

Rapid communication

Designing functionalized gold surfaces and nanostructures for Laser Desorption Ionisation Mass Spectrometry



Rosa Pilolli ^{a,1}, Nicoletta Ditaranto ^{a,*}, Antonio Monopoli ^a, Angelo Nacci ^a,
 Francesco Palmisano ^{a,b}, Luigia Sabbatini ^{a,c}, Nicola Cioffi ^{a,b}

^a Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", via Orabona 4, 70125 Bari, Italy

^b Centro Interdipartimentale di Ricerca S.M.A.R.T., Università degli Studi di Bari "Aldo Moro", c/o Dipartimento di Chimica, via Orabona 4, 70125 Bari, Italy

^c Laboratorio di Ricerca per la Diagnostica dei Beni Culturali, Università degli Studi di Bari "Aldo Moro", c/o Dipartimento di Chimica, via Orabona 4, 70125 Bari, Italy

ARTICLE INFO

Article history:

Received 10 June 2013

Received in revised form

15 July 2013

Accepted 19 July 2013

Keywords:

Gold nanoparticles

Surface functionalization

XPS

MALDI-MS

ABSTRACT

The present work is aimed at developing gold nanostructures functionalized with antenna systems to exploit the synergistic nanostructure/antenna desorption-ionization efficiency. A potential Matrix-Assisted Laser Desorption Ionisation (MALDI) organic matrix has been modified introducing specific functional groups or molecular linker and used as a capping agent for gold nanostructures.

In particular, conjugated naphthyl-thio-derivative, i.e. 4-mercaptanaphthalene-1,8-dicarboxylic acid, was synthesized and characterized by means of nuclear magnetic resonance, UV–visible and X-ray photoelectron spectroscopies. Afterwards, the thio-derivative was used as covalent surface modifier for flat gold surfaces and nanostructured gold films. These surfaces were thoroughly characterized by means of parallel angle-resolved X-ray photoelectron spectroscopy to obtain quantitative information about elemental composition, chemical speciation, and in-depth distribution of the target chemical functional groups. Finally the compound was preliminarily tested as a non-conventional matrix in Laser Desorption Ionisation Mass Spectrometry (LDI-MS) analysis of low molecular weight biomolecules in order to assess its capability of acting as the antenna system and proton donor after covalent bonding to gold nanomaterials.

© 2013 Elsevier Ltd. All rights reserved.

The research activity in the field of nanoparticle-promoted desorption ionization (DI) processes has greatly increased in the last few years [1–9]. Despite this, a universal method providing efficient energy transfer and ionization processes for different classes of analytes and real samples is still missing. The DI efficiency remains strongly analyte-dependent. Furthermore, the positive ion mode mass spectra obtained using gold nanoparticles (AuNPs) as well as their derivatives as DI promoters often resulted in analyte fragmentation and/or in the massive presence of alkali ions adducts.

Previous studies showed that the presence of a proton donor is crucial for the ionization of polar biomolecules [10–12]; 4-

aminothiophenol (4-ATP) and 4-mercaptobenzoic acid (4-MBA) functionalized AuNPs were proposed by Russell and co-workers as proton sources [13]. The rationale was that capping AuNPs by an organic monolayer acting as an efficient proton donor, would enhance the ionization efficiency while maintaining the advantages provided by the nanomaterials.

Simplified mass spectra were obtained, due to the reduction of (i) alkali-adducts of analyte molecules, (ii) analyte fragmentation, and (iii) interfering ions ascribable to gold clusters. The tentative explanation for this observation was that the presence of an organic capping agent at the surface of the nanoparticle reduced the analyte fragmentation by decoupling the analyte from the nanoparticle itself. The chemisorbed monolayer inhibited the direct adsorption of analyte molecules onto the nanoparticle surface, thus lowering the energy required for analyte desorption and allowing a softer desorption/ionization process (lower internal energy ions). Another advantage was an increase of the useful analyte mass range for LDI-MS as a consequence of the increased analyte ions production and survival.

Recently, AuNPs functionalized by α -cyano-3-hydroxycinnamic acid (CHCA) have been proposed as an improved DI promoter

* Corresponding author. Università degli Studi di Bari "Aldo Moro", Dipartimento di Chimica, via Orabona 4, 70125 Bari, Italy. Tel./fax: +39 0805442026.

E-mail addresses: rosa.pilolli@ispa.cnr.it (R. Pilolli), nicoletta.ditaranto@uniba.it (N. Ditaranto), antomono@libero.it (A. Monopoli), angelo.nacci@uniba.it (A. Nacci), francesco.palmisano@uniba.it (F. Palmisano), luigia.sabbatini@uniba.it (L. Sabbatini), nicola.cioffi@uniba.it (N. Cioffi).

¹ Present address: Istituto di Scienze delle Produzioni Alimentari, CNR, Via Amendola, 122/O, 70126 Bari, Italy.

