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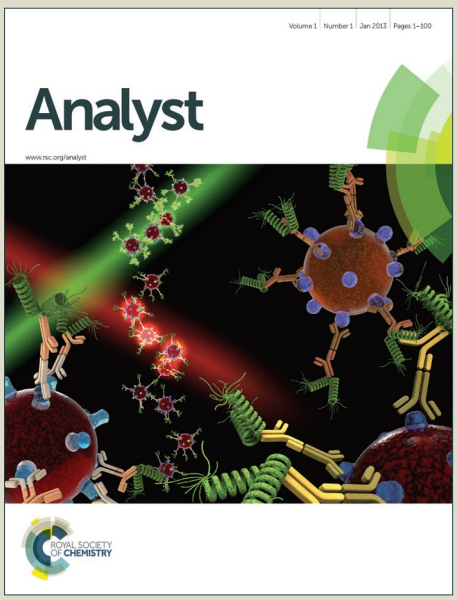

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ARTICLE

Portable Microcolumn Based on Silver Nanoparticle Functionalized Glass Fibers and Its SERS Application

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Hai-Xin Gu,[a,b] Da-Wei Li,[a] Lin Xue,[b] Yong-Feng Zhang[b] and Yi-Tao Long*[a]

We presented a facile method for the preparation of portable detection column integrated with silver nanoparticle (Ag NPs) functionalized glass fibers for surface-enhanced Raman scattering (SERS). Ag NPs were immobilized onto the surface of fibers through a two-step self-assembly process, and the cycle of assembly process was repeated to optimize the SERS activity. The optimized fibers coated with homogeneous and dense Ag NPs were combined with a glass column, displaying a good reproducibility. This combination could construct more "hot spots" and the spatial intra-channel structure for high mass transfer, and provide more sufficient interaction between probing laser and metallic nanoparticles. The capability of the prepared column for high sensitivity to dyes was demonstrated by the measurements of rhodamine 6G, alizarin red and methyl orange, with low concentrations of 28 pM, 64 pM and 0.36 nM, respectively. The SERS-active column fabricated by a facile, low-cost and high-yield approach is expected to be an effective and practical means for on-site application when rapid separation and detection of analytes in liquid sample is needed.

Introduction

The rapid detection and analysis under on-site condition has been an increasing demand for forensic investigation, environmental monitoring, food safety, and so forth. For analysis outside laboratory, portable spectrum instrument equipped with optical fiber probe giving quick and direct-read test results is considered as a more suitable candidate. Surface-enhanced Raman spectroscopy (SERS) is capable of providing both spectroscopic information of molecular structure and high-level sensitivity to trace analytes.[1, 2] Additionally, SERS is available for almost all the samples even within aqueous and biological system. Hence, SERS as a powerful and versatile analytical technique has received much attention from a wide variety of disciplines, and the rapidly increased applications of SERS have been witnessed in recent years.[3–6]

For the portable SERS detection, a multitude of research works have been undertaken on integrating SERS-active materials into inner-flow-through structured devices. White and DeVoe synthesized discrete polymer monoliths in silica capillary, and then physically functionalized silver nanoparticle aggregations within the monolith matrix for SERS detection.[7] Li et al. injected a silver colloid and analyte mixtured solution into monolithic column to develop an ultrasensitive SERS detection method.[8] These kinds of portable SERS detection devices possessed the good operability and adaptability over traditional vial colloids. However, there are several issues taken into account for real-world samples. Organic monolithic matrix may complicate the analysis as the matrix itself has Raman signals interfering spectral background. Meanwhile the uniformity of floating nanoparticles may be uncontrollable for the aggregation on the surface of the monolithic substrates. Fortunately, the immobilization of SERS-active nanoparticles onto capillary's interior surface could highly improve the reproducibility,[9] and extended the application and functionality.[10] However, this hollow structure with a thin nanoparticle layer assembled on the inner surface may provide smaller loading area and low mass transfer of samples, thus suffering from the less amount of analytes adsorption and limiting the interaction between SERS substrates and probing laser. More recently, microfluidic channel chips were developed as independent detection elements.[11–14] Whereas, micro-channel may risk blocking when injected by solid impurity contained solution.

