Grafting of polymeric platforms on gold by combining the diazonium salt chemistry and the photoiniferter method

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**Abstract**

The grafting of stable and strongly attached polymeric platforms on gold is a key factor for successful applications in biology, catalysis and sensing. Here, we report on the use of a combination of the iniferter method and the diazonium salt chemistry for preparing smart polymeric platforms attached through covalent bonds on gold. For this, bifunctional molecules bearing aryl diazonium coupling agents for anchoring on gold and N,N-diethyldithiocarbamate groups for initiating the growth of polymer chains were used. These two moieties were separated by oligo(ethylene oxide) spacers of various lengths allowing a fine tuning of the hydrophilic properties of the grafted photoinitiator layers. Cross-linked copolymers of methacrylic acid (MAA) and N,N-methylenebisacrylamide (MBAm) were then grown from the gold surfaces under UV light. The polymer films were characterized in terms of chemical composition and wettability by X-ray photoelectron spectroscopy and contact angle measurements, respectively. The grafting procedure was simple, rapid and effective in producing polymer-grafted Au surfaces at room temperature. The diethyldithiocarbamil groups remaining at the end of the growing tethered chains could then be easily exchanged by a UV-light induced radical-exchange experiment in order to obtain terminal amino moieties able to immobilize citrate-capped gold nanoparticles, through electrostatic interactions. The results obtained in the present work highlight the efficiency of the diazonium salt chemistry coupled to the photo-iniferter based surface grafting approach to spontaneously functionalize gold surfaces through covalent bonds. This strategy open new opportunities for the preparation of “smart” hybrid platforms made of pH-responsive polymers and nanoparticle assemblies.

**Keywords:**
- Diazonium salts
- Iniferter polymerization
- Gold nanoparticles

**1. Introduction**

Surface-initiated polymerization (SIP) on gold has received an increasing interest these recent years because gold surfaces are compatible with a large range of analytical techniques (SPR, SERS) and present unique properties at nanoscale. The use of photochemically activated initiators is especially convenient for grafting polymers to gold surfaces, since the process can readily be controlled and confined by the selective application of long wavelength UV light. Dithiocarbamate species, introduced as photoinitiators (or iniferter: initiator-transfer-terminator agents) by Otsu [6–8], have the peculiarities of cleaving upon UV irradiation, forming a radical pair constituted by a reactive carbon radical that initiates the polymerization and a less reactive, sulfur-centered radical that can act as a reversible capping agent during the polymerization process. This polymerization process addresses a wide range of economical and ecological concerns, compared to corresponding thermal reactions, with low cost and mild reaction conditions. Conventionally, the universal platform for grafting iniferter based surface grafting approach to spontaneously functionalize gold surfaces through covalent bonds. This strategy open new opportunities for the preparation of “smart” hybrid platforms made of pH-responsive polymers and nanoparticle assemblies.
lamps emitting at 300 nm coupled with a 280 nm cut-off filter to perform the photopolymerization and avoid any degradation of the starting monolayer. However, the Au–S bond at the interface between the organic polymer coating and the gold surface remains labile upon certain conditions (UV light or heating) which causes instability problems for storage under light or any post-functionalization reaction above 60 °C.

Therefore, the development of versatile and efficient surface modification iniferter strategies able to provide strong and stable linkages between the gold surface and the polymer coating still remains challenging. We address this issue in the present paper by developing a facile methodology to surface-initiated photopolymerization (SIP) of vinylic monomers from gold surfaces via an aryl diazonium salt-derived iniferter. Aryl diazonium salts have been shown recently to be useful coupling agents for the grafting of polymer coatings on carbon-based [21–27] and metallic [28–40] (gold, platinum, palladium, ruthenium and titanium) planar or nanoparticle surfaces, affording strong carbon or metal–carbon linkages. Nevertheless, the combination of the diazonium salt chemistry and the iniferter method, which has proved to be efficient in order to grow dense polymer layers from the surface of aluminum [41] and oxide nanoparticles [42–44] has never been extended till now to the functionalization of gold surfaces.

