Bare gold nanoparticles mediated surface-enhanced Raman spectroscopic determination and quantification of carboxylated single-walled carbon nanotubes

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HIGHLIGHTS

- c-SWNTs have been determined in spiked river water samples by SERS spectroscopy.
- Bare AuNPs are microfiltrated on a membrane forming the SERS active substrate.
- Measured SERS intensity data were closely fit to a Langmuir isotherm.
- The use of a portable Raman spectrometer enables in situ determination of SWNTs.
- The limit of detection of the proposed methodology is $10 \, \mu g \, L^{-1}$.

GRAPHICAL ABSTRACT
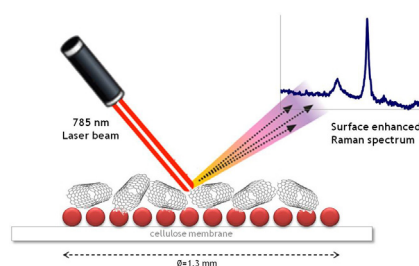
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ABSTRACT

The paper proposes a simple and portable approach for the surface enhanced Raman scattering (SERS) spectroscopy in situ determination of carboxylated single walled carbon nanotubes (SWNTs) in river water samples. The method is based on the subsequent microfiltration of a bare gold nanoparticles solution and the water sample containing soluble carbon nanotubes by using a home-made filtration device with a small filtration diameter. An acetate cellulose membrane with a pore size of $0.2 \, \mu m$ first traps gold nanoparticles to form the SERS-active substrate and then concentrates the carbon nanotubes. The measured SERS intensity data were closely fit with a Langmuir isotherm. A portable Raman spectrometer was employed to measure SERS spectra, which enables in situ determination of SWNTs in river waters. The limit of detection was $10 \, \mu g \, L^{-1}$. The precision, for a $10 \, mg \, L^{-1}$ concentration of carbon nanotubes, is 1.19% intra-membrane and 10.5% inter-membrane.

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1. Introduction

Carbon nanotubes (CNTs) have attracted much attention since their discovery [1]. The increasing use and disposal of these nanoparticles (NPs) will lead to their accumulation in the environment. The effectively monitoring of their occurrence requires the development of quantitative analytical techniques for determining their concentration in the environment. Probabilistic material flow analysis from a life-cycle perspective of engineered nanomaterials containing products has been used in order to predict the environmental concentration at which carbon nanotubes may be present.

In this sense, Gottschalk et al. [2,3] predicted CNTs concentration at the ng L^{-1} range in sewage treatment plant (STP) effluent in Europe, which is a constraint from the point of view of the actual analytical methods available for CNT detection.

Carbon nanotubes are highly water insoluble and tend to aggregate, which hampers their characterization and determination in aqueous environments [4]. In order to reduce aggregation and improve their solubility, different strategies of carbon nanotube functionalization have been developed [5–7]. Among them, carboxylation is commonly employed in industry to achieve aqueous dispersion of CNTs and further functionalization via carboxyl group [8]. As much de-bundled and individually suspended CNTs are, they will remain longer in the water column [9]. Oxidized carbon nanotubes are, thus, likely to be present in aqueous environmental compartments [10] and hence the importance of developing methodologies for their determination and quantification. There are still few approaches to their quantification in natural media. Carboxylic carbon nanotubes from surface waters have been preconcentrated by using a filter modified with carbon nanotubes and subsequently determined by capillary electrophoresis [11]. In addition, carboxylated single walled carbon nanotubes (c-SWNTs) in waters have been subjected to microliquid–liquid extraction in ionic liquid, microfiltrated in a membrane and finally determined by Raman spectroscopy [12].

Surface-enhanced Raman scattering (SERS) spectroscopy is a powerful technique for carbon nanotube characterization. SERS enhancement is produced at the so-called hot spots, consisting of two or more coupled metallic nanoparticles with closely spaced features [13]. Two mechanisms – electromagnetic and chemical – are responsible for the enhancement, the electromagnetic being the most predominant [14]. SERS substrates have been traditionally composed by highly ordered arrays of metallic nanoparticles in order to obtain high sensitivity and reproducibility [15]. An impediment for a widespread use of SERS-based sensors is the lack of facile fabrication strategies for reproducible SERS substrates with large and stable Raman enhancement [15]. SERS studies of carbon nanotubes using metallic periodic structures have been described [13,16–18], in order to investigate defects [19] and transformations [20,21] in CNT structure as well as the influence of different conditions (i.e. low temperature) [22] on the feature bands which appear in the SERS spectrum [23]. Other attempts have included the mixture of Au hydrosols and SWNTs to form a solid film [24], the deposition of a nanometric Ag layer by electron-beam metal evaporation at high pressure [25] and the use of metal-coated filter paper to study defect, diameter and SERS mechanism of SWNTs [26]. Furthermore, a modified silver electrode has been also used as substrate [27]. Recently, a 3D substrate formed by gold nanoparticles deposited at the end of vertically aligned CNTs has been described [28].

