Infrared and UV-Vis spectroscopic study of 3,7,10-substituted-phenothiazine derivatives adsorbed on gold nanoparticles

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Abstract. Absorption of 3,7,10-substituted-phenothiazine derivatives on gold nanoparticles was investigated by optical spectroscopic methods. Gold colloids provide active surfaces for the self-assembly of redox-active thiolate and disulfide phenotiazine compounds monolayers by forming one Au-S bond. The coverage of their surfaces is a long term process being accompanied by stability of the functionalized gold nanoparticles.

1. Introduction

Several studies have been reported dealing with preparation and characterization of self-assembled monolayer on various type of substrates due to their applications ranging from nanotechnology to fundamental surface science [1,2]. Particularly, gold nanoparticles (GNP) have been the subject of intense research due to their unique properties: \textit{i}) gold can be functionalized through tiol functional groups[2,3], \textit{ii}) the synthesis of size controlled GNP is quite easy, following the reduction of a gold(III) compound by a reducing agent [4,5], \textit{iii}) their plasmon characteristics can be tuned from visible domain to the near infrared one, making them ideal candidates for sensing and biolabelling [6].

Obtaining of modified nanoparticle surfaces by organic molecules is a topic of great interest. Thus, heterocyclic compounds such phenotiazine derivatives, which present remarkable pharmaceutical applications[7], represent a challenging option from this point of view. Moreover exhibiting low oxidation potential, phenotiazines can generate radical cations playing important roles in physiology [8].

In this work we report on the interaction of 3,7,10-substituted phenothiazine derivatives[9], bearing tiol and disulfide functional groups, with gold nanoparticles in colloidal organic solutions, by using optical spectroscopic (UV-Vis and FTIR) methods. These results represent primary steps for applications in chemical and biological sensing.
2. Experimental

2.1. Chemicals
The tetrachloroauric (III) acid (HAuCl₄, 99.5%) and tetrahydrofuran (THF, spectroscopic grade) were purchased from Merck. The trisodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O, 99%) and sodium borohydride (NaBH₄, 98%) were purchased from Sigma Aldrich. Deionized water (18 MΩ-cm⁻¹) was added to prepare all aqueous solutions and THF to prepare all organic solutions.

2.2. Preparation of gold nanoparticles (GNP)
GNPs were prepared by direct reduction of tetrachloroauric (III) acid with sodium borohydride in the presence of trisodium citrate[5], in order to limit the size of colloidal gold nanoparticles. Then they were subjected to repeated centrifugal purification to obtain a concentrated colloidal solution.

2.3. Preparation of functionalized GNPs
3,7,10-substituted-phenothiazine derivatives, denoted Tiol8CH₂ and BTiol8CH₂ respectively, have been synthesized according to the protocols previously described[8]. Each compound was dissolved in THF to achieve 10⁻³ M homogeneous solutions, and then was added in 3:1 v/v ratio to the colloidal concentrated aqueous solution. The samples were kept at room temperature in dark sealed vessels and investigated by optical spectroscopic methods after 24 h and seven months, respectively.

2.4. Instrumentation
The UV-Vis absorption spectra were recorded on a Jasco V550 UV-Vis spectrophotometer in the 190-900 nm wavelengths range with a 2 nm resolution, using 10 mm length quartz cells. FTIR measurements were performed in the range 4000 to 350 cm⁻¹ on a JASCO 6100 spectrometer (single beam) with a 2 cm⁻¹ resolution, and 512 scans were performed to collect each spectrum. KBr pellet technique for measurements in absorbance mode was employed.

3. Results and discussion
Obtaining of functionalized gold nanoparticles with 3,7,10-substituted-phenothiazine derivatives consisted of two main steps: the first, GNPs synthesis and centrifugal cleaning, the second, adsorption of organic molecules onto the obtained gold nanoparticles.

3.1. UV-Vis characterization
The bare and the functionalized GNPs, in their appropriate solutions, were characterized by UV-Vis spectroscopy. The visible absorption spectra of the gold solution (figures 1 and 2) presents a well-defined peak with maximum at λ_max = 528 nm, characteristic for plasmon (SPR) absorbance of nanometric Au particles ascribed to an average size bellow 10 nm.

