolute ethanol (Ajax Finechem) for 5 days at room temperature with mild stirring. The disc was washed with ethanol. Drying was carried out using nitrogen gas followed by an overnight drying under vacuum.

2.2. RAFT-RIGP adiation grafting of abaca fibers

Prepared gold-SAM samples were immersed in a solution containing 3% glycidyl methacrylate (GMA, Sigma Aldrich), 0.6% Tween 20 (Scharlab) and 0.26% 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPPA, Sigma Aldrich) in deionized water, emulsified at 6000 rpm for 30 mins. The emulsion was bubbled with nitrogen gas for 1 h, sealed and irradiated with gamma rays at 1 kGy/h. The disc was washed with tetrahydrofuran and methanol and dried under vacuum. Homopolymers formed in the solution were precipitated with methanol, collected, and dried.

2.3. Characterization

The gold discs were subjected to several characterization techniques after each modification step. Successful modification was verified using Frontier FTIR Spectrophotometer (Perkin Elmer, Japan) in ATR mode, scanning at 650-4000 cm^{-1} with 4 cm^{-1} resolution. SPR measurements were carried out using the KEI ESPRIT scanning angle SPR. Measurements were taken using 0.6% Tween 20 in deionized water at 670 nm, with the range of 4000 mdeg and angle resolution of <0.02. The resulting data were normalized using Origin® 2016. Relative resonance angle and standard deviation were taken from 2-3 measurement replicates.

2.4. Simulation and fitting of SPR data

Layer-by-layer thickness simulation was calculated by fitting these experimental SPR curves with a Fresnel equation algorithm (Winspall software version 3.20) [11]. Approximations were drawn from the following inputs:

Table 1. Thickness and reflectivity constants used in Winspall Simulation

Layer	**Thickness (nm)**	**Refractive Index**
BK-7 prism	0	1.5151[12]
Gold	50	0.1377 [13]
DDT	0-4.0	1.4590 [14]
PGMA	0-10	1.4490 [15]
Water	0	1.3334 1[12]

It should be noted that the program assumes each modification as separate layers with distinct optical constants that is not affected by the nature of their attachment. Linear regression taken from the resonance angle and thickness of simulated plots were used to calculate thickness of the layers as a function of resonance angle shifts from SPR measurement. For simplicity and given limited literature values for the optical properties, pure water was considered the medium in lieu of 0.6% Tween 20 in water.

3. Results and Discussion

Self-assembled monolayers (SAMs) of thiol compounds on gold substrates are one of the most popular model systems for probing self-assembly of organic molecules on metal surfaces. The robustness of Au-S interaction between thiols and gold surfaces serves as platform for fabrication of SAMs for diverse applications [16]. In this study, SAM serves as the base for the generation of carbon radicals through gamma radiolytic reactions. DDT is an alkanethiol with 12 C-H chains at any point of which can generate a carbon-centered radical after irradiation. Figure 2 confirms the successful SAM formation of DDT onto the gold surface as indicated by peaks at 1465 and 880 cm^{-1} corresponding to CH_2 bending of the alkane chain and C–S stretch of the thiol group [17]. Expected C-H stretching at around 3000 cm^{-1} was obscured by surface impurities of the bare gold specimen (not shown).

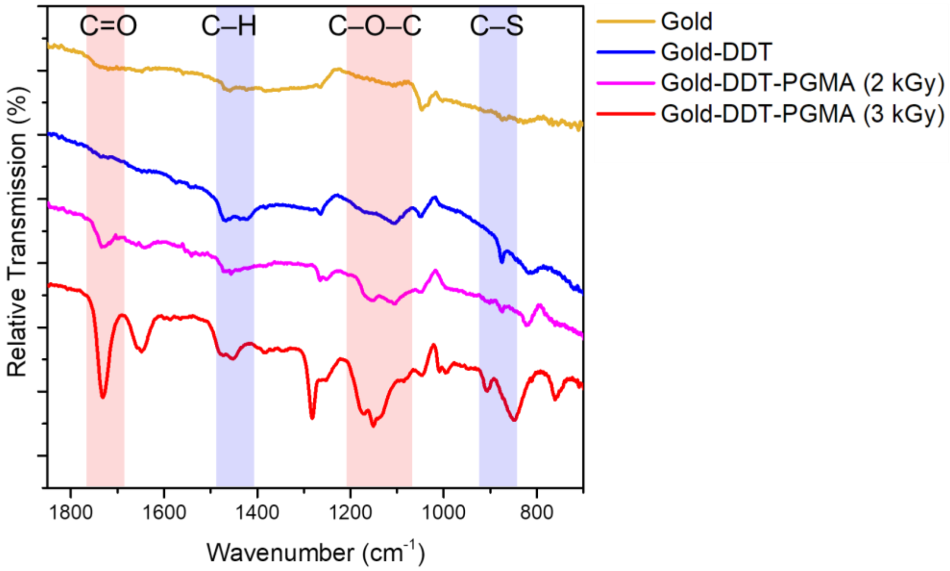


Figure 2. FTIR spectra of the gold surface before and after modification.

