

# Synthesis *in situ* of gold nanoparticles by a dialkynyl Fischer carbene complex anchored to glass surfaces



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## ABSTRACT

In this work we present a detailed study of classic reactions such as “click reaction” and nucleophilic substitution reaction *but* on glass solid surface (slides). We used different reactive center of a dialkynyl-alcoxy Fischer carbene complex of tungsten(0) to be anchored to modified glass surface with amine, to obtain aminocarbene, and azide terminal groups. These cycloaddition reaction showed regioselectivity to internal triple bond of dialkynyl Fischer carbene complex without Cu(I) as catalyst. Anyway the carbene anchored was able to act as a reducing agent to produce *in situ* very stable gold nanoparticles fixed on surface. We showed the characterization of modified glasses by contact angle measurements and XPS. Synthesized nanoparticles were characterized by SEM, XPS, EDS and UV–vis. The modified glasses showed an important enhancement Raman-SERS. This simple, fast and robust method to create a polifunctional and hybrid surfaces can be valuable in a wide range of applications such as Raman-SERS substrates and other optical fields.

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## 1. Introduction

The miniaturization of devices is an emergent technology in many areas, that go from electronic up medicine [1,2] which could result in significant progress for society. In recent decades the chemical functionalization of solid substrates has aroused significant attention among scientists due to the possibility to tailor the surface properties, e.g. the wettability, frictional resistance, adhesiveness and conductivity among others, in a controlled fashion by covering the surface with monolayers of molecules with specific characteristics [3,4]. The modifications of glass with organosilanes provide advantages over other systems like gold with sulfurs compounds, which represent the most popular combination. Silane coupling agents has the ability to form a durable bond between organic and inorganic materials. The general formula shows three important parts: the hydrolysable group directly bound to silicon atom, the linkage or carbon chain and the functional group bonded to it. Extended linker length is important in oriented applications such as self-assembled monolayers (SAMs) because if the linker length is long the functional group has greater mobility and can extend further away from the inorganic substrate. Also, it is

possible to control the stability of the monolayer or packaging by varying the alkyl chain length (distance control) due to van der Waals interactions that have a significant influence on the ordering of the monolayers [5]. On the other hand the functional end group imparts desired characteristics to the glass surface. The variety of organosilane coupling agents offers a broader range of terminal reactive groups to continue with the synthesis of the following layers [6]. The substrate glass is optically transparent at wavelengths >320 nm, it has a low intrinsic fluorescence, high mechanical stability and it is cheaper than gold. For all these reasons, SAM's on glass provides a simple, economic, robust and fast technique to set up functional surfaces. One of the most advanced applications of SAM's on solid surface is the design of biosensors. Immobilization of proteins with retention of their activity on highly ordered monolayers is a key factor behind of the successful of a biosensor to be used in diagnostic, affinity separation, and biomaterials technology [7]. In order to obtain a certain control during binding of a biomolecule with modified surface is very important study the classics reactions used in detail.

The versatility and utility of Fischer carbene complex as tools in organic synthesis have been widely demonstrated during the past two decades. Particularly alkynyl Fischer carbene complexes are multifunctional molecules that allow a variety of transformations under mild conditions [8,9]. The pentacarbonyl metal fragment is a powerful electron-withdrawing group makes the conjugated

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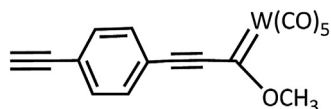


Fig. 1. Pentacarbonyl-[(1,4-diethynylphenyl)-methoxycarbene]-tungsten(0) **1-W**.

alkyne group considerably electron-deficient and polarized. So, a triple bond conjugated with the pentacarbonyl metal moiety is highly activated toward cycloaddition reactions [10]. Some years ago we reported stereoselective cycloaddition of dithioethiones to monoalkynyl Fischer carbene complexes at  $-40^{\circ}\text{C}$  to obtain dithyafulven unit [11]. Sierra et al. [12] showed that the [3+2] cycloadditions between an 1,3-dialkynyl Fischer carbene complex and organic azides in solution are regioselective to terminal triple bond with Cu(I) as catalyst. Somewhat later, Sarkar et al. [13] using monoalkynyl Fischer carbene complexes, obtained moderate yields of [3+2] cycloaddition product without the need of Cu(I) catalyst which allow to work in suitable conditions for biomolecules [14–16]. They had also shown the reducer capacity of Fischer carbene to generate gold nanoparticles (AuNp) in solution [17]. More recently, the reducing capacity of the Fischer carbene complexes was demonstrated against  $\text{K}_2\text{PdCl}_4$  obtaining palladium nanoparticles in aqueous solution [18].

