



# Coupling shell-isolated nanoparticle enhanced Raman spectroscopy with paper chromatography for multi-components on-site analysis

Kun Zhang<sup>a,1</sup>, Jiang Qing<sup>b,1</sup>, Han Gao<sup>a</sup>, Ji Ji<sup>a</sup>, Baohong Liu<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Institute of Biomedical Sciences and State Key Lab of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China

<sup>b</sup> Technical Center for Industrial Products and Raw Materials Inspection and Testing, Shanghai Entry-Exit Inspection and Quarantine Bureau, No. 1208 Minsheng Road, Shanghai 200063, China

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## ABSTRACT

By coupling shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) with paper chromatography, two birds with one stone method were developed for simultaneous on-site separation and optical detection of multiple components. The established method features high sensitivity of plasmon-enhanced sensing strategies and sufficient temporal and spatial resolution of planar chromatographic techniques.

## 1. Introduction

The development of portable, sensitive and rapid methods to detect pollutants [1], pesticides [2], antibiotics [3] and illegal additives in foodstuffs [4] is still a major goal in food and drug safety, environmental monitoring fields. Currently, surface-enhanced Raman spectroscopy (SERS) is considered to be a promising method owing to its increased sensitivity, cost efficiency and simplicity. The combination of dramatic signal amplification with the narrow line width of SERS spectra in principle allows for multi-components detection at ultralow concentrations down to single-molecule level. However, the actual application of SERS in real-world scenarios is limited by two basic issues: (1) the abundance of molecular structure information from SERS spectra makes extracting the individual component spectral from that of a mixture a challenging obstacle. (2) most enhancing media composed of Au, Ag, or Cu suffer from a lack of substrate generality.

One of feasible strategies to solve the problem is integrating Raman detection with separation capability into a single sensing system. Several efforts have been devoted to the coupling of SERS with gas chromatography [5], high performance liquid chromatography (HPLC) [6,7] and thin layer chromatography (TLC) [8,9], where SERS was used as a readout method after the chromatographic separation, and chromatography was used as the sample pre-treatment before SERS detection. However, these techniques have some limits such as requiring expensive instrumentation, skilled personnel, or tedious process of component identification. Recently, paper-based SERS strips with high sensitivity have been developed through inkjet printing [10], deposi-

tion [11], in situ growth [12] and filtration [13]. Paper-based SERS strips possess several advantageous features in terms of simplicity, cost-effectiveness, and on-site detection. Moreover, paper strips could separate the mixtures with their inherent ability of capillary-action fluidic [14,15]. The coupling of paper chromatography (PC) with SERS has been previously performed for detection of dyes [16] and drugs [17]. All these studies involve the use of bare noble metal particles as enhancing media. The binding interaction between analytes and bare metal nanoparticles could lead to overlap and tail, interfering the spectral signatures. In addition, the exposure of enhancing media goes against the substrate stability.

Therefore, another endeavor is establishing a stable and general enhancing media for paper strips. Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) developed by Tian' group brings a key to conquer this barrier [18]. SHINERS utilizes Au nanoparticles isolated by an ultrathin silica/Al shell as the enhancing media, thus significantly extends the versatility of SERS to conform to different contours of samples and prevents the direct contact of metal nanostructures with the test molecules. Since the establishment in 2010, SHINERS has found its applications in a wide range of fields, such as detecting chemical and biological species [19,20], and probing the molecular behavior at the electrode-electrolyte interface [21,22]. Despite these advances, SHINERS by itself still cannot diminish or eliminate the spectral overlap between components, since it is essentially a vibrational spectroscopic technique evolved from SERS.

Herein, we report the first combination of PC with SHINERS for the simultaneous on-site measurement of multiple components. The PC/

\* Corresponding author.

E-mail address: [bhliu@fudan.edu.cn](mailto:bhliu@fudan.edu.cn) (B. Liu).

<sup>1</sup> K. Zhang and J. Qing contributed equally to this work.

SHINERS substrate was achieved via simple dip-coating of chromatographic paper in the colloidal suspension of Ag@SiO<sub>2</sub> core/shell nanoparticles. Using Ag nanosphere that is isolated by a thin layer of SiO<sub>2</sub> as the enhancing unit not only avoids the direct contact of metal cores with the probed species, but also protected the Ag surface from oxidation. Moreover, the SiO<sub>2</sub> layer could improve the capability of separation. The efficient blocking of the pores in the cellulosic framework by the silica could result in a more concentrated sample on the top surface of the substrate and a less binding interaction between the analyte and the cellulose. The separation and detection capabilities of such a paper-based sensing method were evaluated for analysis of sample mixtures from molecules of diverse structures and optical properties.

## 2. Experimental

### 2.1. Chemicals and materials

All chemicals were of analytical grade and used without further purification. AgNO<sub>3</sub>, ethylene glycol, ammonia aqueous solution (28 wt %), acetone, NH<sub>4</sub>NO<sub>3</sub>, tetraethyl orthosilicate (TEOS), malachite green (MG), Rhodamine 6G (R6G), 4-nitrothiophenol (4-NTP) and fluorescein were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polyvinylpyrrolidone (PVP, Mw=55000), 2,2'-di-pyridyl and 4,4'-bipyridine were obtained from Sigma Aldrich. Chromatography paper (1CHR, No.3001-917) was purchased from Whatman. Deionized water was used in all experiments.

