

Surface photografting of arylazide derivatives on chalcogenide glasses



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ABSTRACT

Arylazide derivatives have been used for the surface functionalization of chalcogenide glasses. These compounds are photografted by a deposition step followed by an irradiation step under UV light. Two photosensitive molecules were studied: the so-called “molecular clip” which is a phenylazide moiety linked via a propylene chain to a succinimidyl ester (**4**), and the perfluoro-4-azido-1-benzoic acid coupled to a hexaethyleneglycol chain (**3**). Two approaches have been considered: the indirect approach that consists in the binding of the azido compound onto a primary organic layer (made of the PEGylated molecules **1** and **2**) previously deposited on the glass surface, and the direct approach that is the reaction of the azido compound directly with the native glass surface. After photografting, the samples were analyzed by water contact angle measurement (θ_w), X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS). The “molecular clip” **4** binds strongly to the surface and also forms multilayers by intermolecular linkages, either in the direct or the indirect approach. According to the θ_w values, the perfluorophenylazide **3** reacts weakly with the surface; however, the ToF-SIMS spectra confirm the presence of photografted molecules. In this case, intermolecular reactions are highly favored and therefore responsible of the poor surface coverage. The binding of **4** leads to a reactive surface, functionalized by succinimidyl ester groups, the surface reactivity of which has been assayed by coupling 3,5-bis(trifluoromethyl)benzylamine, followed by XPS analysis. An ATR (attenuated total reflection) prism has been functionalized as above and used for the immobilization of an insulin specific antibody. This device allowed the detection of insulin in an aqueous solution by FTIR (Fourier transform infra-red) spectroscopy.

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1. Introduction

Arylazides are known since many years as useful photoaffinity labeling agents in biology because of their ability to form highly reactive species (nitrenes) when irradiated under UV light [1–7]. They are also employed for surface functionalization [8–10]; for this latter purpose, arylazides coupled to another reactive moiety are grafted on several types of surfaces [11]. One approach consists in binding the other functional group to an inorganic surface and using the azide function for the next step of the desired construction. Another approach uses the azide function to bind with different surfaces such as organic surfaces, polymers or any carbon-based material, while the other functional group remains available for various surface post-functionalizations [12]. A widely used functional group, in the context of biosensors for instance, is the carboxylic ester derived of *N*-hydroxy-succinimide (NHS ester) able to react with the amine functions generally found in bio(macro)molecules [12].

Several inorganic surfaces can undergo azide photografting when their surface contains carbon chains which are provided by the deposition

of a primary organic layer before the photochemistry. Such a construction has been already reported on crystalline germanium in order to build an infrared biosensor [13,14]. The carbon chains can also be found as contaminants on the material surface, which is likely the case for chalcogenide glasses according to the XPS study of these surfaces [15,16]. The carbonaceous contamination comes mainly from the glass preparation process. Chalcogenide glasses are vitreous materials comprising chalcogen elements (Se, Te or S) in their atomic bulk composition. They have a good transparency towards infrared and can be manufactured by molding process to prepare optical devices such as fibers and prisms. Therefore these glasses are useful for applications like infrared detection or thermal imaging [17–22].

In a previous work, we already disclosed a new route for the surface modification of chalcogenide glasses, namely the photo-assisted grafting of disulfide and silane derivatives [15,16]. In the present article, we have investigated a novel route for surface modification of these glasses using azide derivatives directly photografted on the substrate, or grafted on a primary organic layer made of disulfide and/or silane derivatives involving short polyethyleneglycol (PEG) chains in order to favor the photografting of azides.

The organic molecules used in this work are prepared from thioctic acid, 3-(triethoxysilyl)propyl isocyanate and 4-azido-2,3,5,

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6-tetrafluoro-1-benzoic acid coupled to hepta- or hexa-ethyleneglycol chains (named PEG) via an amide, carbamate or ester link, giving the molecules **1**, **2** and **3** respectively (Fig. 1). The so-called “molecular clip” **4**, to be grafted on a primary PEG layer, is a phenylazide connected to the NHS ester via a propylene chain. 3,5-Bis(trifluoromethyl)benzylamine **5** is used as a fluorinated probe for labeling the NHS-activated surfaces and further quantification by X-ray photoelectron spectroscopy (XPS). Two glasses, namely IG2 and IG4 differing by their Ge/As ratios have been studied. The best conditions of surface functionalization have been applied to an ATR (attenuated total reflection) prism of IG4 used for the immobilization of an antibody of insulin.

2. Materials and methods

2.1. Chalcogenide glasses

Two types of chalcogenide glasses (IG2 and IG4) were purchased from Vitron Spezialwerkstoffe GmbH (Jena-Maua, Germany). According to the manufacturer, the bulk composition of the glass is Ge₁₀As₄₀Se₅₀ for IG4 and Ge₃₃As₁₂Se₅₅ for IG2. The lenses received from the manufacturer have a 50.8 mm diameter and are 2.0 mm thick. The ATR prisms have 50.0 × 20.0 mm² dimensions and are 2.0 mm thick. For the experiments, a lens was cut into several 10 × 10 mm² squares. The samples named “native” are used as received. All the other samples are washed overnight in refluxing chloroform in a Soxhlet apparatus, prior to the surface modification processes described below. ATR prisms having the IG4 atomic composition were used for the FTIR measurements.

