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Simultaneous Photografting of Two Organic Groupson a Gold Surface by using Arylazo Sulfones As the Single Precursors.

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Abstract

Arylazo sulfones have been exploited as photoactivable substrates for the simultaneous photografting of both aryl and methanesulfonyl groups on a gold surface. The obtained samples have been characterized by different spectroscopic techniques including Infrared reflection absorption (IRRAS), Surface-enhanced Raman (SERS), XPS spectroscopy and AFM.

1 INTRODUCTION.

The surface of many objects for industrial use or daily life is modified either for aesthetic purposes (plating of metals by chromium or gold), for preventing corrosion (painting of mild steel objects), or for adding new properties to a material (self-cleaning glasses). As concerning organic coatings, the simplest one is painting that protects a steel gate from rusting, but there is an interest in modifying surfaces with more strongly bonded organic films.

A significant example of the potentialities of surface modification in medicine is provided by stents insertion into arteries, where the release of an antimitotic agent (Paclitaxel for example) prevents restenosis.^{1,2} Binding of the drug on the metal surface must be strong enough to resist friction during implantation; this has been achieved by electrochemical reduction of a diazonium salt in the presence of butyl methacrylate, using the stainless steel stent as a cathode.^{1,2}

Several methods to obtain such strongly (covalently) bonded films are available. Self-assembled monolayers (SAMs) of silanes,^{3,4,5} and phosphonates,⁶ have been prepared on oxide surfaces, whereas alkenes and alkynes have been covalently bonded to hydrogenated silicon^{7,8} or carbon.⁹ Analogously, long alkyl chain thiols SAMs have been attached to different metals, including Au, Ag and Cu.¹⁰ Electro-grafting strategies were also adopted in the presence of diazonium salts as grafting agents, able to provide aryl films covalently bonded to a variety of surfaces (carbon, metals, oxides, polymers).^{11,12}

Photoinduced functionalization of surfaces by means of visible- or UV-light irradiation of benzoin derivatives,¹³ azobisisobutyronitrile¹⁴ and benzophenone¹⁵ was likewise exploited in radical-triggered polymerization.¹⁶ Benzophenone has been commonly used as a

photoinitiator, since the biradical character of its triplet excited state, acts as a hydrogen atom abstractor to generate the radical responsible of the polymerization event. For example, the photografting of porous three-dimensional materials has been achieved via the benzophenone photoinitiated surface polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid within the pores of a macroporous polymer monolith contained in a fused silica capillary.¹⁷ In another a hydrogen donor (the *N,N*-dimethyl aminophenyl group, DMA) was first electrografted on the surface, and benzophenone in solution was used as the photosensitizer to strip hydrogen from the grafted DMA. This system permitted efficient surface initiation of photopolymerization of 2-hydroxyethyl methacrylate.¹⁸

Short lived intermediates such as singlets or triplets carbenes and nitrenes presenting free doublets¹⁹ can be involved in insertion processes occurring into alkyl and aryl C–H and X–H (X = O, N, S) bonds for the surface modification of polymers. Among these species, diarylcarbenes, obtained by thermolysis or photolysis of the corresponding diazo compounds, have been investigated²⁰ for the preparation of highly colored polystyrene beads.²¹

Diazonium salts (Ar-N_2^+) or iodonium salts ($\text{Ar-I}^+-\text{Ar}'$) under UV²² or visible light exposure (in the presence of a photoredox catalyst)^{23,24,25,26} cleave to aryl radicals that react with metals or polymers. In this way it was possible to pattern gold surfaces,²⁴ polyethyleneterephthalate (PET)²⁵ or paper.²⁶