Glass fiber is an inexpensive, flexible and widely available material that has a long history as the separation medium in real-world situation. It is also a typical material for extraction and absorption as glass fiber affords much higher surface area than that of common packing materials for the same filter volume.[15] Specially, a fine capillary structure could be constructed by numerous extremely fine fibers and the glass based material is intrinsically tolerant to biochemical or chemical circumstance,[16] serving as suitable support material for surface compounds over porous glass and silica gel.[17] And traditional glass fiber has been extended to wider usage for analytical matrix by chemically modified active coatings.[18–19]

[a] Key Laboratory for Advanced Materials and Department of Chemistry, East China University of Science and Technology, Shanghai 200237, P. R. China. E-mail: ytlong@ecust.edu.cn； Fax/Tel: +86-21-64250032
[b] Shanghai Fire Research Institute of Ministry of Public Security, Shanghai 200438, P. R. China.
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Moreover, silicon materials have been employed as a promising and effective candidate for the construction of high-performance SERS substrates, fulfilling excellent sensitivity and reproducibility.[20] Functional glass fibers for SERS detection could be prepared by Tollen's reaction to cover a silver layer onto the surface of the glass fiber filter.[21] However, this chemical reaction has to need several complicated processes prior to the accomplishments of final products. And as the reaction was undertaken under swirling or stirring, a homogeneous silver coating could hardly be formed.

A uniform and highly dense gold nanorod (AuNR) could be assembled on electrospun polycaprolactone (PCL) fibers through electrostatic interaction, and the fibrous mesh fabricated by AuNR-PCL nanocomposite achieved the detection with the concentration of 10^{-7} M for 4-mercaptopyridine and Rhodamine 6G in solution.[22] However, apart from its potential disadvantages in terms of suffering from the chemical environment and producing interfering signals, the SERS effect may be negatively influenced when the contaminant covers the surface of mesh in the case of actual situation. Moreover, a flat and thin filter or mesh may just allow smaller amount of solution and SERS-active area compared to a transparent column filled with abundant SERS-active materials.

Herein, silver nanoparticles (Ag NPs) functionalized glass fibers were fabricated as the SERS-active substrate with a facile method. The homogeneous and dense Ag NPs were immobilized onto the surface of fibers through a two-step self-assembly treatment, and the cycle of assembly was repeated to maximize the SERS activity. The flexible modified fibers were integrated with glass column as the detection device, feasible for aqueous or analytically soluble sample to separate and pre-concentrate the analytes of interest from complex substrate. Apart from its portability and practicability, this microcolumn device would also exhibit a higher enhancement of Raman signals of molecules due to its inner 3D structure constructed by the compacted fibers.[22] The schematic representation of the designed SERS-active microcolumn is shown in Fig. 1.

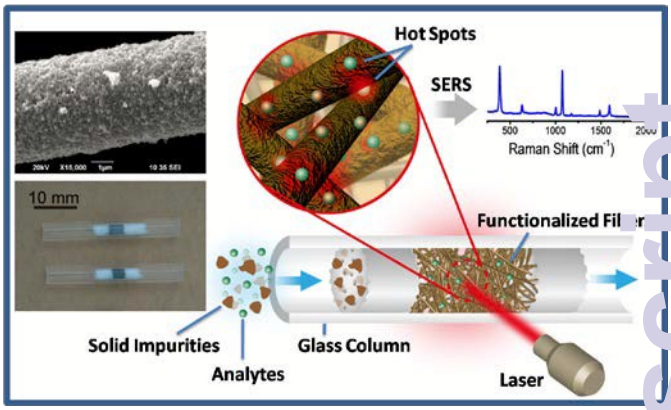

Fig. 1 Schematic illustration for SERS detection by the portable microcolumn.

Experimental

Materials

All the chemicals were used directly. Silver nitrate (99%), (3-aminopropyl) trimethoxysilane (APTMS, 97%), sodium citrate (99%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). H_2O_2 (30%), H_2SO_4 (95%–98%), methanol were obtained from sinochem Co., Ltd. (Shanghai, China). p-Aminobenzenethiol (p-ATP, 99%), rhodamine 6G (R6G, 99%), alizarin red (AR, 99%), methyl orange (MO, 99%) were purchased from Aladdin-Reagent Co., Ltd. (Shanghai, China). 18MΩ•cm deionized water produced by a Mili-Q equipment (Billerica, MA, USA) were used for washing and sampling. Glass fiber w… purchased from Perkin Elmer Co., Ltd. (Shanghai, China). Gla… column of 2.5 mm inner diameter, 4 mm external diamete… and 3 cm length was obtained from Shanghai Tokun Biotech… Co., Ltd. (Shang, China).

