



# Modified nanocellulose as promising material for the extraction of gold nanoparticles

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## ABSTRACT

Increasing number of engineering nanoparticles (NPs) in consumer products is unstoppable even after the toxic effect of metallic-based nanomaterials stated more than a decade ago; thus, selective methods for detecting metallic NPs are highly demanded and of great importance. A simple and rapid approach for detecting gold NPs (AuNPs) using ecofriendly sulfonated nanocellulose (s-NC) as sorbent material is described. The interaction between s-NC and AuNP is based on the affinity of sulfur atoms towards metals. We found that the use of cationic surfactant substantially benefitted the extraction and preconcentration of AuNPs by virtue of the NP stabilization. Good linear correlations were found in a concentration range spanned from 7 to 20 µg/mL with a detection limit of 0.26 µg/mL. Furthermore, the proposed method was successfully applied to detect AuNPs in presence of other nanowastes, opening new opportunities of creating functional materials to collect and store nanoobjects for further uses. Further experiments are directed for reaching a generalized method towards the analysis of a bigger variety of NPs covering the trending topic third facet of the analytical nanoscience and nanotechnology.

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## 1. Introduction

In recent years, the fascinating physicochemical properties of nanomaterials had entailed an exponential growth of applications, which includes many areas such as medicine, electronics, catalysts, cosmetics, food, and textile. With the nanotechnology promise to benefit the Society, this progress has forced the market with a vast of consumer goods containing large quantities of nanomaterials. As all revolutionary technologies, the impact of this growth on human health and environment is undeniable and a myriad of problems and consequences is coming to be faced. Nanotoxicology [1] is still in its infancy and there exist controversy around nanoparticle (NP) safety, which is stated to be dependent not only on their particle shape and size distribution but also on their chemical composition and stability, i.e., which is governed by their surface (both functionalities and charges) [2].

In this respect, pollution caused by nanotechnology has become one of the most urgent concerns for protecting the ecosystem [3]. Of great interest is the case of metallic NPs [4,5] by virtue of their antimicrobial

properties, being able to interact with biomolecules, cells and even organs of living organisms for its nanosize and large surface area. On the other hand, it is expected that NPs accumulate in environment, for instance after their recent applicability as promising pesticides [6], or by their released from wasted consumer products. In reaction to this, the analytical community has paid attention in creating low-cost sophisticated analytical methods with ecofriendly sorbent materials for the detection, quantification and storage of hazardous NPs.

Most of methods described for separating and detecting AuNPs involved expensive instrumentation (i.e., field-flow fractionation [7], size exclusion chromatography [8], graphite furnace atomic absorption spectroscopy [9], electrothermal atomic absorption spectrometry [10], inductively coupled plasma mass spectrometry (ICPMS) [11]) with tedious enrichment steps (i.e. liquid-liquid and solid phase extractions, cloud point extraction (CPE) [10] or disintegration of the sample (i.e., enzymatic digestion [12,13]). No digestion of AuNPs were required in a reported method [14] in which an elaborated NPs (Al<sup>3+</sup>-immobilized Fe<sub>3</sub>O<sub>4</sub>@silica@iminodiacetic acid) were used as sorbent materials for magnetic SPE to avoid gold ion interferences by ICPMS. Resins like Amberlite were also used for selective extracting plasmonic NPs via electrostatic interactions [9], being their elution easily performed with formic acid (8%) in methanol.

On the contrary of these expensive methods, the optical properties (fluorescence, absorbance, scattering) of NPs have been also explored for AuNP monitoring using inexpensive optical instrumentation like fluorescence [15] and especially UV spectrometer [16–19] by using

*Abbreviations:* AuNPs, gold nanoparticles; AgNPs, silver nanoparticles; CAPS, 3-(cyclohexylamino)-1-propanesulfonic acid; CTAC, hexadecyltrimethylammonium chloride; CTAB, hexadecyltrimethylammonium bromide; EC, capillary electrophoresis; LVSS, large-volume sample stacking; ICPMS, inductively coupled plasma mass spectrometry; TA, thiotic acid; NC, nanocellulose; NPs, nanoparticles; SDS, sodium dodecyl sulfate; SPR, surface plasmon resonance.

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preliminary extraction approaches. This is the case of the ligand-assisted extraction of AuNPs from aqueous samples using dodecanethiol in a reversed phase C-18 column [16]; however, this methodology presented disadvantages such as the use of organic solvents, a prolonged sonication periods (3 h) at low temperatures for eluting AuNPs from sorbent and the need of additional evaporation and reconstitution steps of the eluting residue. Others reported the extraction of AuNPs by their encapsulation with resorcinarene with nonpolar organic solvents like chloroform and toluene [17]. Other interesting methodology demonstrated the extraction of AuNPs using the combination of a cationic surfactant (to stabilized AuNPs) and liquid-liquid extraction in imidazolium ionic liquids (IL) [18]. However, those described methods have the drawback of using toxic liquids such as organic solvents and IL. Recently, a method for AuNP extraction and detection has been reported based on CPE using semiconductor quantum dots (SQDs) via optical incoherent light scattering of the resulting hybrid assembly [19]; however, the potential toxicity of SQDs composed of CdS is a negative aspect of the reported method.