However, all the above reactions allow for the functionalization of the surface by a single chemical group obtained from the starting precursor. On the other hand, the preparation of mixed layers in order to enrich the surface chemistry has received less attention. As an example, mixed monomers providing charge transfer complexes such as styrene and vinyl acetate or maleic anhydride have been photografted to improve the surface properties of PET.^{27,28} Two incompatible enzymes (trypsin and transglutaminase) were separately encapsulated into different poly(ethylene glycol) (PEG) network layer grafted on a polyethylene film via visible light induced living photografting polymerization.²⁹ Electrografting also allows the preparation of mixed layers. Thus, a binary mixture of aryl diazonium salts bearing oppositely charged para substituents ($-\text{SO}_3^-$ and $-\text{N}(\text{CH}_3)_2^+$) has been electrografted and the surface ratio of the two phenyl groups is consistently 1:1 regardless of the ratio of the two aryl diazonium salts in the modification solutions.³⁰ The grafting of the 1-(bithien-2-yl)-4-benzenediazonium (BTB) salt complexed by β -cyclodextrin (CD) provides a layer of grafted BTB oligomers complexed by CD. When CD is removed from the surface, pinholes are created and the 4-nitrobenzenediazonium salt is reduced to graft a second component.³¹ Following the same strategy, after electrografting of the sterically hindered 4-((triisopropylsilyl)ethynyl)phenyl groups, the cleavage of the isopropyl groups and further

grafting of nitrophenyl groups also permits to obtain mixed aryl layers.³² Mixed layers of aminophenyl and perfluoroalkyl groups electrografted on carbon fibers (obtained from aryldiazonium salt and perfluoroalkyliodide) permit to obtained hydrophobic carbon-epoxy composites with improved mechanical properties.³³ Mixed layers have also been prepared by combined electro and photografting: a multilayer film of nitrophenyl groups was electrografted to a carbon surface and 4-aminophenylazide was further photografted to this surface from a spin-coated solution.³⁴

We present herein a protocol for the simultaneous gold surface modification by two different functional groups, starting from arylazo sulfones **1a-c** as photoactivable precursors.

The presence of a *dyedauxiliary group* -N₂SO₂CH₃ in such bench stable derivatives is responsible for both color and photoreactivity of the molecules that, when irradiated, undergo homolytic cleavage of the N-S bond, and the formation of the corresponding aryl radical (Ar[•]).³⁵ Such substrates have found recent application in organic synthesis, for the visible-light induced formation, under metal- and (photo)catalyst free conditions, of both C-C^{36,37,38,39} and C-heteroatom bonds.^{40,41}

In contrast, the use of arylazo sulfones in material chemistry received only few attentions in the past as the use of arylazo tosylsulfones as thermal initiators in the radical polymerization of acrylate monomers.⁴² In this paper we present the photografting of azosulfones and demonstrate that both substituents of the N=N bond are effectively bonded to the surface.

EXPERIMENTAL.

Chemicals. Arylazo sulfones were prepared from the corresponding anilines by following a known method.⁴³ Spectroscopical data of the compounds are in accordance with the literature. Dry and purified acetonitrile was obtained from a Pure Solv system from Innovative Technology.

Photografting was achieved by placing a gold plate in a test tube with a septum screw cap; the tube was filled with argon and a 0.1 mM solution of the chosen azosulfone in ACN was deposited with a needle, through the septum, on the gold surface. Irradiation was performed using a Kessil Lamp (40 W, 456 nm) as the light source for 8 h (Scheme 1).

Scheme 1. Experimental setup.

Substrates. Gold coated (100 nm) silicon wafers obtained from Sigma-Aldrich, were cut into $1 \times 1 \text{ cm}^2$ pieces and successively rinsed in a bath of sulfuric acid (95%) for 2 s, and with distilled water and under sonication in distilled water, acetone, and absolute ethanol (380 s each) and finally dried by an argon stream.

Infrared reflection absorption spectroscopy (IRRAS). Spectra of modified plates were recorded using a purged (low CO_2 , dry air) Jasco FT/IR-6100 Fourier Transform InfraRed Spectrometer equipped with an MCT (mercury-cadmium-telluride) detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm^{-1} . The background recorded before each spectrum was that of a cleaned substrate.