The interaction of GNPs with compound Tiol8CH₂ (figure 1) bring about a significant decrease of the (SPR) peak intensity, as well as a red-shift of 15 nm (λ_max = 543 nm). This effect can be assigned to the chemical adsorption of organic molecules on the gold surface through the sulfur atom, followed by their aggregation. Two additional peaks of low intensity at 686 nm and 731 nm come to support this tendency.

In case of BTiol8CH₂ interaction with GNPs, there are noticeable two maxima of absorption, at 532 nm and at 743 nm (figure 2). Taking into account that both experiments were carried out in the same conditions and the spectra are comparable on the absorbance scale, one can consider that compound BTiol8CH₂ was chemisorbed on the gold surface, but the aggregation tendency of capped nanoparticles is bigger- the red-shift being considerable. The UV-Vis spectra of the considered phenothiazine compounds exhibit no absorption bands in the visible range of wavelengths, their maxima lying in the 200-350 nm UV range.

The S–H bond of the tiol and S-S bonds of the disulfide will be broken during adsorption onto the gold surface resulting in individual fragments stabilizing the metal particles. The generated
nanoparticles were highly stable both in THF solution as well as in the solid state. Solubility characteristics do not change over 7 months, but UV-Vis spectra recorded after 7 months present a dramatically decrease of absorbance and the disappearance of the peaks around 700 nm, ascribed to the higher level of aggregation. However, the main absorption maxima (543 nm and 532 nm) do not shift once the deposition is finished, revealing that the aggregation or decomposition does not occur.

**Figure 1.** UV-Vis spectra of Au colloidal solution and of Tiol8CH2 adsorbed on GNPs in THF solution after 24 h and 7 months, respectively.

**Figure 2.** UV-Vis spectra of Au colloidal solution and of BTiol8CH2 adsorbed on GNPs in THF solution after 24 h and 7 months, respectively.

### 3.2. FTIR characterization

The FTIR spectra of Tiol8CH2 (figure 3) and BTiol8CH2 (figure 4), both neat and chemisorbed on GNPs, were recorded in transmission, in KBr matrix.

**Figure 3.** a) FTIR spectra of Tiol8CH2, neat and adsorbed on GNPs, in KBr matrix, b) Tiol8CH2.

The FTIR spectrum of neat Tiol8CH2 (figure 3) indicates the presence of three C–H stretching modes: two for the –CH\(_2\) group, consisting of one symmetric at 2852 cm\(^{-1}\) and one antisymmetric at 2929 cm\(^{-1}\) and one for the –CH aromatic group at 3056 cm\(^{-1}\). The stretching vibration characteristic of tiol group is located at 2567 cm\(^{-1}\) and those of C=\(\text{C}\) aromatic is located at 1585 cm\(^{-1}\).
The region 1500-1100 cm\(^{-1}\) exhibits medium intensity peaks assigned to the deformation frequencies, characteristic of aromatic and saturated aliphatic compounds. Thus, the 1446 cm\(^{-1}\) peak corresponds to the asymmetric bending frequency of –CH\(_2\) group and the 1342 cm\(^{-1}\) peak corresponds to the symmetric one. A sharp band is observed at 1252 cm\(^{-1}\) is assigned to a skeleton vibration. The intense band at 1110 cm\(^{-1}\) corresponds to a skeleton motion, as well as the highly coupled skeletal vibrations in the region 800-900 cm\(^{-1}\). The C-S stretching vibration is identified at 650 cm\(^{-1}\) as a weak intensity peak.

In FTIR spectrum of Tiol8CH2 adsorbed on GNPs (insert of figure 3) no peak was seen around 2567 cm\(^{-1}\) where the S-H stretching vibration normally occurs. This observation confirms that the thiol proton is lost upon surface adsorption and the resulting anion is in direct interaction with the gold atom of the GNPs surface via the sulfur atom. To avoid any doubt concerning the low intensity of the absorbance peaks in the 7 months after FTIR spectrum, we rescaled it at the intensity of the free molecule FTIR spectrum. In this respect, we have considered as reference the absorbance of the –CH\(_2\) asymmetric stretching vibration peak. Similar procedure was applied for spectrum of BTiol8CH2 adsorbed on GNPs (insert of figure 4).