### 2.2. Synthesis Ag@SiO<sub>2</sub> nanoparticles and PC/SHINERS substrate preparation

The Ag@SiO<sub>2</sub> nanoparticles were synthesized by the ammonia-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) on the surface of water-soluble Ag nanoparticles as described in literature [23]. The Ag@SiO<sub>2</sub> nanoparticles were then impregnated into chromatographic paper by immersing the paper into the colloidal suspension for a certain time, followed by air-drying.

### 2.3. Separation process

0.1 μL of the samples were spotted near the edge of the substrate as indicated in Scheme 1. After the droplets were dried under ambient conditions, a small amount of mobile phase solvent (~3–5) mL was placed into a glass beaker which was then covered with a glass lid to presaturate the beaker volume with solvent vapor. The substrate was then carefully placed upright into the beaker containing the mobile phase reservoir. The sample spots were in proximity to the mobile phase, but did not contact the meniscus. The development process took approximately 5 min for each plate, during which the beaker remained covered to minimize mobile phase evaporation from the paper sub-

strate..

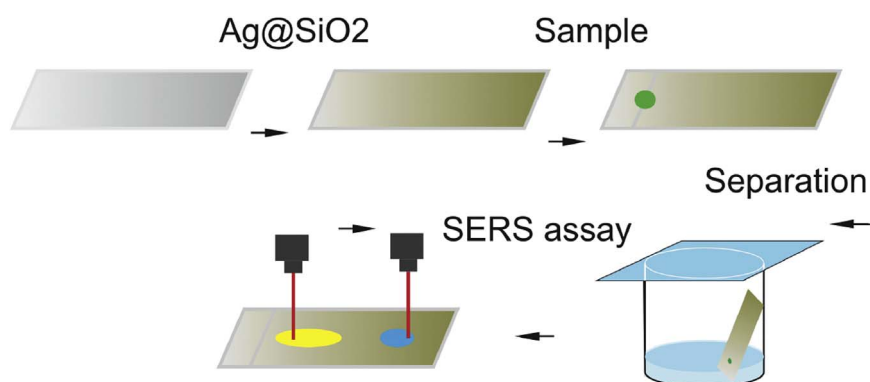
### 2.4. SERS assay

The SERS spectra were recorded from the surface of the PC/SHINERS substrate when it was completely dried using a Horiba XploRA confocal Raman microspectrometer with 632 nm excitation laser (5 mW laser power). A 10-second integration time was used, with averaging of 3 signal acquisitions.

## 3. Results and discussion

Ag nanoparticles with an average size of approximately 50 nm were produced through a solvothermal method by using ethylene glycol (EG) as the solvent, silver nitrate as the silver precursor, and polyvinylpyrrolidone (PVP) as the capping agent (Fig. 1a and Fig. S1a ESI). Particles with this size were employed based on the previously reported size-dependent SERS effect of colloidal Ag nanoparticles, more specifically, the optimal size of Ag nanoparticles for giving a maximum SERS intensity of adsorbates is within a range from 50 to 60 nm [24]. The synthesized shell isolated nanoparticles were torispherical with a plasmon peak centered at about 432 nm (Fig. S1b, ESI). The relatively broad extinction band was due to an increasing contribution of higher-order plasmon modes for larger particles. The thickness of the silica spacer was estimated to be approximately 1.5 nm by using high-resolution transmission electron microscopy (HRTEM) (Fig. S1c, ESI). The Energy dispersive spectroscopy (EDS) analysis also confirmed the successful generation of an ultrathin layer of silica on the surface of Ag nanoparticles (Fig. S1d, ESI). The Ag@SiO<sub>2</sub> nanoparticles were then impregnated into chromatographic paper by immersing the paper into the colloidal suspension for a certain time, followed by air-drying. An incubation time of 16 h was used as the best compromise between enhancing sensitivity and signal reproducibility (Fig. S2, ESI). The loading of Ag@SiO<sub>2</sub> nanoparticles into filter paper was clearly visible to the naked eye through a yellow-green color, which was arisen from the collective localized surface plasmon resonance (LSPR) absorption of Ag@SiO<sub>2</sub> nanoparticles upon assembling on the cellulose fibers of paper (Fig. 1b). It was worth to note that the particles did not desorb upon immersion in various solvents, indicating strong adsorption via van der Waals forces and hydrophobic interactions between the particles and the cellulose fibers. The Ag@SiO<sub>2</sub> impregnated paper was characterized by scanning electron microscopy (SEM) (Fig. 1c and d), which reveals assembly of the NPs into plenty of metal clusters with a surface coverage of around 65%, indicating high density of electromagnetic hot spots created on the paper surface..

We first examined the shelf stability of the paper substrate decorated with Ag@SiO<sub>2</sub> nanoparticles by using 4-nitrothiophenol (4-NTP) as a Raman probe. Fig. 2A in ESI<sup>+</sup> shows the SRES spectra of 4-NTP measured from the freshly prepared plasmonic paper and that after storage for 75 days in ambient conditions. The paper strip still



Scheme 1. Schematic representation of the paper-SERS process.

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