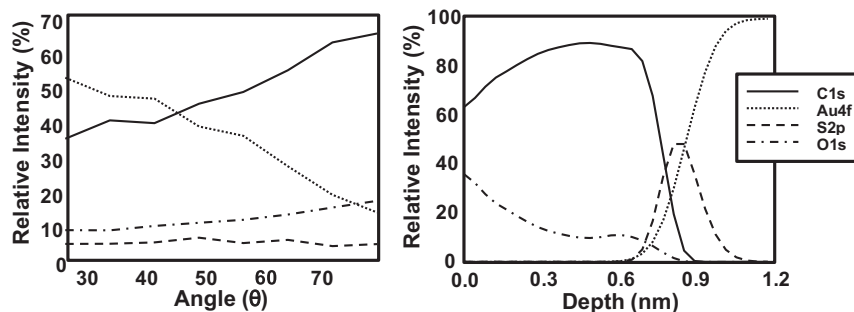


Fig. 1. Typical angle-resolved profiles of self-assembled monolayers of compound M1 on flat gold surface, obtained in AR acquisition mode. Left panel: atomic percentage profile as a function of the acceptance angle. Right panel: concentration depth profile reconstructed by means of Avantage ARProcess software (v. 4.75, © 1999–2010 Thermo Fisher Scientific).

compared to the CHCA matrix itself [14]. Gold nanophasas were capped by means of an organic hybrid shell containing a first cysteamine self-assembled monolayer that acted as a linker for the subsequent covalent binding of CHCA. However, these capped AuNPs tended to aggregate and precipitate at the edge of the sample spot, resulting in inhomogeneous spot composition. Therefore, additives, such as glycerol and citric acid, were required. Presumably, the efficiency of this hybrid nano-system is still limited, when applied to the analysis of complex samples and in our opinion this method strongly recalls the “two-phase” MALDI approach by Tanaka et al. [10], rather than being exclusively based on nanophasas.

Starting from this background, the present work aimed at developing engineered nanostructures functionalized with antenna systems to exploit the synergistic nanostructure/antenna desorption-ionization efficiency. MALDI organic matrices and/or analogous molecules have been modified introducing specific functional group or molecular linker and used as capping agent for gold nanostructure.

In particular, a conjugated naphthyl-thio-derivative, i.e. 4-mercaptanaphthalene-1,8-dicarboxylic acid (M1), was synthesized and characterized by means of nuclear magnetic resonance

(NMR), UV–visible and X-ray photoelectron spectroscopies. Afterwards, the thio-derivative was used as covalent surface modifier for flat gold surfaces, and nanostructured gold films by conventional functionalization approaches based on Au–S linking chemistry. The functionalized surfaces were thoroughly characterized by means of X-ray photoelectron spectroscopy (XPS) which provided quantitative information about elemental composition and chemical speciation of the outermost layers. Finally the compound was tested as a non-conventional matrix in MALDI-MS analysis of low molecular weight biomolecules, such as amino acids and peptides, in order to assess its capability of acting as an antenna system and proton donor after covalent binding to gold nanomaterials.

The gold flat surfaces were prepared by thermal evaporation of a 100 nm thick gold layer on silicon wafer. A thin layer of adhesion promoter (Cr) was added underneath the gold film in order to avoid peeling-off issues in solution. The resulting substrates were cleaned in freshly prepared piranha solution, exhaustively rinsed with deionized water, and dried by nitrogen.

The surface functionalization was carried out from solution as follows: the substrate was incubated for 8 h in a 5 mg/ml solution of the compound (M1) in acetonitrile/tetrahydrofuran (ACN/THF) 1:3.

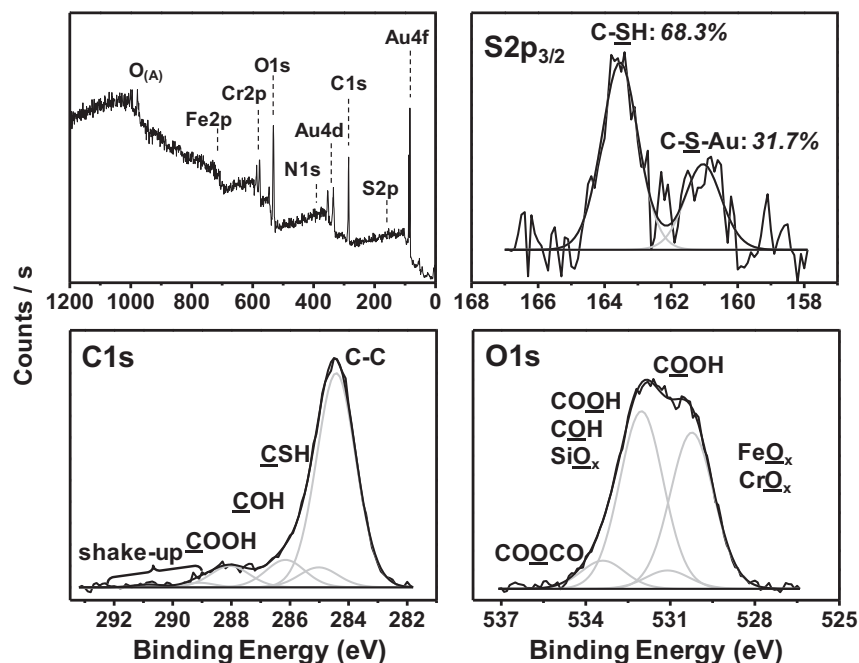


Fig. 2. Typical XPS spectra of self-assembled monolayers of compound M1 on AuNP-film in conventional acquisition mode: wide scan, C1s, S2p_{3/2} and O1s high resolution regions.

Download English Version:

<https://daneshyari.com/en/article/1688422>

Download Persian Version:

<https://daneshyari.com/article/1688422>

[Daneshyari.com](https://daneshyari.com)