Surface-enhanced Raman spectroscopy (SERS). The SERS spectra were recorded on gold SERS substrates modified by arylazo sulfone using a Horiba XploRA PLUS Raman microscope with an excitation wavelength of 633 nm and a power of 0.6 mW. The spectral resolution was less than 3 cm^{-1} and the accumulation time was set to 20 s with two repetitions.

XPS Spectra. XPS measurements were performed using a K-Alpha system (Thermo Fisher Scientific, East-Grinstead, UK) fitted with a microfocused and monochromatic Al $K\alpha$ X-ray source (1486.6 eV, spot size: $400 \mu\text{m}$). The pass energy was set to 150 and 40 eV for the survey and the high-resolution spectra, respectively. The spectra were calibrated against the C–C/C–H C 1s component set at 285 eV. The chemical composition was determined with version 5.9902 Avantage software, by using the manufacturer sensitivity factors. The spectra were calibrated against C 1s set at 285 eV.

Contact Angle Measurements. The water interaction properties were characterized with a drop shape analysis system Krüss DSA30S and a Drop Shape Analysis 1.92.1.1 version software.

AFM Images. AFM images were recorded with a NT-MDT Solver pro equipment. AFM topography was performed in the intermittent contact mode with standard silicon cantilevers. Image analysis was achieved with the free software WSxM.

RESULTS AND DISCUSSION

IRRAS. After irradiation of the azosulfone solution deposited on a gold plate (in deoxygenated ACN), the plate was ultrasonicated for 180 s in EtOH and dried under argon, an *IRRAS* spectrum was recorded. The modified gold plates are referred as *Au-NO₂*, *Au-CN*, *Au-COCH₃*. The IR and Raman spectra indicate the presence of the aromatic groups and also of the substituents (NO₂, CN, C(=O)CH₃), in the absence of irradiation these IR signals are not observed (Table 1, Figure 1). We also searched for the presence of azo bonds either as *Au-N=N-* or as *-N=N-* inside the film. The Ar-N=N-SO₂Me stretching bands are weak in the starting azosulfones (1414, 1404 and 1407 cm⁻¹ for, respectively, **1a**, **1b**, **1c**) and are not observed in *Au-NO₂*, *Au-CN*, *Au-COCH₃*.⁴⁴ SO₂ stretching ($\nu_{\text{sym}}(\text{SO}_2)$ at *ca.* 1110–1170 cm⁻¹) and bending ($\delta_{(\text{SO}_2)}$ at *ca.* 325–365 cm⁻¹) vibrations^{45,46,47} cannot be safely assigned by IR while they clearly appear in the surface-enhanced Raman spectrum at 1174 cm⁻¹ and 1363 cm⁻¹ (Table 1, Figure 2).

Table 1. IR and Raman spectra of *Au-NO₂*, *Au-CN*, *Au-COCH₃*, wavenumbers (cm⁻¹)

Azosulfones		Aromatic bands	NO ₂ ^{a)}	CN	COCH ₃	CH ₃ S(=O) ₂
1a , R = NO ₂	IR	1598	1528			-
		1580	1350			
	Raman	1591	1335			1174, 1363
1b , R= CN	IR	1577		2229 ^{b)}		-
1c , R = COCH ₃	IR	1560,			1694 ^{c)}	-
		1604,				
		1576				

By comparison,⁴⁸ nitrobenzene signals were observed at 1521 and 1347 cm⁻¹; b) benzonitrile at 2230 cm⁻¹; c) acetophenone at 1686 cm⁻¹

Figure 1. IRRAS spectra of Au-NO_2 , Au-CN , Au-COCH_3 .

Figure 2. Surface-enhanced Raman spectrum of Au-NO_2 .