Nanocellulose (NC), which is obtained from abundant renewable resources, is a good candidate in this matter because of their non-toxic features and impressive properties (e.g. compatibility, biodegradability, lightness, large surface area, high porosity and stiffness, mechanical and thermal stability, reactive surface, rheological properties, etc) [20,21]. Although the NC developments are still in its infancy, there are great expectations as a competitor of graphene. In the last years, functionalization approaches of the NC surface for the development of innovative analytical tools had become crucial in the adsorption efficiency, the selectivity towards the target and also the separation capacity [22,23]; Few are the analytical methods which demonstrated the advantages rendered by NC related to detection of other nanomaterials [24,25] such as silver nanoparticles (AgNPs). Thus, in those examples, NC acted as sorbent material (stem from its multiple groups, porosity and large surface area) [24] and as sensing platform (resulted from the optical transparency and suitability to accommodate specific fluorophores) [25].

Herein, this paper proposes an ecofriendly method to extract, storage and quantify AuNPs using a low-cost material consisting on NC with superficial sulfonate groups (s-NC) based on simply monitorization of the surface plasmon resonance (SPR) absorption of AuNPs. The method displayed a good sorption towards plasmonic NPs by virtue of the binding ability of sulfur towards metals.

This straightforward strategy fitted for the analysis of the nanoworld by means of using analytical nanotools, being an excellent example of the trend known as the third way of Analytical Nanoscience and Nanotechnology [26]. In this case, our method integrates low-cost instrumentation and biodegradable sorbent materials for targeting other nanosized contaminants.

## 2. Materials and methods

Information of instrumentation and reagents are given in the electronic supplementary material (EMS).

### 2.1. Synthesis of nanoparticles

The synthesis of gold nanoparticles was performed as described elsewhere [27] following the Turkevich method [28]. An aqueous solution of  $\text{HAuCl}_4$  was mixed with trisodium citrate under reflux conditions. After cooling down, the red solution was stored in an amber bottle until further use. The average size of AuNPs resulted to be 35 nm.

The preparation of s-NC by acid hydrolysis of microcrystalline cellulose (MCC) was as reported elsewhere [24]. For more details, see EMS.

### 2.2. Protocols

#### 2.2.1. Determination of the superficial charge of nanocellulose

The net surface charge of s-NC was obtained by titrating a diluted suspension containing NC with NaOH (0.5 and 0.1 M) and HCl (0.5 M) with Zetasizer instrument coupled with a titrator. The suspension was sonicated with a sonicator tip to enhance the debundling. The charge density is the average of several measurements of each suspension.

#### 2.2.2. Extraction and elution of metallic nanoparticles with nanocellulose

Previous to each experiment, the sorbent was activated by passing ultrapure water through an amount of s-NC (6 mg) placed in a 1.5 mL Eppendorf tube. Then, 50  $\mu\text{L}$  of CTAC (200 mM) was added to the solution containing metallic nanoparticles (ca. 1 mL) and then subjected to the dispersive solid phase extraction with the s-NC as sorbent. The extraction steps followed are: stirring on a vortex for 10 s, followed by sonication for 10 min, and then, centrifuged for 3 min at 1800 rpm; thus, the separation of the sorbent containing the analyte from the aqueous sample is achieved. Afterwards, the supernatant was discarded and sorbent was washed with double distilled water. Then, sonication of the sorbent with a TA solution (75 mM) for 10 min followed by centrifugation enabling the separation of the supernatant containing the eluted AuNPs. The sorbent was then washed once with methanol: water (ratio 1:1) and reused for further uses. The eluted NPs were monitored by their SPR absorption band centred at 527 nm. The morphology of eluted AuNPs was proved to be intact after the extraction process by single particle measurement using nanosight.

#### 2.2.3. Evaluation of other metal nanoparticles as interference in the determination of AuNPs

The selectivity of the method was evaluated in presence of other metal nanoparticles as  $\text{TiO}_2$  and plasmonic AgNPs. Samples containing the target analyte and the interference were tested. On the one hand,  $\text{TiO}_2$  resulted to be adsorbed onto the s-NC although no elution occurred under the protocol of the method, not altering the quantification of AuNPs. On the other hand, citrate AgNPs were retained by the sorbent and also eluted following the method conditions. Capillary electrophoresis was used to evaluate the effect of AgNPs eluted towards the determination of AuNPs; thus, electrophoretic mobilities of eluted nanoparticles were monitored by CE to inspect any AgNP-AuNP interaction. It is reported a "large-volume sample stacking" (LVSS) mode CE method that uses thiomalic acid (0.1% (w/v)) as buffer additive. In this electrophoretic modality, a large volume of sample is introduced in the capillary followed by a plug of buffer to increase the AuNP-additive interaction. Subsequently, a high negative voltage was applied for 4 min, and finally, the polarity is returned to positive to start the separation. All solutions were filtered through 0.45  $\mu\text{m}$  pore-sized nylon membranes before the analysis. The fused-silica capillary (57 cm length and 75  $\mu\text{m}$  inner-diameter) was conditioned using sequentially HCl (1 M) for 5 min, NaOH (0.1 M) for 10 min and double distilled water for 5 min. The electrophoretic running buffer was composed of SDS (40 mM) and CAPS (10 mM) with 0.1% methanol at pH 9. Eluted metallic NPs were injected into the capillary (0.5 psi for 50 s) and subsequently separated (voltage of 20 kV for less than 12 min). Between runs, the capillary was washed following the addition of HCl (1 M) for 1 min, NaOH (0.1 M) for 2 min, double distilled water for 5 min and the running buffer for 5 min.

## 3. Results and discussion

### 3.1. Sorbent material suitability

To succeed in the determination of AuNPs, the insertion of appropriate superficial groups in the sorbent material is required. Two negatively charged NC containing diverse ionizable groups (i.e. sulfonate esters (s-NC) and carboxylic groups (c-NC) on surface) were evaluated,

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