In this paper, we fill this gap by exploring the propensity of aryl diazonium coupling agents bearing N,N-diethyldithiocarbamate (DEDTC) [9] groups to photo-initiate the growth of polymer chains from gold surfaces, as depicted in Fig. 1. The diethyldithiocarbamyl groups remain at the end of the growing tethered chains [6,7], which allows one to tune the chain length by variation of the irradiation time. In addition, the use of this polymerization reaction gives control over the end groups, which can be easily exchanged or chemically modified. The biocompatibility of this technique should also be underlined: no organic solvents are used and no toxic metal/compounds are involved in the polymerization process. By introducing oligo(ethylene oxide) spacers of various lengths between the aryl anchoring moieties and the DEDTC groups, we could play on the hydrophilic character of the initiating layer, which is of prime importance when the functionalization steps have to be performed in a water environment. We demonstrate this approach by grafting cross-linked copolymer layers of methacrylic acid (MAA) and N,N'-methylenebisacrylamide (MBAm) on gold surfaces. This grafting procedure is simple, rapid and effective in producing

![Fig. 1. General method for the functionalization of gold surfaces by bifunctional molecules bearing a diazonium moiety and an iniferter end group separated by oligo(ethylene oxide) chains of various lengths.](image-url)
polymer-grafted Au surfaces at room temperature with controlled thickness. Moreover, this strategy not only harnesses the advantages of UV-light photoinitiated polymerizations, but also overcomes the problem caused by the lability of the Au–S bond through the formation of stable Au–C bonds at the interface between the polymer layer and the Au surface. In order to demonstrate the potential applications of this approach, we show that it can be used to immobilize gold nanoparticles on the polymer layer through a simple modification of the polymer chain extremities under UV light.

2. Materials and methods

2.1. Materials

Methacrylic acid (MAA), N,N'-methylenebisacrylamide (MBAm), gold-coated silicon wafers, diethyldithiocarbamate (DEDTC), ethylene glycol, diethylene glycol, triethylene glycol, 4-nitrophenol, triethylamine methysulfonyl chloride, sodium nitrite (NaNO₂), terbutylnitrite, thionyl chloride (SOCl₂), and tri-sodium citrate were purchased from Sigma-Aldrich and used as received. Chloroauric acid (HAuCl₄) was obtained from Alfa Aesar. All the solvents were obtained from Acros organics and used as received. Water was deionized using a Millipore purification system.

2.2. Synthesis of diazonium salts

2.2.1. Synthesis of diethyldithiocarbamyl phenyldiazonium tetrafluoroborate (BF₄⁻, 2N–C₆H₄(O–CH₂–CH₂)ₙ⁻[1–3]–DEDTC)

This diazonium salt was prepared in three steps, as described previously [45]. First the 4-nitrobenzyl chloride reacts with DEDTC to give the 1-diethyldithiocarbamate-(4-nitrophenyl)methane in a good yield. This last intermediate was hydrogenated using Raney Nickel and led to the corresponding primary amine in quantitative yield. A cold solution of tert-butyl nitrite in anhydrous acetonitrile was added drop wise to a cold solution (in an ice bath) composed of this compound, tetrafluoroboric acid and anhydrous acetonitrile. The reaction was conducted at −20 °C during 24 h. The viscous diazonium salt was washed 3 times with ether, dissolved in acetone and dried at room temperature.

2.2.2. Synthesis of Cl⁻, 2N–C₆H₄(O–CH₂–CH₂)ₙ⁻[1–3]–DEDTC

The synthetic strategy was similar for the three salts (with n varying from 1 to 3) following the procedure described in a previous reference [42]. Briefly, diazonium salts were synthesized by the diazotization of aniline derivatives. These salts were prepared by suspending aniline derivatives in a 50/50 by volume hydrochloric acid and distilled water. The mixture was cooled to 3 °C in an ice bath, and then 1 equivalent of sodium nitrite was slowly added. The mixture was stirred for 15 min. A summary of the procedure is proposed in the form of a scheme in Fig. 2.

2.3. Grafting of aryl-terminated iniferters on planar gold surface

Gold-coated silicon wafers were cut into slides of 2 cm × 4 cm, ultrasonically rinsed with water and ethanol, dried in a stream of argon, cleaned in a UV cleaner (Boekel, Inc., Model 135500) and rinsed with ethanol in order to remove the organic residues on the surface. The grafting of aryl layers was conducted by immersing the Au plates for 1, 5 and 24 h in aqueous solutions of the diazonium salts (3.10⁻³ M) at room temperature. The substrates were washed by sonication in water and ethanol during 5 min in order to remove all the non-grafted species from the surface.

2.4. Photopolymerization from iniferters grafted on gold surface

The Au plates modified with DEDTC groups were immersed in a polymerization mixture containing MAA as the functional monomer, N,N'-methylenebisacrylamide (MBAm) as the cross-linker.