XPS. The modified Au plates were also examined by XPS. The three samples present a contribution of Au4f, this indicates that the organic is thinner than 5-10 nm. The observation of the signals assigned to the substituents confirms the grafting of the substituted aryl rings and of the sulfone group on the gold surface (Table 2, Figure 3). It is difficult to differentiate a grafted substituted phenyl ring from a substituted azophenyl group; however, the Au-N=N-Ar structure has been observed during the grafting of diazonium salts on Au through an N1s signal at 397.5 eV.⁵² In our case, the deconvolution of the N1s peaks, does not indicate the presence of this bond except after grafting the NO₂ substituted azosulfone where a very small contribution is observed at this energy. In addition, the XPS spectra indicate the presence of oxidized sulfur that corresponds to sulfone groups, but also of unoxidized sulfur similar to that of thiol SAMS, the origin of reduced sulfur results, most probably, from a reduction by the X-ray beam.

The spectrum of Au-NO₂ present a N1s contribution at 406.0 eV characteristic of the nitro groups, the N1s contribution at 399.1 and 400.1 eV (corresponding to a nitrogen and its protonated form), result respectively from i) some contamination, ii) the reduction of the nitro group under the X-ray beam, but could also be assigned to iii) azo bonds inside the film as with diazonium salts. The C1s peak presents three contributions at 284.8, 286.0 and 288.4 eV that can be assigned to aromatic carbons but also to the carbons bonded to sulfur (284.7, 285.3 and 286.3 for polyethersulfone⁵¹). The sulfur is mostly present in its oxidized form at 166.9 eV assigned to the sulfone group (Figure 4).

Au-CN presents two N1s contributions at 399.3 and 401.7 eV that can be assigned to the cyano group but also to some contamination. Nearly equal amounts of oxidized and reduced sulfur are observed. The C1s peak also presents three contributions at 284.8, 286.3, 287.9 eV). Au-COCH₃, the C1S peak presents three contribution at 284.8, 286.2, and 287.8 eV, the last two correspond to oxidized carbon C(=O) and C-S.

Table 2. XPS Spectra (Binding Energy eV, and % elemental composition)

<i>Au</i> -NO ₂ , CN, COCH ₃	NO ₂	CN	COCH ₃	Au-N	S	
R = NO ₂	N1s 406.0 (2.1)			N1s 397.5 ^{c)} (<0.1)	S2p 168.9 ^{d)} (0.3)	S2p 161.8 ^{e)} (1.0)
R = CN		C1s 286.3 ^{a)} (6.2) N1s 400.0 5.2		-	S2p 168.9 ^{d)} (0.4)	S2p 162.2 ^{e)} (1.9)
R = COCH ₃			C(1s) 287.9 ^{b)} (5.5)	-	S2p 168.7 ^{d)} (0.6)	S2p 162.3 ^{e)} (1.3)

a) Polyacrylonitrile N1s at 399.6 eV,⁴⁹ benzonitrile N1s at 399.2,⁵⁰ polymethacrylonitrile C1s at 286.4 eV⁴⁹, b) poly(3-methyl-but-3-en-2-one) at 287.4 eV.⁵¹ c) see reference.⁵² d) corresponds to an oxidized sulfur, for example Na₂SO₄ at 168.4 eV e) corresponds to an Au-S-R bond, for example Au-S-C₁₈H₃₇.

Figure 3. XPS spectra (N1s contribution) of A) *Au-NO₂* and B) *Au-CN*.

Figure 4. XPS spectra (S2p contribution) of *Au-NO₂*

AFM. The images obtained by AFM are presented in Figure 5. The gold surface modified by 4-nitroazosulfone presents a film reaching 12 nm on most of the surface, but on some places very high and sharp needles appear with a height up to 80 nm. With COCH₃ as the substituent these needles are much smaller reaching only 12 nm with a film height of 4-6 nm. These values can be compared with the length (from molecular models) of –C₆H₄–NO₂, –C₆H₄–CN, –C₆H₄–COCH₃ groups (0.68, 0.73, 0.80 nm, respectively) and indicate the formation of multilayers. If one compare the images recorded on a

200 nm scale with that of unmodified gold, the Au(111) domains are still visible but somewhat blurred by the grafted film.