Apparatus

Scanning electron microscope instrument equipped with energy dispersive X-ray spectroscopy (JEOL Inc., J… 6390LA/EX-54175LMU) was used for the observations a… measurements of Ag NPs modified fibers. The Raman spectr… were recorded by a hand-held Raman spectrometer (BWS46… 785S, B&W Tek. Inc., USA) with a 785 nm excitation wavelength.

Preparation of Ag NPs modified glass fibers

Ag NPs were synthesized on the basis of a literature method.[2…] In brief, 100 mL of deionized water contained 18 mg of silver nitrate was stirred and heated from room temperature to boiling. Then, 2 mL trisodium citrate solution (1.00 wt%) w… s dropwise added. After cooling down to the room temperature, the obtained silver colloid was concentrated by centrifugation.

Microscope regular glass fiber was dispersedly soaked fo… in piranha solution (7 volume H_2SO_4 and 3 volume H_2O_2), and then rinsed by deionized water and methanol. The dried fiber was immersed in 10% APTMS methanol solution at roo… temperature for 4 h. The amino-modified glass fiber w… s rinsed with methanol, dried under vacuum, and fina… immersed in concentrated Ag NPs sol for 5h. The product w… rinsed by deionized water and left to dry under vacuum. … order to deposit abundant particles onto fiber surface, th… processes of deposition were repeated for several times.

Fabrication of SERS detection column

The produced Ag NPs-coated glass fiber was filled and condensed in glass column with the two ends fixed. …e packed column was connected to a syringe. 1mL of aqueous