To the best of our knowledge, there is nothing reported about the behavior of Fischer carbene complexes with two triple bonds on surfaces, so we considered interesting to exposing a modified glass surface with azide terminal groups to a solution containing dialkynyl Fischer carbenes complex, [pentacarbonyl-(1,4-diethynylphenyl)-methoxycarbene]-tungsten(0), **1-W** Fig. 1. This system would allow us to know whether the cycloaddition reaction can occur with or without Cu(I) catalyst, and to establish if there is selectivity regarding the triple bond (internal or terminal) on which it is produced. Besides, the triple bond that do not take part in the cycloaddition reaction would be available for subsequent modifications on this surface.

With **1-W** already bonded to the surface we demonstrate that the reaction can be easily pursued with high regioselectivity and

without catalyst. Besides we demonstrated that a Fischer carbene complex anchored in a glass surface is capable to produce gold nanoparticles *in situ* on the surface, indicating that the complex has not lost its reducing capacity. We also attached **1-W** to a surface containing free amino groups [19] and found that these modified glass is also able to reduce Au(III) forming nanoparticles.

These AuNp have a proper size and arrangement to produce a substantial SERS effect. The generation of nanoparticles on the surface *in situ*, prevents agglomeration, which is very important in terms of efficiency in producing increased Raman signal [20].

## 2. Experimental section

### 2.1. Materials

The glass slides used were commercially available Microscope cover glasses,  $20 \times 20$  mm obtained from by Marienfeld Laboratory glassware GmbH y Co. KG.

The organosilanes used for the silanization were 1-aminoundecyltrimethoxysilane ( $\text{C}_{17}\text{H}_{39}\text{NO}_3\text{Si}$ ) 95% (**AUTES**) and 11-bromoundecyltrimethoxysilane ( $\text{C}_{14}\text{H}_{31}\text{O}_3\text{BrSi}$ ) 95% (**BUTS**), they were purchased from ABCR GmbH and Co. and used as received. In both cases, we prepared a solution 0.01% v/v of these silanes in dry toluene. These solutions were used and stored under  $\text{N}_2$  atmosphere. The same solutions were used more than once for silanizing several sets of glasses.

The glass surfaces were characterized by XPS using a Mg K $\alpha$  source (XR50, Specs GmbH) and a hemispherical electron energy analyzer (PHOIBOS 100, Specs GmbH) operating at 40 eV pass energy. Before analysis, the samples were kept for 1 h in a separate vacuum system in order to remove all volatile substances. The base pressure in the chamber was around  $5 \times 10^{-10}$  Torr. The C 1s line at 285 eV was used as charging reference. Images of AuNps onto surfaces were taken by a scanning electron microscope (SEM) (Zeiss, SIGMA). SEM observations were carried out at 10–25 kV. The EDS information was obtained with a spectrometer Oxford AZtec and InLens detector.