After DDT assembly on the gold surface, RAFT-RIGP was performed in simultaneous mode where the substrate is irradiated with the monomer solution such that radicals are formed on the SAM layer or monomer molecules by either direct bond breaking or reaction with solvent radiolytic species. Propagating radicals in this system may now be either free (initiated from an activated monomer molecule) or tethered (initiated from the activated substrate). Both types of chain adds to the chain transfer agent, CPPA which controls the reversible chain inactivation allowing for even growth of chains and reduction of premature termination reactions [10,18]. FTIR analysis (Figure 2) also confirms successful grafting of PGMA onto the gold-SAM substrate with the appearance of peaks at 1730 and 1160 cm^{-1} correspond to the C=O stretching and C–O–C vibrations of PGMA respectively [19]. Effect of dose on grafting is shown as an increase in intensity of carbonyl peak suggesting a higher degree of grafting. This may be attributed to the progression of polymerization sustained by the RAFT mechanism, leading to an increase in molecular weight of the grafted polymer [10]. To verify, molecular weights of grafted chains were indirectly measured using the homopolymers co-generated in the reaction. As the formation of grafted polymers and homopolymers exist in dynamic equilibrium, RAFT control exerted is expected to result in similar polymerization rates [9]. The homopolymers were analyzed using ^{1}H-NMR analysis (Figure 3), which showed the characteristic profile of PGMA as well as chemical shifts corresponding to the ring of the thiocarbonylthio end group at 7.2–8.0 ppm. The ratio between the peak area for the aromatic protons and the main chain protons were used to calculate the molecular weight of the polymers. As can be seen in Table 2, calculated values closely corresponded to theoretical values. These observations indicates the successful addition of propagating PGMA to CPPA and supports that RAFT-mechanism was in effect [20].

Table 2. Effect of absorbed dose on conversion and molecular weight

Dose, kGy	Conversion, %	Molecular weight, kDa	
		Calculated*	NMR
2	62	2.3	2.8
3	92	3.3	4.3

[*] Calculated as M(PGMA) = n(GMA)/n(CPPA) x M(GMA) x conversion + M(CPPA)

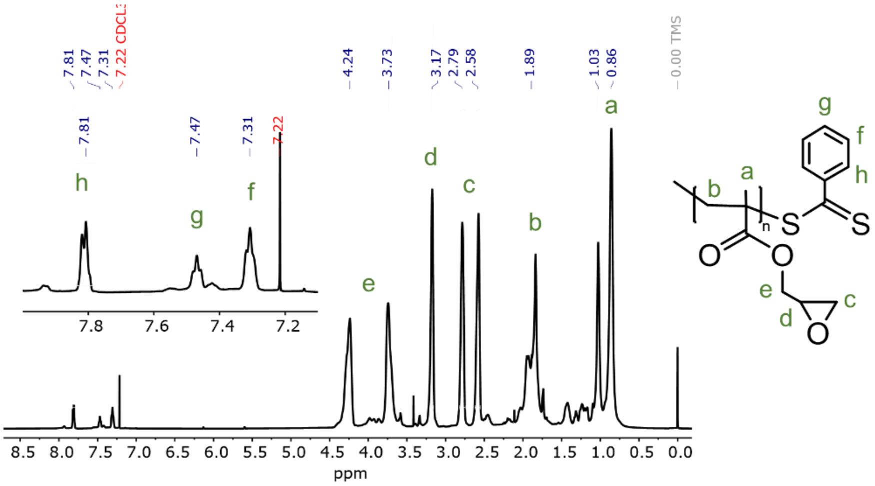


Figure 3. Representative ^{1}H-NMR profile of PGMA homopolymer generated simultaneously in the grafting solution (3 kGy).

