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Rapid fabrication of silver nanoparticle-coated filter paper as SERS substrate for low-abundance molecules detection

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ABSTRACT

Silver nanoparticles (Ag NPs) were fabricated on the fibers of the filter paper by the reaction between silver nitrate ($AgNO_3$) and hydrazine hydrate ($N_2H_4 \cdot H_2O$). By using the Ag NPs-coated paper, the limit of detection as low as 10^{-11} M for Rhodamine B (RhB) and 10^{-10} M for crystal violet (CV) was achieved. Moreover, the uniformity, reproducibility and stability of the Ag NPs-coated paper were also involved. Meanwhile, the detection of 10^{-4}–10^{-6} M moxifloxacin in deionized water and tap water was also carried out successfully by using the paper-based substrates. The fabrication process is easy to handle, cost-efficient and the as-prepared paper-based SERS substrate is ideal for rapid and simple detection of low-abundance molecules.

1. Introduction

Surface enhanced Raman spectroscopy (SERS) is a technique which overcomes the low sensitivity of normal Raman spectroscopy [1,2], and has a wide application prospect in various fields such as medical diagnosis [3,4], food safety [5,6], environment monitoring [7,8] and explosives [9].

The fabrication of the SERS substrate is one of the key processes for SERS analysis [10], thus a wide variety of materials such as glass [11], silicon wafer [12], capillary [13], adhesive tape [14] and cotton swab [15] have been used to prepare SERS substrates to accelerate the transformation of SERS technique into a practical analytical tool. However, these fabrication methods have some shortcomings such as high price, time-consuming, and the analysis of aqueous samples always requires extensive time to evaporate the water to concentrate the analyte at the silver nanoparticles (Ag NPs) [16].

Filter paper is considered to be an ideal solid substrate because of its low-cost, portability, good absorbency and biodegradability. Various methods have been developed to fabricate the metal nanoparticles onto the filter paper, such as physical vapor deposition [17], silver mirror reaction [16,18], ink-jet-printing [19] and soaking [20,21], and it is found that the paper-based SERS substrates are highly-sensitive and can be utilized for rapid, portable and in situ detection of trace amounts of samples [22,23].

Ag NPs have become the most commonly used nanostructures for SERS owing to their large enhancement factors [24]. In this paper, silver nanoparticle-coated filter paper was fabricated as SERS substrate via the reaction between silver nitrate and hydrazine hydrate, and the SERS performance of the as-prepared Ag NPs-coated paper was analyzed while crystal violet (CV) and Rhodamine B (RhB) were used as test SERS probes because these dyes are highly toxic and disturb the ecological system [25]. Besides, it is known that fluoroquinolone moxifloxacin is a fourth-generation antibacterial agent with enhanced in vitro activity against gram-positive and anaerobic bacteria widely [26]. Therefore, the Ag NPs-coated paper was also applied in the analysis of moxifloxacin in deionized (DI) water and tap water respectively. It is found that the fabrication process is easy to be applied and the paper-based substrate is ideal for the detection of low abundance molecules in water.

2. Experimental Section

2.1. Materials

All the chemical reagents used in this work, including silver nitrate ($AgNO_3$), hydrazinehydrate ($N_2H_4 \cdot H_2O$, 85 wt.%), ethylene glycol (EG), Polyvinyl pyrrolidone (PVP), RhB, CV and moxifloxacin hydrochloride ($C_{21}H_{24}FN_3O_4 \cdot HCl$) are analytically pure, and all the chemical reagents were used as received without further purification. Qualitative filter papers (medium) were obtained from Hangzhou WoHua Filter Paper Factory, and deionized water was used for all procedures.

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2.2. Characterization

The phase purity of the products was characterized by X-ray diffraction (XRD, German Bruker AXSD8 ADVANCE X-ray diffractometer) using an X-ray diffractometer with Cu KR radiation (λ = 1.5418 Å). Scanning electron microscope (SEM) images were obtained using a HITACHIS-4800 microscope (Japan). Raman spectra were measured using a Britain Renishaw inVia Raman spectrometer with a solid-state laser (excitation at 532 nm) at room temperature in the range of 500–1800 cm^{-1}.

2.3. Preparation of Ag NPs-coated Paper

85% $N_2H_4 \cdot H_2O$ was diluted with water into concentration of 10% and then mixed with 1 mol · L^{-1} PVP/EG solution by 1:1 in volume. The filter papers were cut into 1 cm × 3 cm strips and treated with 10% ammonia for 3 h to enlarge spaces between cellulosic fibers for better growth of the Ag NPs in the inner layers of the fibers [16], then the filter papers were dipped vertically into 0.5 mol · $L^{-1}AgNO_3$/EG solution. After that, the filter papers were dipped into $N_2H_4 \cdot H_2O$/PVP solution to form Ag NPs. Finally, the Ag NPs-coated papers were rinsed thoroughly with distilled water and then dried in air.

2.4. SERS Analysis

A piece of Ag NPs-coated paper (about 2 mm × 2 mm) was immersed in 200 μL of probe molecules solution for 2 h and dried in air before SERS analysis. During the SERS experiments, the excitation laser power was set at about 0.2 mW with an accumulation time of 10 s. A 20× objective was used and the laser beam was directly focused on the surface of the substrates.