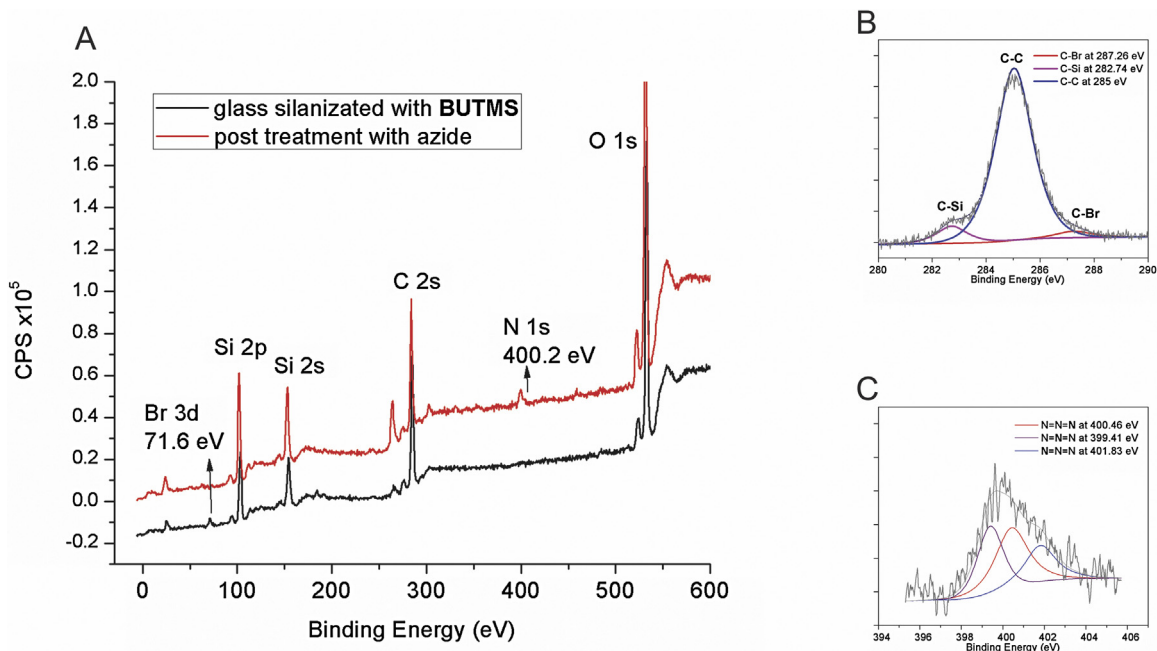
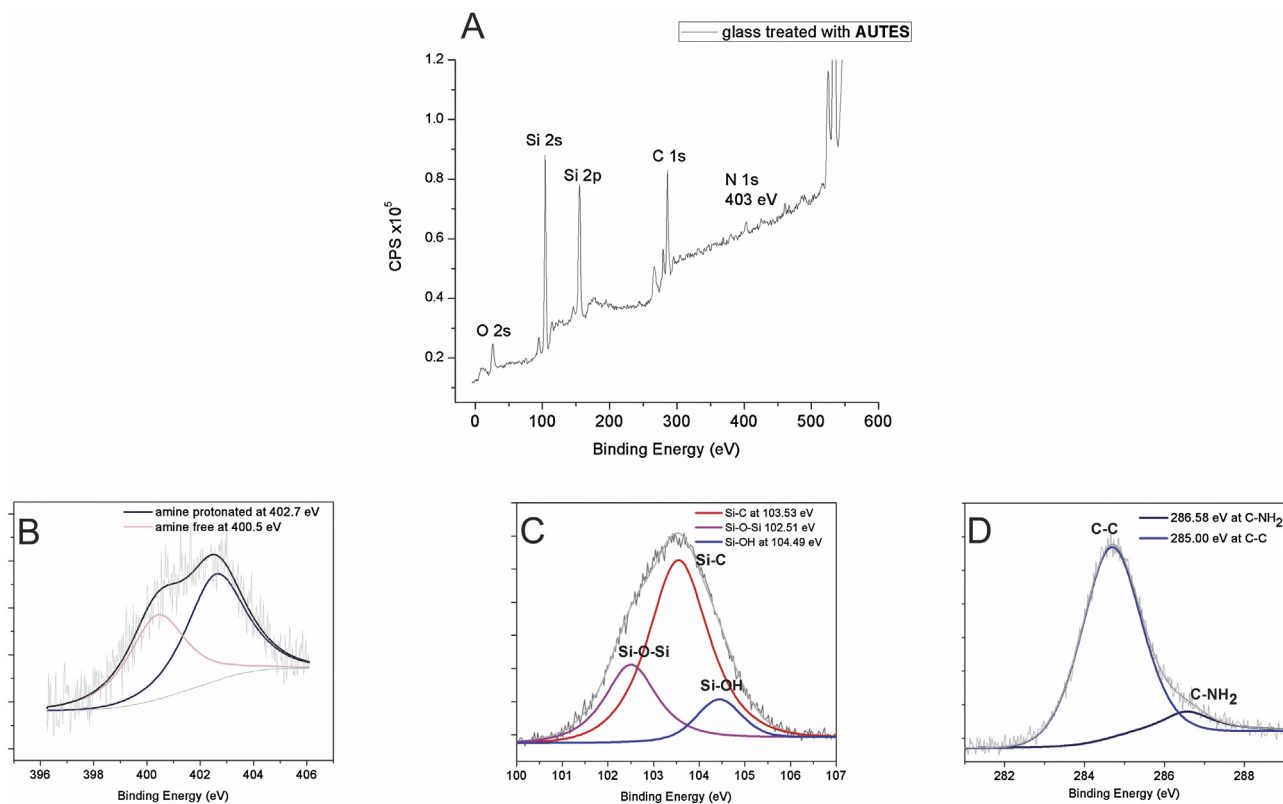


Fig. 2. (A) XPS survey spectra for silanized glass slide with **BUTMS** (black line) and post-treated with azide (red line), (B) Deconvolution of C 1s signal corresponding to glass treated with **BUTS**. (C) Deconvolution of N 2s signal post-treated with sodium azide. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** (A) XPS survey spectra for silanized glass slide with **AUTES** (B) Deconvolution of C 1s signal corresponding to glass treated with **AUTES**. (C) Deconvolution of Si 2p to the same surface. (D) Deconvolution of N 1s from samples treated with **AUTES**.

The UV–vis spectra were recorded on a double beam spectrophotometer placing a single glass in the optical path of the spectrophotometer. Static contact angle determinations were made with a KSV CAM200 instrument, with the water sessile drop method. Raman and SERS spectra were obtained with a Horiba LabRam 800HR Raman instrument. Excitation was provided by the 632.817 nm line of a HeNe 20 mW laser. The laser beam was coupled to a dried sample of glass slide by means of 100 × microscope objective lens.