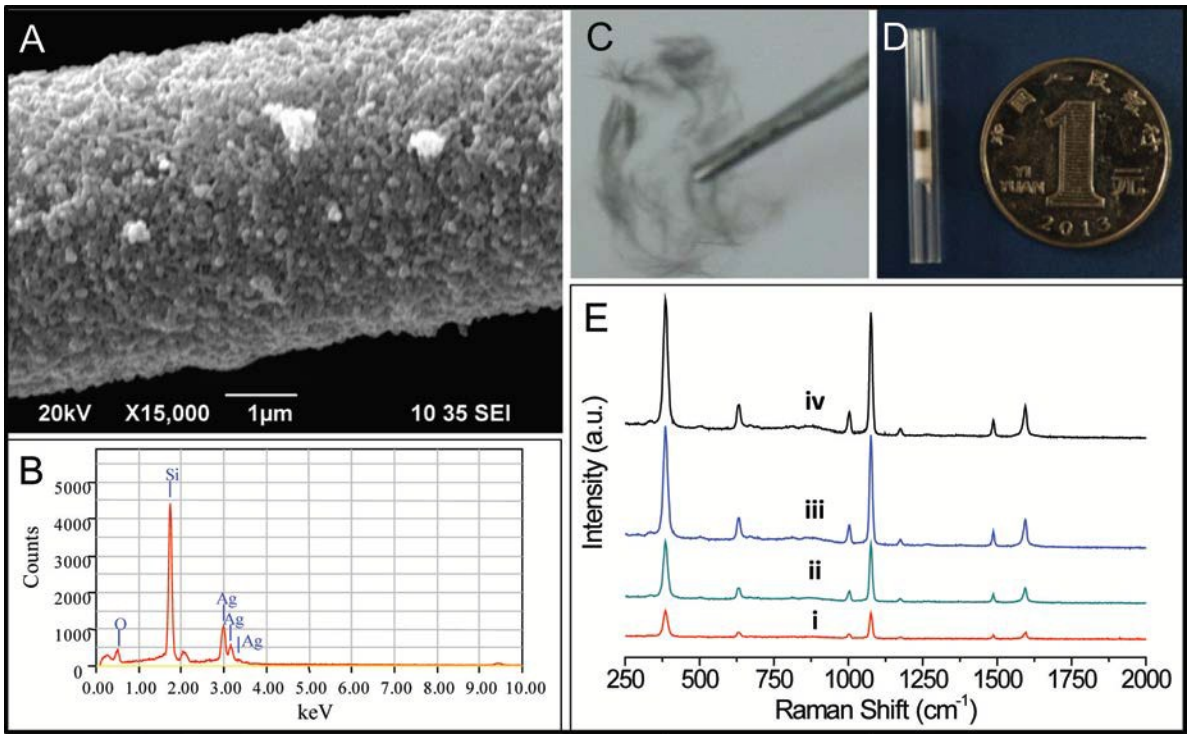

Fig. 2 (A) SEM image of Ag NPs deposited on glass fiber after three times assembly. (B) EDX spectrum of the surface of Ag NPs coated glass fiber. (C) The digital photograph of modified fibers. (D) The digital photograph of the fabricated column. (E) SERS spectra of 10^{-6} M p-ATP acquired on detection column filled with glass fibers coated by Ag NPs with one time (curve i), two times (curve ii),three times (curve iii) and four times (curve iv) deposition.

solutions with different concentrations were slowly injected through the column via the syringe, and then subjected to SERS measurements.

Results and discussion

Ag NPs prepared by wet-chemical synthesis exhibit excellent SERS activity,[23] and have become very effective base materials as SERS substrate. In order to immobilize Ag NPs onto glass fiber, the surface of glass fiber was previously hydroxylated under oxidation of piranha solution, and APTMS was bonded with exposed hydroxyl group to enable aminopropyl group to anchor Ag NPs via $-NH_2$ group by self-assembly. And the repeated self-assembly process increased density and uniformity of Ag NPs layers (see Fig. S1, S2 in ESI† and Fig. 2A). Unlike the metallic nanoparticles in native colloids, the Ag NPs were tightly bonded with silicon substrates via metal-affinitive functional group, which can effectively prevent random movement and aggregation, thus providing higher activity, stability and reproducibility for SERS measurements. The product of fabricated glass fibers after three times deposition is shown in Fig. S3 (see Fig. S3 in the ESI†). The presence of assembled Ag NPs could be verified by the measurement of EDX spectrum, as shown in Fig. 2B. It indicates that this facile fabrication method made it feasible for high-yield production.

For practical application, Ag NPs coated fibers (see Fig. 2C) were integrated with the common glass column (see Fig. 2D) as the portable SERS detection device. SERS performance of the detection column was investigated by p-ATP as the molecule probe. The compared SERS spectra of p-ATP in Fig. 2E show that SERS activity increased with the increased amount of nanoparticles. And the intensity of signals hardly improved after three times of assembly. Meanwhile, the whole surface of glass fiber was coated with uniform and dense Ag NPs aggregation layer (see Fig. 2A). In order to examine its reproducibility and reliability, we tested the different positions of the SERS-active microcolumn at random after 1mL of 1uM p-ATP solution was slowly injected through the microcolumn. Figure 3 shows the SERS spectra from the recorded 25 positions and their distributions of relative SERS intensities characterized at

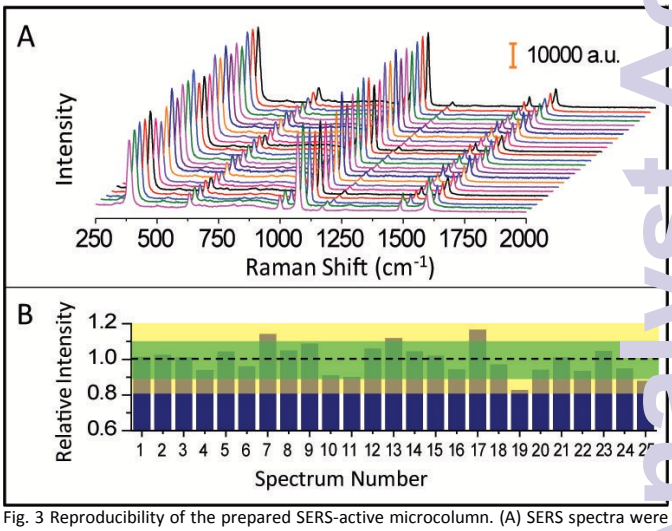

Fig. 3 Reproducibility of the prepared SERS-active microcolumn. (A) SERS spectra were randomly obtained from 25 positions. (B) Intensity distribution of the 25 spectra at the peak of 1075 cm^{-1}. The green and yellow zones represent ±10 and ±10–20% intensity variation, respectively.

the band of 1075 cm^{-1}. There located 20 records within ±10% and other 5 records within the variation range of ±10−20%. It may demonstrate a good reproducibility of SERS detection.[9, 24] This could be attributed to the regularity of the immobilized Ag NPs and inner-compacted fibers, spatially accomodating a uniform amount of Ag NPs within the laser explored region.