![FTIR spectra of BTiol8CH2, neat and adsorbed on GNPs, in KBr matrix, b) BTiol8CH2.](image)

**Figure 4.** a) FTIR spectra of BTiol8CH2, neat and adsorbed on GNPs, in KBr matrix, b) BTiol8CH2.

The FTIR spectrum of neat BTiol8CH2 (figure 4) reveals very similar assignments with those of Tiol8CH2. The major difference consists of the lack of –SH stretching vibration. Unfortunately, the S-S vibration, located in the 450-550 cm\(^{-1}\) region, exhibits a very weak peak without relevance in infrared spectra.

FTIR spectrum of BTiol8CH2 adsorbed on GNPs (figure 4) is similar to that of Tiol8CH2 adsorbed on GNPs. It is worth mentioning that BTiol8CH2 molecule represents in fact a linear dimer of Tiol8CH2 molecule, connected through a disulfide bridge. During the adsorption of BTiol8CH2 onto the gold surface the S-S bonds are broken [10] and generate thiolate (Tiol8CH2) fragments that will bind with the gold atoms from the GNP surface. In this situation, we have the same functionalized gold nanoparticles as if we should deposited Tiol8CH2 on GNPs. However, one cannot support the chemisorption by the missing of S-S vibration but one can consider the CH\(_2\) group peak as an internal standard to validate the functionalization process comparison to Tiol8CH2, when identical sample quantities were taken into account.

To avoid any doubt concerning the low intensity of the absorbance peaks in the 7 months after UV-Vis spectra, we rescaled them at the 24h molecule UV-Vis spectra, using as reference the intensity of the absorbance peaks with maxima at 543 nm and 532nm, respectively.
4. Conclusions

In conclusion, a combined UV-Vis and FTIR spectroscopic study converge in the evidencing that phenotiazine derivatives Tiol8CH2 and BTiol8CH2 chemisorb on the surface of gold nanoparticles by forming Au-S bonds. The chemical binding of the considered organic molecules on the gold surface is accompanied by a capped-GNPs aggregation, supported by a significant red-shift of SPR absorption peak relatively to the bare GNPs. Gold colloids functionalization is a long term process, which evolves at room temperature long time after the 24 h “well-established” period for deposition. Tiol and disulfide group bearing phenotiazine derivatives in conjunction with gold nanoparticles offer a good approach for building molecular defined “blocks” useful to design chemical and biological sensing devices.

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References

[1] Ulman A 1996 Chem. Rev. 96 1533-54
[2] Love J C, Estroff L A, Kriebel J N, Nuzzo R G and Whitesides G M 2005 Chem. Rev. 105 1103-69
[3] Gooding J J, Mearns F, Yang W and Liu J 2003 Electroanal. 15 81-96
[4] Frens G 1972 Nature 241 20-2
Patil V, Malvankar R B and Sastry M 1999 Langmuir 15 8197-206
Premkumar T, Kim D, Lee K and Geckeler K E 2007 Gold Bull. 40 321-7
[5] Brown K R, Lyon L A, Fox A P, Reiss B D and Natan M J 2000 Chem. Mater. 12 314-23
[6] Barbillon G, Bijeon J-L, Plain J, Chapelle M L, Adam P-M and Royer P 2007 Gold Bull. 40 240-44
[7] Silberg I A, Cormos G and Oniciu D C 2006 Adv. Heterocycl. Chem. 90 205-37
[8] Elisei F, Aloisi G G, Latterini L, Mazzucato U, Viola G, Mioio G, Vedaldi D and Dall’Acqua F 2002 Photochem. Photobiol. 75 11-21
[9] Turdean R, Bogdan E, Terec A, Petran A, Vlase L, Turcu I and Grosu I 2009 Cent. Eur. J. Chem. 7 111-7
[10] Gropeneanu R A, Tintas M, Plion C, Morin M, Breau L, Turdean R and Grosu I 2007 J. Heterocycl. Chem. 44 521-7.