## 2.2. Synthesis of pentacarbonyl-[(1,4-diethynylphenyl)methoxycarbene]-tungsten(0) 1-W

In a three neck r.b. flask, 317.8 mg 1,4-diethynylbenzene (96% purchased from Sigma-Aldrich) (2.5 mmol) was taken in a 10 ml dry THF under Nitrogen. The stirred solution was cooled to  $-40^{\circ}\text{C}$  and 1.26 ml of *n*-buthyllithium in cyclohexane (1.6 M, 2.5 mmol, purchased from Sigma-Aldrich) was added drop wise, stirring was continued for 1 h. The monoanion generated was controlled by  $^1\text{H}$  NMR, following the 50% disappearance of the signal corresponding to de H acetylenes around at 3:14 pm taking as 100% the integral of the aromatic signals equivalent to 4H. In another r. b. flask, 885.5 mg (2.5 mmol) of  $\text{W}(\text{CO})_6$  was taken in 30 ml dry anhydrous THF under  $\text{N}_2$  and the suspension was cooled to  $-40^{\circ}\text{C}$ . The monoanion solution was then added to the tungsten hexacarbonyl suspension. The temperature was raised to  $0^{\circ}\text{C}$  and stirred for 1 h. The orange solution obtained was cooled to  $-40^{\circ}\text{C}$  and 0.3 ml (2.5 mmol  $\delta = 1.5$  g/ml) of the Methyl trifluoromethanesulfonate ( $\text{CF}_3\text{SO}_2\text{OCH}_3$  SigmaAldrich >98%) was added. The solvent of the resulting dark red solution was evaporated and purified by column chromatography (pet hexane:dichlorometane 80:20) under

$\text{N}_2$ . Yield 35%. The product was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and HRMS (see SI).

## 2.3. Synthesis of modified glass surfaces

### 2.3.1. Substrate preparation: activation

The cleanliness of the surfaces is of critical importance in the experiments. The cover glass slides were cleaned carefully and active following reported procedure [21]. For modifications of the surfaces a specific glass reactor was used and Teflon support designed to keep the slides in a vertical position while avoiding contact between the slide with one another allowing the results to be reproducible (see reactor in SI). The surface modification was confirmed by contact angles measurements. The difference in hydrophobicity between a normal glass and an activate glass surface enable the control of the effectiveness of the successive steps. The contact angle changed from  $(58 \pm 2)^{\circ}$  for the glass without surface activation to  $(21 \pm 2)^{\circ}$  for the hydrophilic glass.

### 2.3.2. Silanization with organosilanes BUTMS and AUTES

After that, the activated and dry glasses were immersed in a dilute solution of organosilane **AUTES** or **BUTMS** in dry toluene (0.01% v/v) at room temperature under  $\text{N}_2$  atmosphere overnight. Then, the glasses were rinsed with ultrasonication in toluene, ethanol and acetone for several times. The organosilanized glasses were dried with  $\text{N}_2$  and stored for characterization. Contact angle measurements showed again changes in the hydrophobicity of the treated surfaces. The bromo terminated surface show a contact angle value of about  $(73 \pm 2)^{\circ}$  and amine terminated surface  $(66 \pm 2)^{\circ}$ .

### 2.3.3. Modification by $S_N$ reaction with sodium azide of bromo terminal containing surface

Nucleophilic displacement of bromide by azide on SAM was carried out in DMF with sodium azide. The slides were immersed in a saturated solution of  $\text{NaN}_3$  in dry DMF allow to reflux for 48 h. Then they were washed thoroughly with DMF, ethanol and acetone and dried under  $\text{N}_2$ . After that treatment the contact angle was  $(84 \pm 3)^\circ$ .

### 2.3.4. Grafting of Fischer carbene complex 1-W on surface

The two types of surfaces obtained allowed attaching the Fischer carbene complex to them in two different way. The first was called “Via amine” because involves a formation of amine carbene by the reaction between amine terminal surface and the carbenic carbon of the **1-W**. The second method was called “Via click” by cycloaddition reaction with azide and a triple bond of **1-W**.

**2.3.4.1. By Cu-free “Click” chemistry: “Via click”.** The glasses with azide terminated monolayer were treated with **1-W** (10 mM in dry acetonitrile) under  $\text{N}_2$  atmosphere with stirring at RT overnight. Then they were washed with pure acetonitrile and dried under  $\text{N}_2$ . The contact angle was  $(79 \pm 3)^\circ$ .

**2.3.4.2. By nucleophilic substitution: “Via amine”.** The glasses with amine terminated monolayer were treated with 10 mM solution of **1-W** in dry acetonitrile at RT following the same procedure described above, and stored for characterization. Contact angle was measured again being  $(81 \pm 3)^\circ$ .

### Generation of nanoparticles of gold

Both modified surface (“Via amine” and “Via click”) were immersed in an aqueous solution of  $\text{HAuCl}_4$  (1 mM in MilliQ water) for 48 h at  $T^\circ$  ambient. After that time the glass turned rosy. The pink glasses were then rinsed thoroughly with MilliQ water and washed in an ultrasonic bath to remove the nanoparticles that have not been anchored to the surface. The slides were dried with a nitrogen stream and stored to UV-vis, XPS, SEM-EDS and Raman-SERS measurements. In all cases, the negative controls with glass without carbene complex were done.