Moreover, the capability of the column for label-free SERS detection of dyes was demonstrated by determining organic dyes of the rhodamine 6G (R6G), alizarin red (AR), methyl orange (MO), which would display its potential application in food safety, environmental monitoring and forensic purpose. Additionally, the concentrations as low as 2.8×10^{-11} M, 6.4×10^{-11} M and 3.6×10^{-10} M were achieved for R6G (see Fig. 4), AR (see Fig. 5) and MO (see Fig. 6) respectively. Moreover, compared to flat SERS detection substrate,[25] this column device may possess superiorities on the amount of solution volume and the efficiency of sample processing. It was also found that when the molecules covered the entire surface of fibers, a higher concentration could hardly contribute to a higher SERS effect (see Fig. S4 in the ESI†).

The presence of "hot spots" and the incoming light induced interaction between molecule and nanostructured metals are two critical factors for an effective SERS detection. It demonstrates that the dense Ag NPs immobilized on the surface of fibers generated abundant and homogeneous "hot spots" from gaps between the closely packed particles. When filled into column, the flexible fiber matrixes compacted and intersected with each other, spatially increasing the additional amount of "hot spots" from junctions between the Ag NPs on two or more contacted fibers. Meanwhile, this constructed intra-channel structure could provide a high diffuse efficiency and mass transfer of analytes between sample solution and

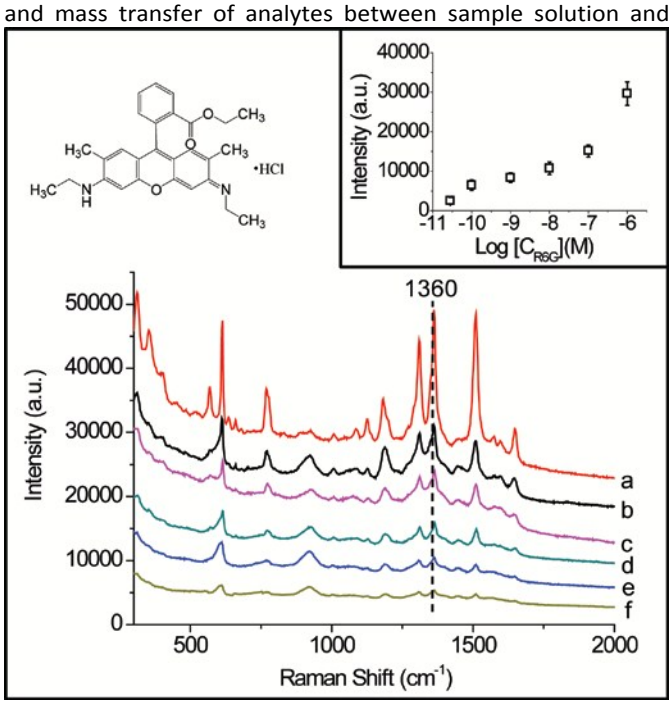

Fig. 4 SERS spectra of R6G at different concentrations of (a) 1×10^{-6} M, (b) 1×10^{-7} M, (c) 1×10^{-8} M, (d) 1×10^{-9} M, (e)1×10^{-10} M, and (f) 2.8×10^{-11} M. The insert shows a plot of signal intensities vs logarithmic R6G concentrations for the band at 1360 cm^{-1}.