2.2. Organic compounds

The synthesis of molecules **1**, **2** and **4** has been described earlier [12–14]. The synthesis of **3** is reported in the Supplementary data. 3,5-Bis(trifluoromethyl)benzylamine **5** was purchased from Sigma-Aldrich-Fluka (Bornem, Belgium).

2.3. Biological materials

Insulin and its specific antibody were obtained from DiaSource-ImmunoAssay S.A. (Louvain-la-Neuve, Belgium). The antibody is a monoclonal anti-human mouse antibody. The mother-solution of

1 mg of antibody in 273 μL of Borate Buffer Saline (BBS, 0.1 M, pH 8) was diluted 10 times to give a concentration of 366 μg/mL. The insulin mother-solution was of 0.15 mg in 100 μL of 0.01 N HCl.

2.4. Water contact angle measurement (θ_w)

Water contact angles were measured in a static mode at 25 °C with a home-made equipment using the sessile drop method and an image analysis system of the droplet profile. The volume of MilliQ water is 10 μL/droplet. The reported results are the average of 8 to 10 measurements (± standard deviation).

2.5. X-ray photoelectron spectroscopy (XPS)

The analyses were performed on a Kratos Axis Ultra spectrometer from Kratos Analytical (Manchester, UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV) and an eight channeltron detector. The spectrometer is interfaced with a Sun Ultra 5 workstation. Instrument control and data acquisition are performed with the Vision 2 program. The samples were fixed on a standard stainless steel multispecimen holder by using a piece of double sided isolative tape. The pressure in the analytical chamber was about 10⁻⁶ Pa. The angle between the normal to the sample surface and the direction of photoelectron collection was 0°. Analyses were recorded in the hybrid lens mode and the analyzed areas were 700 μm × 300 μm. The pass energy of the hemispherical analyzer was set at 160 eV for the survey scan and 40 eV for the narrow scans. In the latter conditions, the full width at half maximum (FWHM) of the Ag 3d_{5/2} peak of a standard silver sample was 0.9 eV. Charge stabilization was achieved by using the Kratos Axis device. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, N 1s, S 2p, F 1s, Se 3d, As 3d, Ge 3d, Zn 2p, Na 1s, Si 2p and C 1s again to check for charge stability as a function of time, and the absence of sample degradation during the analysis. The C-(C,H) component of the C 1s peak of carbon has been fixed at 284.8 eV to set the binding energy scale. Spectra were decomposed with the CasaXPS program from Casa Software Ltd (UK) with a Gaussian/Lorentzian (70/30) product function. Molar fractions are calculated using the peak areas normalized on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors and transmission factors

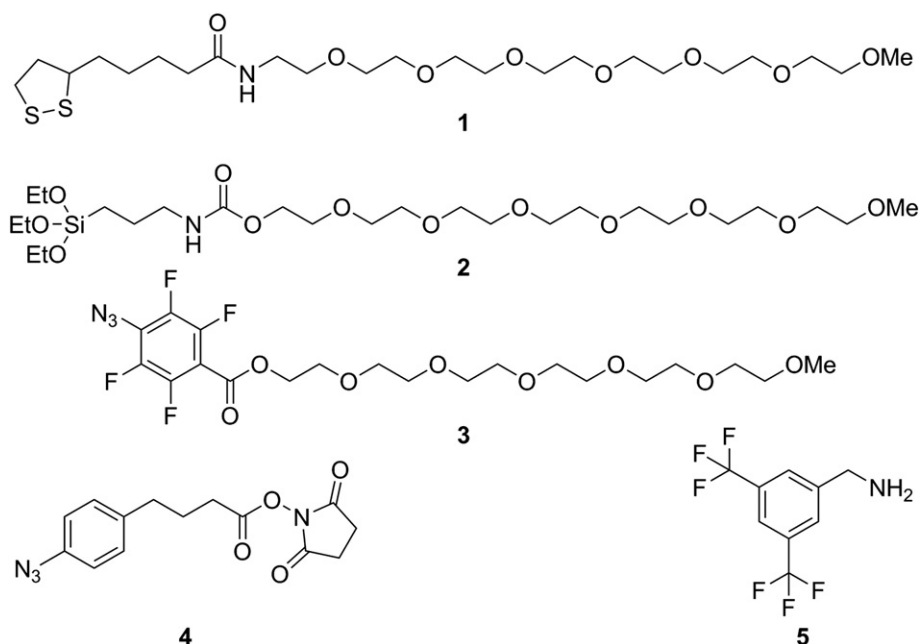


Fig. 1. Structures of the organic compounds used to form primary layer (**1**, **2** and **3**), to activate (**4**) and to assess the reactivity (**5**) of the chalcogenide glass surface.

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