## 3. Result and discussion

### 3.1. Silanization of glass surface

The glass surfaces functionalization was started by formation of terminated bromo mono-layer and characterized firstly by contact angle and then by XPS in order to analyze the superficial chemical composition after the silanization process. First, a broad scan survey spectrum was obtained (from 1000 to 0 eV) to identify the elements presents in each sample. After that, narrower detailed scans of selected peaks were taken and deconvoluted with a FWHM in the range of 1.4–2.5 eV. The survey spectrum (Fig. 2A, black line) obtained, show three main elements signals, one at 285.0 eV corresponding to C 1s, one peak at 102.2 eV relating to Si 2p signal, and another at 71 eV corresponding to Br 3d which clearly indicates successful modification of glass surface treated with **BUTS** agent [22]. Deconvolution of the high-resolution C 1s spectrum (Fig. 2B) based on electronegativity and the possibility of bonding arrangements show that the major contribution is at 285.0 eV from C atoms solely bond to C or H atoms, others contributions found at 282.7 eV and 287.3 eV would corresponds to C-Si bond, and C-Br bond respectively. The lower intensity of that peak is related with the radiation-sensitive of that kind of atoms [23]. In the high resolution N peak (Fig. 2C) is possible to see three kinds on nitrogen in azide moiety in excellent agreement with literature data [24]. These results are consistent with observed changes in contact angles mentioned in the experimental section.

The hydrophilic glass surfaces were treated with **AUTES**; following the procedure described in the experimental section and characterized by XPS. In survey spectrum (Fig. 3A) the signal corresponding to N 1s at 399.7 and C 2p at 285.0 eV appeared among others. The peak corresponding to N 1s was resolved in two components (Fig. 3B) that according to data from literature they are assigned to the free amino group (lower energy, at 400.5 eV) and to protonated or hydrogen-bonded nitrogen (higher energy at 402.7 eV) [25]. Deconvolution of the Si 2p peak (Fig. 3C) was performed to examine in detail the different covalent bonds present in the silanized glass which was divided into three components at 104.5, 103.5 and 102.5 eV that correspond to Si-OH, Si-O-Si and Si-C surfaces group respectively [26]. The observation of the Si-C signal confirms the attachment of the organic material to the surface although it is not totally covered as evidenced by the appearance of Si-OH signal.

In addition two components were identified by deconvolution of the C 2s peak of the amino-silaned glass. The lowest energy peak at 285.0 eV was attributed to C-C bond and the higher energy peak at 286.6 eV to C-N bond (Fig. 3D). These results are also consistent with changes in contact angles mentioned above.

### 3.2. 1-W binding to modified glass surfaces

Azide terminated surface was converted into **1-W** terminated surface by click reaction called “Via click”. This statement is supported by the appearance of the signal of W at 36.4 eV (Fig. 4A, red line) and peak of N 1s at 402.2 eV. Beside the deconvolution of the high resolution N peak shows three components, consistent with the formation of the triazole ring typical product of cycloaddition (Fig. 4B). Since the reaction occurred without Cu(I) as catalyst, it is reasonable to assume that it was through the more activated internal triple bond. On the other hand, **1-W** was anchored to the amine terminated surface by nucleophilic displacement. The peak of W on survey XPS spectrum appeared at 37.9 eV. (Fig. 4A, black line) which confirmed the anchoring of **1-W**. For both modified surfaces, “Via click” and “Via amino”, deconvolution of W signal showed the typical split of this element with a separation of 2.15 eV between electronic levels 4f 5/2 and 4f 7/2 (Fig. 4C) [23].

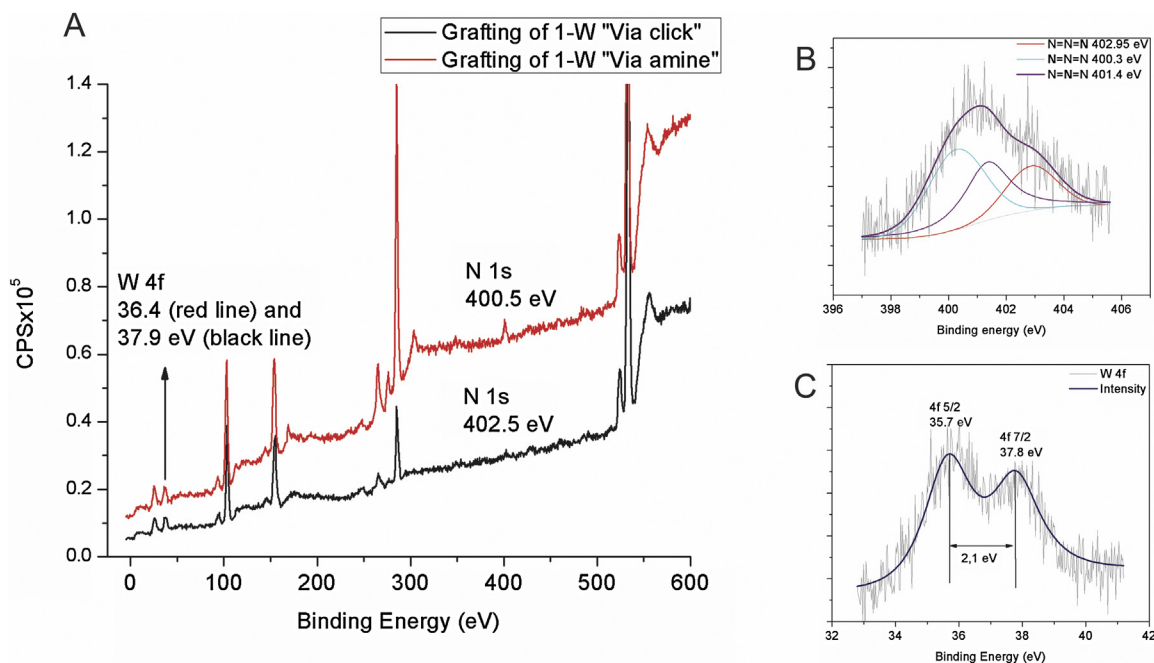
In Scheme 1, we present schematically the summary of the results described above.