![Fig. 2. Schematic illustration of the procedure employed in order to synthesize the iniferter molecules bearing aryl diazonium end groups Cl⁻, 2N–C₆H₄(O–CH₂–CH₂)ₙ⁻[1–3]–DEDTC.](image-url)
monomer and water as the solvent. The glass vessel was degassed by bubbling argon for 10 min. The slides were then exposed to UV light at 365 nm at room temperature for 5 h. The slides were rinsed with copious amounts of water and ethanol to remove the unreacted monomers, and dried in a nitrogen stream.

2.5. Immobilization of gold nanoparticles (AuNPs)

In order to immobilize AuNPs on the aryl-terminated iniferter grafted on gold surface, the substrates were first placed in a quartz flask containing 5 ml of 0.01 M aqueous solution of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TMPO) and were irradiated for 25 min by UV light (365 nm) at room temperature. The substrates were subsequently rinsed with water and ethanol and stored under argon. In a second step, they were incubated with gold nanoparticles suspensions during 12 h, and then washed several times with water and ethanol.

2.6. Instrumentation

Photopolymerization was performed using the commercial ultraviolet processor Spectrolinker XL 1500 UV (Spectronics Corp.). This processor was equipped with 6 tubes (8 W) with a wavelength range of 365 nm and intensity of 17.6 mW cm⁻². XPS spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a microfocused, monochromatic Al Kα X-ray source (hv = 1486.6 eV; spot size = 650 μm; power = 15 kV, 200 W). The pass energy was set at 150 and 40 eV for the survey and the narrow regions, respectively. Spectral calibration was determined by setting the main C1s component at 285 eV. The surface composition was determined using the integrated peak areas and the corresponding Scofield sensitivity factors corrected for the analyzer transmission function. Scanning electronic microscopy (SEM) images were obtained using a Zeiss SUPRA 40 FESEM equipped with a thermal field emission gun. Images were created using SMARTSEM. Wetting properties was characterized with a Contact Angle Digi- drop PX 500. The contact angle measurement were performed using the image of a sessile drop at the points of intersection between the drop contour and the projection of the surface (baseline). Moreover, the polynomial method was used to determine the contact angle. In the polynomial method, the parameters of a polynomial function are fitted to the drop contour. The drop is unsymmetrical so contact angles are measured on both sides of the liquid drop profile, and the values are averaged.

3. Results and discussion

3.1. Grafting of aryl-terminated iniferter on planar gold surface

The spontaneous grafting of the diazonium-derived iniferter layer at the surface of gold was performed by simply incubating the substrates with the corresponding diazonium salts in water at room temperature. Strong modifications in surface chemical composition were observed by XPS after functionalization of the gold substrates. Indeed, the gold signal appears strongly attenuated while the carbon and oxygen content increase and new peaks assigned to sulfur and nitrogen appear, indicating the covering of gold by the iniferter layers (see Table 1). Depending on the size of the oligo(ethylene oxide) spacers between the diazonium anchoring moieties and the iniferter groups, the proportion of oxygen changes, increasing for longer spacers.

The peak fitting of the C1s signal displayed in Fig. 3 clearly reveals all the components contained in the grafted iniferter layers. The intense peak at 285 eV is assigned to C–C and C=O environments, the one at 286.6 eV corresponds to the C–O

<table>
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<th>Au</th>
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component, while the small peak at 288 eV is due to the dithiocarbamate S–C=S group. It is noteworthy that a shake-up satellite π−π* is observed at ca. 291 eV, which is the characteristic signature of the presence of aryl groups. Furthermore, the differences in the oligo(ethylene oxide) spacer size are clearly visible in the C1s high resolution spectra, with an enhancement of the C–O component at 286.6 eV when the number of ethylene oxide units increases in the spacer.

The growth of the iniferter layer at the surface of gold was then investigated by varying the time of incubation between the gold substrate and the N₂–C₆H₄–O(CH₂)₂–DEDTC iniferter-derived diazonium salts. The gold signal attenuation due to the progressive covering of the substrate by the iniferter layer as a function of time was used to provide an estimation of the organic layer thickness evolution.

From these results, it appears that, contrary to alkylthiols molecules which tend to form monolayers on surfaces [46], the diazonium-derived iniferter layers grow progressively with time, forming functional poly(phenylene) multilayers as previously reported in the literature [47]. The thickness of these iniferter layers varies from less than 1 nm after 15 min of incubation to almost 20 nm after 24 h of incubation.

A comprehensive study of the chemical nature of the interface was performed by closely examining the high resolution spectra of all the elements present in the XPS survey spectrum at low iniferter layer thickness (after incubation time of 15 min). Three types of chemical bonding between the Au substrate and the iniferter grafted groups were considered: (i) the interaction of Au with the sulfur atoms from DEDTC units; (ii) the direct reaction of diazonium salts with the gold surface leading to Au–N interfacial bonds, as already observed by G. Deniau et al. [48], or (iii) the presence of Au–C bonds explained by the grafting of aryl cations or radicals on the surface, arising from dediazoniation.