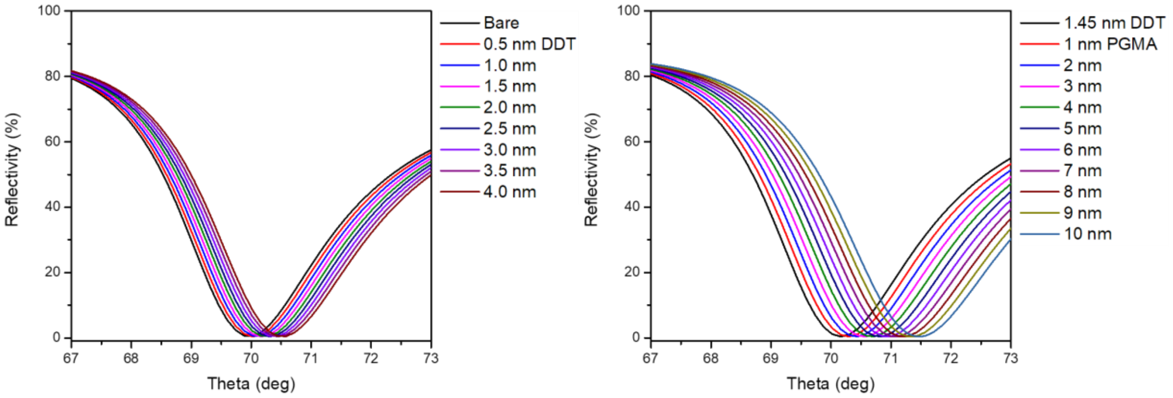
The sensitivity of surface plasmons to changes in the optical properties enables the monitoring and characterization of a metal-dielectric interface upon coating, deposition, or immobilization of organic molecules. In the Kretschmann configuration, SPR is measured from the evanescent wave propagated when a light source hits the back of the gold/glass substrate, which creates the surface plasmon wave that propagates through the metal-dielectric layer. The energy transfer between the evanescent wave to the surface plasmon wave at different angles translates to changes in reflectivity which undergoes a sharp dip when energy transfer is complete – this is known as the resonance angle. The position of the resonance angle depends on the refractive index and thickness of the metal film [21]. Therefore, any changes on the metallic substrate can be quantified by analyzing the resulting SPR reflectivity curves and resonant angles. As can be seen from Table 3, there is significant shifting of the relative resonance angle with every modification step compared to the bare gold surface. This points to the successful immobilization of the SAM and graft polymer layer. To measure the theoretical layer thickness, reflectivity curves were simulated using Winspall 3.02 software which is based on the Fresnel equation [11]. Using refractive index values from literature (Table 1), resonance angle shifts can be correlated to the thickness of the SAM and grafted polymer layers (Figure 4b-c) [22]. Shifts in reflectivity are minimal as the layer changes are in the nanometer scale (< 10 nm). Results of fitting are shown in Table 3. There was close correspondence between theoretical layer thickness (taken from literature and calculation based on bond lengths) and the values calculated from simulation. These results will be verified by atomic force microscopy in the next phase of the study. It should also be noted that the standard deviation values of angle shifts are relatively high, which may indicate some degree of nonuniformity in the modified layer.

Table 3. Relative resonance angle from SPR measurements and calculated layer thickness using Winspall simulation and fitting.

Layer	**Relative Resonance Angle (°)**	**Calculated Thickness (nm)**	**Theoretical Thickness (nm)**
Gold	1.93 ± 0.33	n.a.	n.a.
DDT	2.13 ± 0.33	1.45 ± 0.18	1.7[a]
PGMA (2 kGy)	2.63 ± 0.30	4.25 ± 0.69	4.6[b]
PGMA (3 kGy)	3.18 ± 0.39	8.10 ± 0.43	6.9[b]

[a] **Taken from literature** [23].

[b]**Calculated from bond lengths of PGMA** [24] based on molecular weights from NMR analysis.



(a).

(**b**)

Figure 4. Calculated SPR curves for gold modified with (**a**) DDT then (**b**) PGMA.

4. Conclusion

In the endeavor to develop SPR-based sensors using a facile and environment-friendly technique, RAFT-RIGP was employed in the modification of gold surfaces. The process involves an initial self-assembly of a thiol-based compound, whose carbon skeleton will serve as the initiation sites once exposed to ionizing radiation. This was then followed by simultaneous grafting using glycidyl methacrylate and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid in Tween 20 emulsion. Successful surface modification was verified using FTIR analysis and SPR measurement. Winspall simulation and linear fitting of layer thickness with the resonance angle indicate nanometer-scale layers were successfully immobilized. The calculated thickness values correspond well with theoretical values based on literature. Standard deviation of resonance angles indicates some possible issues with the uniformity of the modified layers across the substrate that needs further probing. Nevertheless, the control extended by the RAFT mechanism over RIGP seems very apparent and with some improvements will lead to a more reproducible synthetic process. Additional characterizations and further functionalizations will be done in subsequent studies.

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