3. Results and Discussion

3.1. Characterization of Ag NPs-coated Paper

In this study, a convenient procedure was introduced to fabricate Ag NPs on filter paper. $AgNO_3$ and $N_2H_4 \cdot H_2O$ solutions interacted through the reaction (Eq. 1) and Ag NPs were directly synthesized and grown on the surface of the filter paper as well as within the paper.

$$2AgNO_3 + 2N_2H_4 \cdot H_2O = 2Ag + 2NH_4NO_3 + N_2 + 2H_2O \quad (1)$$

XRD analysis was performed and the results were shown in Fig. 1. The four distinct peaks with 2θ values of 38.1°, 44.3°, 64.5° and 77.3°could be attributed to the (111), (200), (220) and (311) crystalline planes of Ag, while the other diffraction peaks at 34.2° and 46.8° were attributed to cellulose from filter paper (marked with▽) [27]. No other peaks of impurities were detected. Therefore, it can be found that the filter paper was coated with crystallized Ag.

The SEM images in Fig. 2 exhibit that plenty of Ag NPs were formed on the fibers of the filter paper. As shown in Fig. 2a, low magnification SEM image shows uniform speckled surface morphology of the paper, indicating highly uniform and dense adsorption of Ag NPs on the surface of the filter paper. Higher magnification image shows the Ag NPs decorating the fibers of the paper surface (inset of Fig. 2a).

The silver nanoparticle distribution on the filter paper was analyzed by the software of SEM image analysis (Nano Measurer System, 1.2.5). The silver nanoparticles were treated as round particles and the silver nanoparticle-aggregates were ignored because the boundaries were not clear. Totally 67 nanoparticles of the image (inset of Fig. 2a) were calculated. The results showed that the size distribution of Ag NPs varies from about 40 nm to 90 nm with an average size of about 60 nm (Fig. 2b).

According to the XRD and SEM results, it can be concluded that the filter paper was coated with dense and uniform Ag nanoparticles, and can be used for the SERS analysis.

3.2. Sensitivity, Uniform and Stability of the Ag NPs-coated Paper

SERS performance including sensitivity, uniformity, reproducibility and stability of the as-prepared paper-based substrates was analyzed in this work.

Fig. 3 presents the SERS spectra collected by using the Ag NPs-coated paper for RhB solutions of various concentrations (10^{-11}–10^{-7} M). The typical Raman peaks of RhB at 623 cm^{-1} (aromatic bending),

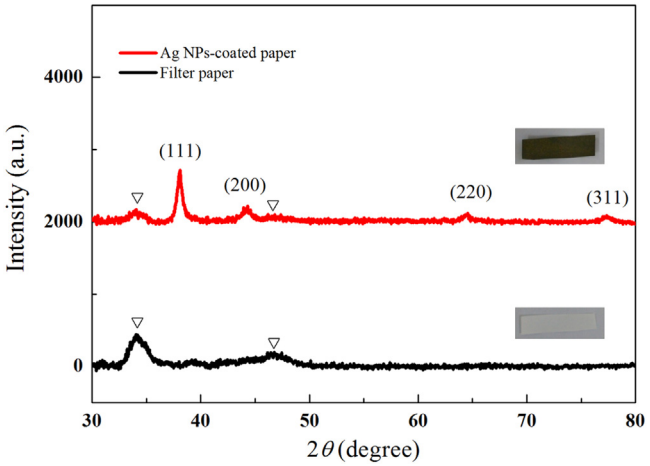

Fig. 1. XRD spectra. Insets are the photographs of filter paper and the Ag NPs-coated paper.

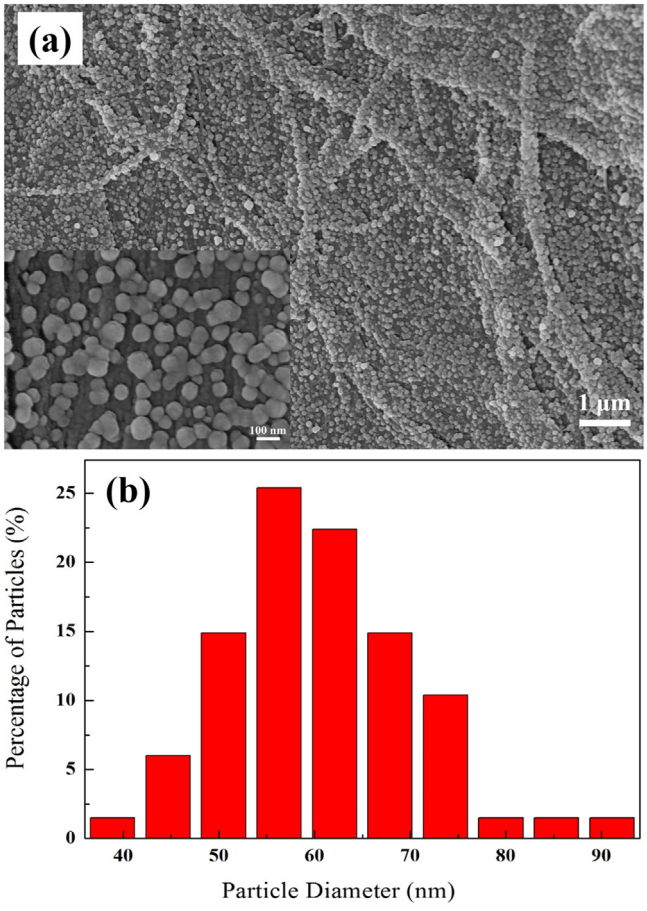

Fig. 2. (a) SEM image and (b) particle size distribution of Ag NPs-coated paper (totally 67 nanoparticles were calculated). Inset is the higher resolution image.