In this work, a simple SERS substrate is fabricated by using a home-made microfiltration device that allows the subsequent microfiltration of gold nanoparticles – forming the SERS active substrate – and c-SWNTs water solutions on an acetate cellulose membrane. Due to the simplicity of the procedure and the low quantities of nanoparticles needed, a new substrate is prepared for each measurement which overcomes the limitations of substrate shelf-life and reusability. The suitability of gold nanoparticles obtained by using a new synthetic procedure in which stainless steel acts as reductant agent, leading to nanoparticles without ligands or stabilizers on their surface, has been proved. Moreover, its performance has been compared with those of gold nanoparticles synthesized by citrate reduction method. The procedure shows relatively low variability being possible to fit the data with a Langmuir isotherm. Thus, the potential of the proposed procedure to quantify carboxylic carbon nanotubes in water has been demonstrated.

2. Methods

2.1. Materials and reagents

SWNTs were obtained from Shenzhen Nanotech Port Co. Ltd (NTP) (China), with a purity over 90%, an outer diameter of <2 nm, a length of 5–15 μm and a special surface area of 500–700 m^2 g^{-1}. H$_2$SO$_4$ and HNO$_3$ were purchased from Panreac (Barcelona, Spain). Acetate of cellulose membranes of 0.2 μm pore size and nylon membranes with a pore size of 0.45 μm were purchased from Sartorius Stedim Biotech (Germany) and Supelco (USA), respectively. HAuCl$_4$ (Sigma Aldrich), sodium citrate dihydrate 99.5% (Sigma Aldrich) were used to synthesize the gold nanoparticles. Before synthesis the materials were washed with a mixture 1:3 of nitric acid and hydrochloric acid (PANREAC). Chemicals were used as received with safety precautions taken as according to their respective material safety data sheet.

2.2. Equipment

Raman measurements were performed with a portable Raman spectrometer system provided by B&W TEK Inc., known as inno-Ram with a wavelength of 785 nm and a maximum laser output power of 285 mW in the probe. For measurements the laser power at the probe was 5.7 mW in order to avoid sample damage.

UV/vis measurements were performed using a halogen lamp as excitation and the monochromator and photonic detector of a PTI fluorescence Master system as a detector. TEM images were recorded using a PHILIPS CM-10 system. Characterization of the nanoparticles was performed using an AFM 5500 by Agilent equipped with NCL-W Point probe-Silicon SPM-cantilevers. For AFM studies at AuNPs, a piece of silicon wafer was covered with AuNP suspension, dried, and then imaged by AFM in tapping mode with a resonance frequency of 190 kHz and a force constant of 48 N m^{-1}. SEM measurements were performed with a Quanta 3D FEG, FEI Company (Eindhoven, Nederland) equipped with an EDX detector.

2.3. Stainless-steel assisted synthesis of gold nanoparticles

Gold nanoparticles were synthesized by using a new proposed method [29], which is based on the reduction of the HAuCl$_4$ by H$_2$ mediated by the iron contained in stainless steel at ambient conditions. All glassware was cleaned with freshly prepared aqua regia (HNO$_3$:HCl 1:3 mixture) and then rinsed thoroughly with distilled H$_2$O prior to use. A piece of 304-stainless steel (12.9 mm^2 of total surface) was introduced into 100 μL of a 0.2 mg mL^{-1} aqueous solution of HAuCl$_4$. The dimensions of the vial employed were diameter 1.3 cm and 3.3 cm height. Despite the reaction takes place at room temperature, in order to reduce reaction time, synthesis was conducted at 50 °C. The stainless steel substrate is simultaneously used as stirrer during the reaction.

2.4. Citrate reduction synthesis of gold nanoparticles

Gold nanoparticles were synthesized according to the method proposed by Turkevich et al. [30] with some modifications, as described elsewhere [31]. Firstly, the glass material was washed with a mixture 1:3 of nitric acid and hydrochloric acid and then rinsed with distilled water and dry prior use. Solutions of HAuCl$_4$ and sodium citrate were prepared in Milli-Q water and filtered through a 0.45 μm nylon membrane prior use. For the synthesis 50 mL of a 0.01% HAuCl$_4$ solution were heated while being magnetically stirred. After the boiling point, 0.254 mL of a 1% of sodium