Supplementary Information

Facile fabrication of silver nanoparticle-coated silica-C18 core-shell microspheres and their applications in SERS detection

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General Methods

1 Materials and Apparatus

All the chemicals were commercially available and used without further treatment. Silver nitrate (99%), sodium citrate (99%), (3-aminopropyl) trimethoxysilane (APTMS, 97%), rhodamine 6G (R6G, 99%), naphthalene (99%), 2,6-dimethylnaphthalene (99%), and 1- naphthol (99%) were purchased from Aladdin-Reagent (Shanghai) Co., Ltd. Deionized water with 18 MΩ cm was used in all

experimental procedures. n-Octadecane chain (C18) functionalized silica microspheres (Welchrom C18 SPE), polypropylene hollow column, and polyethylene sieve plate with pore diameter of 20 µm were obtained from Shanghai Tokun Biotech Co., Ltd. The morphologies and compositions of the microspheres were characterized by a scanning electron microscopy instrument equipped with an energy dispersive X-ray spectrometer (JEOL, JSM-6390LA/EX-54175LMU). Raman spectral measurements were performed on a portable Raman spectrometer (B&W Tek., BWS465-785S) with 785 nm laser excitation.

2 Fabrication of the silver nanoparticle-coated silica-C18 core-shell microspheres

C18-functionalized silica microspheres were immersed and dispersed in 10% (V/V) APTMS methanol solution for 12 hours. The APTMS treated microspheres were collected on a sieve plate assembled on the bottom of a hollow column, and then rinsed separately with ethanol and water. After that, the microspheres were dried and kept in storage under vacuum. The Ag NPs coated composite microspheres were prepared on the basis of a reported method. Briefly, 300mL of water dissolving 54mg of AgNO₃ was heated to boiling. Then, 6 mL trisodium citrate solution of 1.00 wt% and 15 mg as-prepared microspheres were added slowly, and the boiling was left for 15 min. The cooled solution was concentrated to 30 mL by centrifugation, and placed for a certain time. After that, the produced microspheres were transferred from the solution onto the sieve as previously reported and washed several times with deionized water.

3 Preparation of the small detection device and its SERS detection

The detection device was comprised by a standing column base, and a sieve filled with the SERS-active microspheres was mounted on its bottom. The composite microspheres were dropwise added with 1 mL naphthalenes (naphthalene, 2,6-dimethylnaphthalene and 1- naphthol) sample solutions of different concentrations and subjected to Raman measurements.

In addition, the controlled experiments were performed with the following SERS substrates: i) the concentrated sliver nanoparticles in colloidal solution, ii) the silver

nanoparticle layer deposited on a bare silica support.

Table S1 Comparison of the SERS performance with the reported SERS sensors

Limitations of detection			Complexity	Interference	Development	Direct	Ref.
Nap	Dinap	Napol	of preparation	background	into a detection device	usability for bulk solution	
2.6×10 ⁻⁷ M	2.5×10 ⁻⁸ M	5.4×10 ⁻⁸ M	Easy	No	Yes	good	Our work
1.3×10 ⁻⁸ M	None	None	Complicated	Yes	No	good	Ref. S2
10 ⁻⁵ M	None	None	Complicated	Yes	No	poor	Ref. S3
3.9×10 ⁻⁶ M	None	None	Easy	Yes	No	good	Ref. S4
2.3×10 ⁻⁶ M	None	None	Easy	Yes	No	good	Ref. S5
1.5×10 ⁻⁶ M	None	None	Easy	Yes	No	good	Ref. S6
None	None	$2\times10^{-5}~\mathrm{M}$	Complicated	Yes	No	poor	Ref. S7
1×10 ⁻⁶ M	None	None	Easy	Yes	No	good	Ref. S8
2×10 ⁻⁷ M	None	None	Complicated	Yes	No	good	Ref. S9

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