The high resolution spectra of sulfur S2p and nitrogen N1s are displayed in Fig. 5. The S2p signal, at 163.8 eV is characteristic of DEDTC units which do not interact with Au. This highlights the absence of Au–S interaction (no visible peak at ca. 162 eV). The N1s signal, at 400.3 eV is also characteristic of DEDTC units. The absence of any signal at lower binding energy (around 397.5 eV) indicates that the grafting of the iniferter molecules is not based on Au–N
Concerning the presence of Au–C interfacial bonds, XPS could not bring a direct experimental proof, due to the low difference in electronegativity between carbon and gold atoms (\(\chi_C = 2.55\) and \(\chi_{Au} = 2.54\) using the Pauling scale). Nevertheless, based on the absence of any interfacial Au–\(\ell\)Au or Au–S bonds and on recently reported papers demonstrating the presence of Au–C interfacial bonds on gold nanoparticles modified by diazonium salts using SERS combined to modeling \([49, 50]\), one could anticipate that the grafting of the iniferter layers is based on Au–C covalent bonds.

The influence of the oligo(ethylene glycol) chains upon the chemical properties (hydrophilic/hydrophobic) of the iniferter layers was investigated by measuring the water contact angles (CA) of the bare and modified samples (see Fig. 6). Bare gold substrates have typical water contact angles around \(65^\circ\). After grafting of the iniferter layers, the CA values decrease progressively as the number of ethylene oxide units increases in the diazonium-derived coupling agent. The CA value changes from \(70^\circ\) for \(\text{Au–C}_6\text{H}_4\text{–[O–(CH}_2\text{)\_3–]}\text{DEDTC}\) to \(47^\circ\) for \(\text{Au–C}_6\text{H}_4\text{–[O–(CH}_2\text{)\_3–]}\text{DEDTC}\), in agreement with an enhanced hydrophilic character.

### 3.2. Photopolymerization from iniferter grafted on gold surface

The iniferter pendant groups connected to the gold substrates through oligo(ethylene oxide) chains of various lengths were then used to photo-initiate the polymerization of methacrylic acid (MAA) cross-linked with \(\text{N,N}^-\text{methylbisacrylamide (MBAm)}\), as illustrated in Fig. 7. The gold substrates obtained after 6 h of polymerization were characterized by XPS. Strong variations in the surface chemical composition of the samples were detected, as can be observed in Table 2. The gold signal disappears almost completely, screened by the organic overlayers while the carbon and oxygen contents increase sharply.

The high resolution C1s signal also changes significantly upon polymerization becoming very close to that of PMAA with a main peak at 285 eV due to C–\(\overline{\text{C}}\)–H, a second one at 285.8 eV due to the central C–\(\overline{\text{C}}\)–C and a new intense component at 289.2 eV due to the

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**Fig. 3.** High resolution C1s spectra of the functionalized gold substrates (a) \(\text{Au–C}_6\text{H}_4\text{–CH}_2\text{–DEDTC}\); (b) \(\text{Au–C}_6\text{H}_4\text{–[O–(CH}_2\text{)\_3–]}\text{DEDTC}\); (c) \(\text{Au–C}_6\text{H}_4\text{–[O–(CH}_2\text{)\_2–]}\text{DEDTC}\); (d) \(\text{Au–C}_6\text{H}_4\text{–[O–(CH}_2\text{)\_2–]}\text{DEDTC}\).

**Fig. 4.** Variations of the \((\text{C} + \text{O})/\text{Au}\) atomic ratios versus incubation time between the gold substrate and \(\text{N,N}^-\text{C}_6\text{H}_4\text{–[O–(CH}_2\text{)\_3–]}\text{DEDTC}\) (black curve, circles) and evolution of the iniferter layer thickness \(d\), as estimated by XPS (red curve, up triangles). NB: It is to note that due to the strong attenuation of the gold signal, almost invisible after 24 h (1440 min), it was not possible to calculate the corresponding \((\text{C} + \text{O})/\text{Au}\) atomic ratio. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
O–C=O environments of methacrylic acid units, as displayed in Fig. 8. A fourth component of low intensity is also visible at 287.5 eV, assigned to the amide groups presents in the bis-acrylamide cross-linker.