Figure 5. AFM images of the modified surfaces A) $Au-NO_2$, B) $Au-CN$, C) $Au-COCH_3$, D) bare gold

The above experiments indicate that the film is a thin multilayer with very high needles, they also show that both the aryl group and the sulfone groups are part of this film. The formation of multilayers is a common feature of all radical grafting reactions but the photografting of two groups deriving from the starting compound is unexpected; therefore, the problem arises of determining the structure of the film.

The previously described mechanism permits to get a first insight into the formation of this film. Visible light irradiation of arylazo sulfones resulted in the homolytic cleavage of the N-S bond (via the $^1n\pi^*$ singlet excited state, (Scheme 2, paths a, b) and the generation, of the diazenyl and

methanesulfonyl radicals. The corresponding aryl radical is obtained from N_2 loss of the diazenyl radical (path c).³³ Trapping by the gold surface of the diazenyl radical/ methanesulfonyl radical pair allowed the formation of the mixed functionalized surface (path d, Scheme 2). The presence of the aryl groups in the film and on the surface, has been well documented during of diazonium salts and the IRRAS spectra of surfaces grafted by arylazo sulfones indicate the presence of these groups. On the other hand, the presence of the methanesulfone moiety on the film is attested by Raman and XPS; however, we also noticed that the methanesulfonyl radical can either i) attach to the surface (path d) or ii) react on grafted aryl groups (path d') or both; to test this hypothesis we have abraded the surface with clusters of 2000 Ar^+ ions with a total energy of 4 keV and recorded spectra at different times (note that the total thickness of the film is analyzed). Figure 6 presents the spectra recorded after 0, 60, 120 and 180 s and the profile of the atomic % of the nitro group and of sulfur. The NO_2 % decreases linearly with abrasion time, while S2p % increases slightly (due the decrease of the NO_2 %) and decreases when reaching the surface. This indicates that the methanesulfonyl radical only reacts on the surface and not on the aryl group as in Scheme 2, path d''.

Figure 6. Abrasion of the Au-NO_2 film and profile through the film of the NO_2 and S signals

Scheme 2. The photografting mechanism of azosulfones.

In the case of 4-nitrophenylazo sulfone, early results suggested that trapping of the diazenyl radical could occur faster than N_2 extrusion, and the formation of the $\text{Au-N}_2\text{-Ar}$ bond being in competition with that of the Au-Ar bond (path c'). We thus examined the possibility of grafting a diazenyl radical. This radical generated by photochemistry of arylthiodiazenes has been observed by means of ESR analyses, the decomposition rate of the phenyl diazenyl radical was measured at -96°C : $k = 34 \text{ s}^{-1}$.⁵³ The bond dissociation energy of the Au-N bond in Au-N=N-Ar structures has been calculated by DFT methods, it is much smaller ($7.91 \text{ kcal mol}^{-1}$)⁵⁴ than that of an Au-Ar bond ($38.5 \text{ kcal mol}^{-1}$ in water). Nevertheless, an Au-N bond has been characterized by an XPS signal at 397.5 eV assigned to gold nitride during the spontaneous grafting of 4-nitrobenzenediazonium in unbuffered water.⁵² In the spectra above, there is no sign of -N=N- bonds, however a very small shoulder appears at 397.6 eV on the C1s XPS spectrum of Au-NO_2 (arrow in Figure 3A). Therefore Au-N=N- bonds should be present

only in $Au-NO_2$ (path c'). In this case trapping of the diazenyl radical occurs faster than N_2 extrusion, and the formation of the $Ar-N_2-Au$ bond competes with that of the $Ar-Au$ bond (path d).

Conclusion

The surface modification of gold by photolysis of arylazo sulfone permits the attachment of both the substituted aryl groups and of the $S(=O)_2CH_3$ group; two groups are then grafted from a single precursor. This results from the photocleavage mechanism of azosulfones that provide two radicals, while aryl radicals react both on the surface and the first grafted groups the methanesulfonyl radical reacts only with the surface. Due to its small size it is buried in the polyphenylene oligomers film; it appears as a diluent of the aryl oligomers, a feature that is looked for when attaching large molecules to the extremities of the aryl oligomers.⁵⁵

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