### 3.3. Application of modified surfaces in the synthesis of AuNp

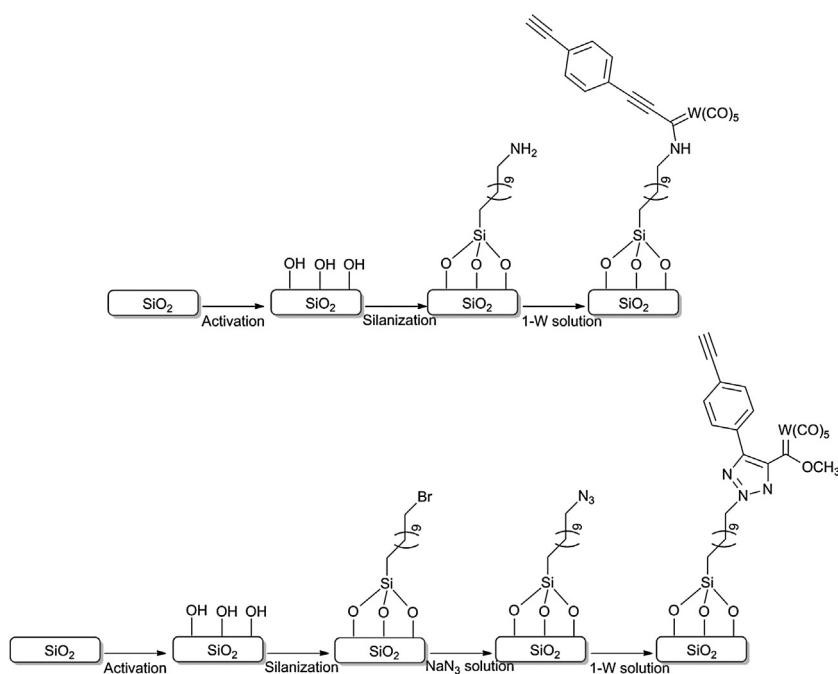
#### 3.3.1. Characterization of slides

As described in the experimental section, after 48 h the reaction between the glasses that have **1-W** attached and Au(III) solution turned the surface rose-colored. Fig. 5A the UV-vis spectrum of one of those glasses is shown. It is well known that the band-width, intensity and position of the localized surface plasmón resonance (LSPR) are related to the size, shape and the dielectric constant of the surrounding medium of the nanoparticles obtained. In this case the LSPR appeared at 549.5 nm and 551.5 nm respectively, which are LSPR characteristic of spherical AuNPs in water with a red shift associated to the surrounding medium. In order to know whether the carbene complex is solely responsible for the reduction, the respective controls were performed. Azide and amine terminated surfaces were immersed in solution of Au(III) for 48 h. After that no change was observed in the UV-vis spectrum of glasses, and EDS spectrum showed no signals corresponding to Au on surfaces.

In Fig. 5B, the ordinary Raman spectrum of the glass surface modified with **1-W** “Via amine” and the SERS spectrum of the same surface after the reaction with Au(III) solution are shown. The signal in the SERS spectrum observed confirms the presence of the gold nanoparticles and the band at  $1570 \text{ cm}^{-1}$  might be associated with the formation of amide group after the oxidation of  $\text{W}(\text{CO})_5$  moiety.