It is noteworthy that while the Au surface is almost completely screened by the polymer chains, the S2p signal is still detectable after 6 h of polymerization, confirming the living character of the polymerization process, leaving the DEDTC moieties at the chain extremities. From the gold signal attenuation, using Equation (1), an estimation of the polymer layer thickness could be obtained. The thickness values were found around 10–15 nm for all the types of initiator-grafted Au surfaces, which confirms the efficient grafting of poly(MAA-co-MBAm) layers from the modified gold surface whatever is the diazonium salt used initially. The initiator method is usually based on benzyl initiating radicals. However, in the initiator molecules reported in this paper, the presence of the hydrophilic spacers located between the diethyl dithiocarbamate moieties and the aryl groups grafted on gold generates alkyl initiating free radicals. Despite this difference, the polymerization process appears to occur efficiently, whatever the length of the oligo(ethylene oxide) chains.

Table 2: Surface atomic percentage determined by XPS for bare and PMAA-grafted Au plates.

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<th>C</th>
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<th>S</th>
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<td>2</td>
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Fig. 5. XPS high resolution spectra of the functionalized gold substrate Au–C₆H₄–[O–(CH₂)₂]–DEDTC (a) S2p and (b) N1s.

Fig. 6. Water contact angles (°) as a function of the number of ethylene oxide units in the initiator molecules grafted on gold.

Fig. 7. General scheme of the chemical procedure for the substrate functionalization by surface-initiated initiator photo-polymerization.
PMAA is known to behave as a pH-responsive polymer, which offers promising potentialities for pH sensing applications (such as biomedical or environmental pH-sensors [51–53]). Therefore, the pH response of the PMAA grafted polymer layers was studied by water contact angle measurements at pH 5.5 and pH 13 (see Fig. 9).

As expected, the CA values reveal a transition between a nearly hydrophobic character (with CA~72°) to a hydrophilic one (with CA~18°) as the pH changes from acidic to basic. This behavior is in agreement with the protonation of MAA units at pH < pKa(PMAA) and their ionization at pH > pKa(PMAA).

3.3. Immobilization of gold nanoparticles

Chemical modification of the diethylidithiocarbamyl groups remaining at the end of the iniferter grafted layers and the polymer chain extremities can be achieved by radical exchange with e.g. stable 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) radicals. In a simple experiment (schematized in Fig. 10), the iniferter layers and tethered polymer chains were irradiated in the presence of 4-amino-TEMPO radicals that irreversibly couple at room temperature with the in-situ formed macroradicals. In the next step, citrate-capped gold nanoparticles were reacted with the primary amine moieties of the exchanged groups.

SEM images of the iniferter-coated gold substrates Au–C₆H₄-[O-(CH₂)₂]-DEDTC and the polymer-coated ones Au–C₆H₄-[O-(CH₂)₂]-PMAA-DEDTC recorded after this two-step procedure (see Fig. 11), evidence the efficient immobilization of a relatively uniform coverage of gold nanoparticles on the amine-coated surfaces.

These gold nanoparticle assemblies were found to be strongly attached and remained at the surface even after a cleaning procedure involving various solvents (water and ethanol) under ultrasound. This chain-terminal-group-exchange strategy therefore offers an easy way to immobilize nanoparticles at the end of tethered polymer layers.

4. Conclusion

In conclusion, we have developed diazonium-derived photo-iniferters for surface-tethered polymerization on gold through stable Au–C anchoring linkages. This process offers a suitable alternative to self-assembled monolayers of iniferters based on thiols or disulfides which are known to be unstable under UV light or heating. In order to finely tune the hydrophilic/hydrophobic properties of the initiator layers, oligo(ethylene oxide) spacers were introduced between the diethyl dithiocarbamate initiating groups and the aryl anchoring moieties. Depending on the length of the spacers (containing a number of ethylene oxide units varying from 0 to 3), the measured water contact angles changed from 70° to 46° evidencing an enhancement of the hydrophilic character of the iniferter-grafted substrates as the number of ethylene oxide units increases. Nevertheless, the presence of the hydrophilic spacers had no influence on the
polymerization process with dense polymer layers obtained after 6 h of UV irradiation, whatever the nature of the iniferter layers. The PMAA coating demonstrated a pH-responsive behavior, as expected, with water contact angle measurements switching from 72° at acidic pH to 18° at basic pH. Furthermore, this method enables control of chain ends and immobilization of nanoparticles, as was proven by a radical-exchange experiment followed by incubation with citrate-capped gold nanoparticles. All these characteristics make this grafting technique a promising tool for producing “smart”, pH-responsive platforms, with potential for the chemical control of the chain-terminating groups.

Financial interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.12.007.

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