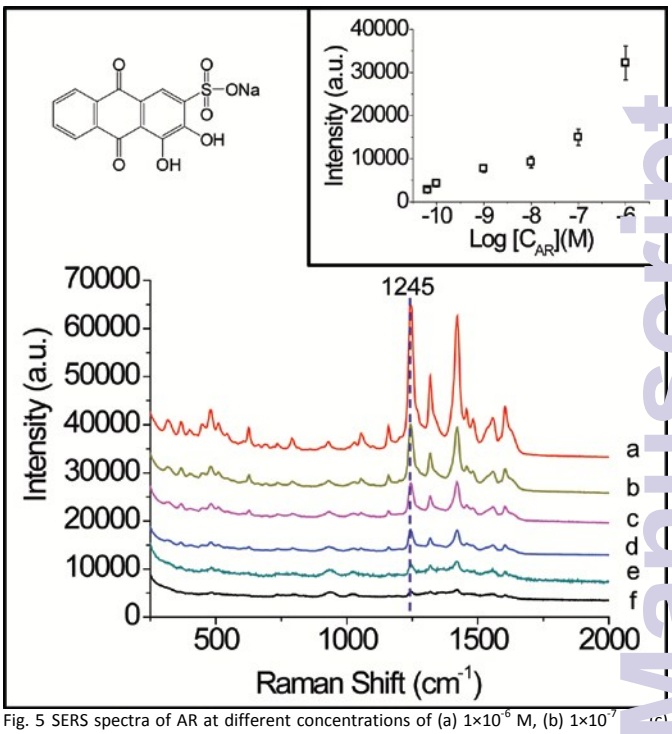

Fig. 5 SERS spectra of AR at different concentrations of (a) 1×10^{-6} M, (b) 1×10^{-7} M, (c) 1×10^{-8} M, (d) 1×10^{-9} M, and (e)1×10^{-10} M, and (f) 6.4×10^{-11} M. The insert shows a plot of signal intensities vs logarithmic AR concentrations for the band at 1245 cm^{-1}.

fillings. Therefore, it would increase the amount of absorbed molecules especially located in hot spots, thus significantly contributing to the overall SERS effect.[26] Moreover, since the incoming laser probes through the transparent glass material the compacted criss-cross structure of fibers could spatially provide more sufficient interaction between probing laser and metallic nanoparticles over the fibers placed on a planar carrier (see Fig. S5 in the ESI†), resulting in a higher SERS effect.

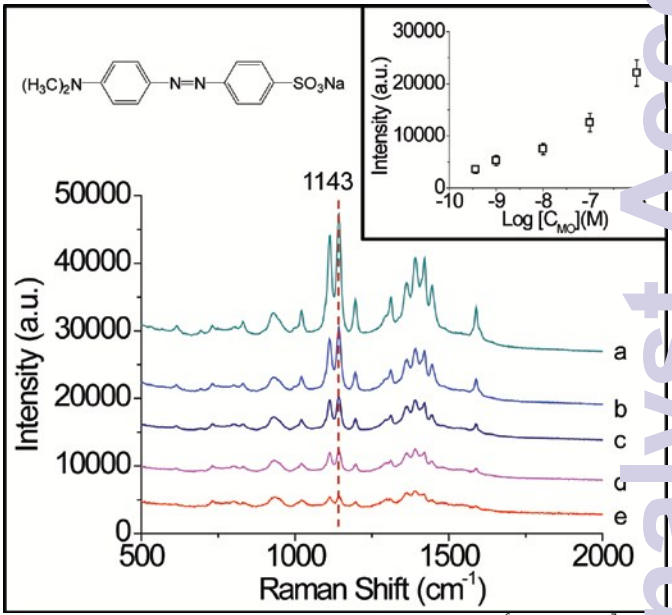

Fig.6 SERS spectra of MO at different concentrations of (a) 1×10^{-6} M, (b) 1×10^{-7} M, (c) 1×10^{-8} M, (d) 1×10^{-9} M, and (e) 3.6×10^{-10} M. The insert shows a plot of signal intensities vs logarithmic MO concentrations for the band at 1143 cm^{-1}.

Conclusions

In this work, the combination of silver nanoparticles functionalized glass fibers and glass column was introduced for rapid SERS detection. The dense and uniform layers of Ag NPs aggregation were assembled onto fibers after a three times self-assembly synthesis. The modified fibers served as functional fillings were constructed into a closed and criss-cross structure in column. In addition to the ability of separation and preconcentration of the analytes, the prepared column exhibited a good reproducibility for SERS measurement. And the high SERS activity was verified by detecting rhodamine 6G, alizarin red and methyl orange with sensitivities of 2.8×10^{-11} M, 6.4×10^{-11} M and 3.6×10^{-10} M respectively. This on-site used device would be promising as a powerful analytical platform for wide-range applications in real-world situation.

Acknowledgements

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