**Fig. 4.** (A) XPS survey spectra for surface with **1-W** anchored “Via click” (red line) and “Via amine” (black line), (B) deconvolution of N 1s signal corresponding to glass treated with **1-W** “Via click”. (C) Deconvolution of W 4f to the same surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

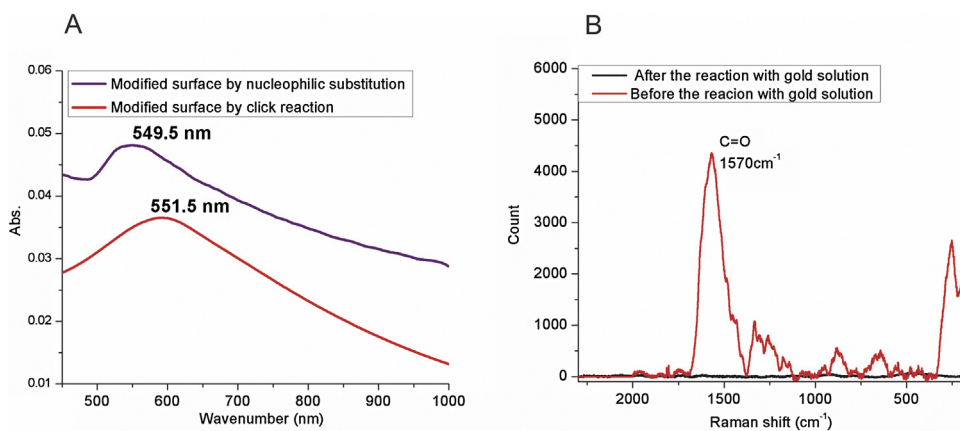


**Scheme 1.** Functionalization of glass by nucleophilic substitution “Via amine” (top) and functionalization of glass by cycloaddition reaction “Via click” (bottom).

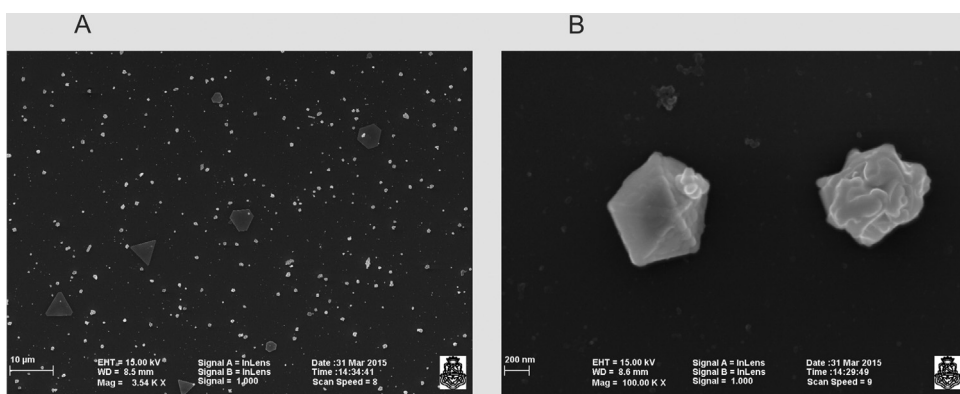
The same surfaces were metalized with Chromo for SEM-EDS measurements. The SEM images obtained are shown in Fig. 6. The 6A image showed a surface with a variety in forms and size of nanoparticles and 6B showed a two different kind of nanoparticles obtained. The crystalline planes could be associated with a slow process of formation (48 hs) or low quantities of reducer agent ( $W(CO)_5$ ) while amorphous nanoparticles could be related with a higher quantities of reducer in that zone. In regard to the size distribution, considering that the maxima of the UV–vis extinction spectra are between 550 nm and 580 nm (Fig. 5A), we can assume

that most of Nps must have a diameter between 50 and 80 nm. Furthermore, the fact that there is light scattering above 600 nm in the UV–vis spectra, is evidence that larger structures have also been generated as can be observed by SEM. The distribution of the Nps on the available surface is random without agglomeration at all.

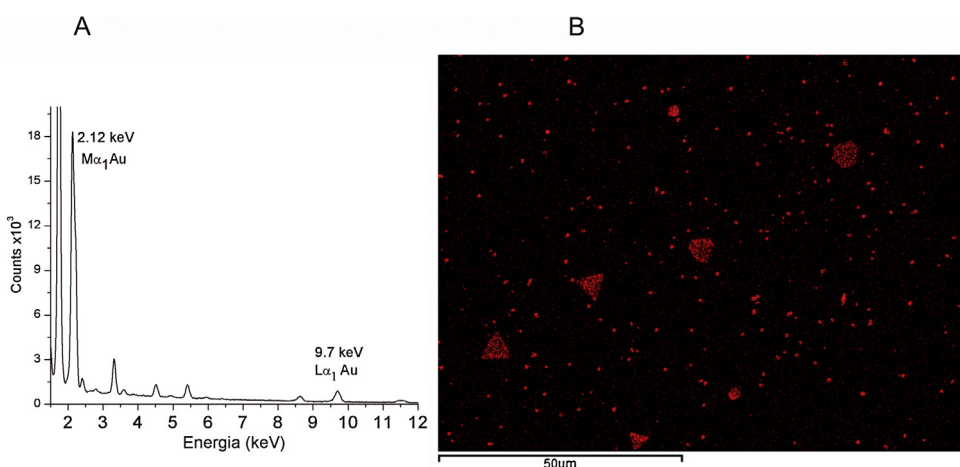
In order to confirm the elemental nature corresponding to nanoparticles observed on the glass surface, EDS and XPS measurements were done. Fig. 7A shows the EDS spectrum with signals corresponding to Au atom. In Fig. 7B is possible to see the mapped



**Fig. 5.** (A) UV-vis spectra obtained with a glass placed in the optical path. (B) Raman and SERS spectra of a glass modified “Via amine” with 1-W before of the reaction with Au(III) (black line) and after the reaction (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 6.** (A) and (B) are SEM images obtained of the surface modified with 1-W “Via amino” after 48 h in Au(III) solution.



**Fig. 7.** (A) and (B) are EDS spectrum and mapped of surface following the signal of the Au atoms, respectively.

surface following the Au signals. Comparing the SEM data (Fig. 6A) with EDS mapped surface confirm the presence of AuNPs.

Additional evidence is obtained from XPS spectral analysis. In Fig. 8A shows the XPS spectrum of the glass modified with 1-W “Via click” and the presence of Au on the surface with their expected signals at 85.5 eV, 345.5 eV and 598.5 eV is observed. Besides it can be seen in Fig. 8B, the typical split of 0.8 eV between electronic levels

5/2 and 7/2 corresponding to the 85.5 eV signals of Au 4f electrons [23].

To check the purity of nanoparticles, measurements of XRD were done (see SI Fig. 2). The sharp diffraction peaks indicate the presence of highly crystallized organization onto an amorphous glass substrate. Two sharp and weak peaks in exactly same position, at 38.3 and 44.5, were found in spectra of “Via click” and “Via amino” surfaces. They were assigned to (111) and (200) planes of crystalline

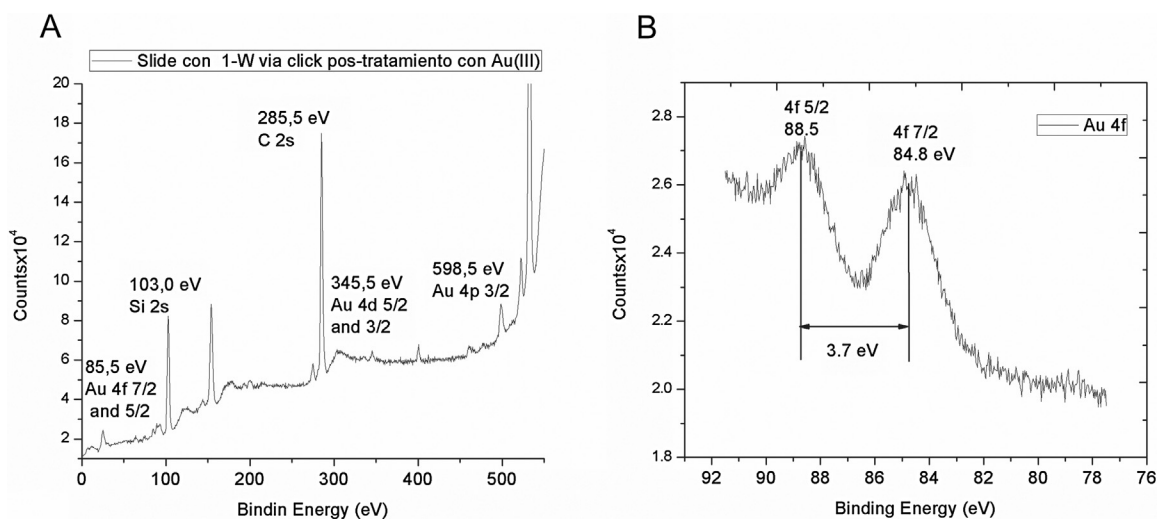


Fig. 8. (A) XPS survey spectra for surface with **1-W** anchored "via click". (B) Deconvolution of Au 4f signal of the same surface.

Gold. The small intensity of the signals is due to the relative thin layer of the nanoparticles.

#### 4. Conclusion

We have demonstrated that it is possible to anchor Fischer dialkynylalcoxy carbene complexes in a silanized glass surface by two ways, through nucleophilic substitution on carbenic carbon with surfaces bearing terminal amino groups, or by cycloaddition reaction with azide terminal groups attached to the surface. Considering the conditions under which the latter reaction is produced, seems reasonable to assume that it is regioselective respect the internal triple bond of **1-W**. It has also been shown that the carbene anchored on the surface does not lose its ability to reduce Au(III) since these surfaces generated in situ AuNPs without any other reducing agent. The AuNPs are fixed well enough to the surface to resist washing with sonication and they were shown to be very stable at ambient conditions for a long time, constituting a robust SERS substrate. In this sense, considering the high affinity of Au by sulfur compounds, these surfaces could be potential sensors of these compounds which are considered contaminants in fuels.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2016.03.214>.

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