Electronic Supplementary Material (ESI) for Chemical Communications.

AuNPs/COFs as a New Type of SERS Substrate for Sensitive Recognition of Polyaromatic Hydrocarbons

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Supporting Information

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Experimental

Reagents and Chemicals

All chemicals used in this work were at least analytical grade and used as purchased without further treatment. 18 MΩ-cm deionized water (DIW) was produced with a water purification system (PCWJ-10, Pure Technology Co. Ltd, Chengdu, China). Melamine (MA), trisodium citrate, dimethylsulfoxide (DMSO), acetone, dichloromethane, methanol and ethanol were purchased from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). The PAHs standards including acenaphthene (AcPy), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR) and benzo[a]anthracene (BaA), 3,4-benzopyrene (BaP), coronene (COR) as well as terephthalaldehyde (TA) and Rhodamine 6G (R6G), were obtained from Aladdin Reagents Co., Ltd. (Shanghai, China). Stock solution of each of the PAHs was 1 mM in methanol and stored at 4 ^{o}C until use.

Instrumentation

A Uwave-1000 microwave reactor for the synthesis of COFs was purchased from Sineo Microwave Chemistry Technology Co. Ltd. (Shanghai, China). The Raman spectra were collected with a JYHR800 (HORIBA Jobin Yvon), equipped with a 50× objective (NA=0.5), 600 lines/mm gratings and an Ar-Kr laser. The PXRD patterns were obtained from an X'Pert Pro MPD (Philips, Netherlands) X-ray diffraction spectrometer using Cu_{ka} radiation. The scanning electron microscopy (SEM) images were recorded with a JEOL JSM-7500F scanning electron microscope at 30.0 kV, and the transmission electron microscopy (TEM) images were obtained from an FEI Tecnai G2 F20 S-TWIN transmission electron microscope. The ^{13}C-NMR spectrum was recorded with a BRUKER AVANCE 400 spectrometer (Bruker, Switzerland) at resonance frequencies of 500 MHz. The FT-IR spectra (KBr pellets) were collected with a Nicolet IS10 Fourier transform infrared spectrometer (Thermo Inc., America), and the UV-vis absorption spectra were collected with a UV-1750 UV-vis spectrophotometer (Shimadzu, Japan).

Synthesis of SNW-1

The SNW-1 NPs were obtained through a one-step polycondensation reaction according to Schiff-base chemistry using a modified microwave-assisted synthetic method reported previously[1]. In brief, MA (2.40 g, 19 mmol) and TA (1.88 g, 14 mmol) were mixed and dissolved in 80 mL of DMSO and then transferred into a 200-mL three-necked round bottom flask. After ultrasonic degassed by N_2 bubbling for 30 min, the obtained clear solution was transferred into the microwave reactor and then refluxed for 4 h under nitrogen and the irradiation of microwave with the output power set at 300 w. Subsequently, the produced offwhite powder was collected by filtration over a Büchner funnel, washed with acetone, dichloromethane, and methanol in sequence, and then dried at 80 ºC under vacuum. The obtained SNW-1 NPs were homogeneously dispersed in water as stock solution for further usage.

Preparation of Au NPs

The Au NPs were prepared by the method of citrate reduction modified from the previously reported[2]. In brief, 25 mL of chloroauric acid (1 mM) in water was heated to boiling, followed by a quick injection of trisodium citrate (1% (w/v)) under vigorous stirring. The obtained solution was boiled for 30 min under continuous stirring, until the color changed from pale yellow to faint blue and suddenly turned brilliant red, which indicated the formation of monodisperse spherical Au NPs. The product was kept as stock solution of Au NPs for further usage.

Fabrication of AuNPs/SNW-1

A facile one-step method was developed herein, to fabricate the size-controlled AuNPs/SNW-1 nanocomposite *via* simple self-assembling, by mixing the obtained stock solution of SNW-1 and Au NPs under ultrasound. The obtained nanohybrids were collected after centrifugation, and then dispersed in water as stock solution until use.

SERS Analysis of PAHs

Aqueous solution of R6G or PAHs was mixed with Au NPs, SNW-1 or AuNPs/SNW-1 dispersed in water with the same volume, with 10 μL of the obtained mixture deposited on a cleaned glass slide for instant Raman scanning. Real samples for SERS analysis were collected from filtered local tap water or pond water. The Raman spectra were collected with the excitation at a wavelength of 633 nm. The data acquisition time was 1 second for R6G and 5 seconds for PAHs unless specified otherwise. The Raman peak of a silicon wafer at 520.7 cm^{-1} was used for calibration.

Figures

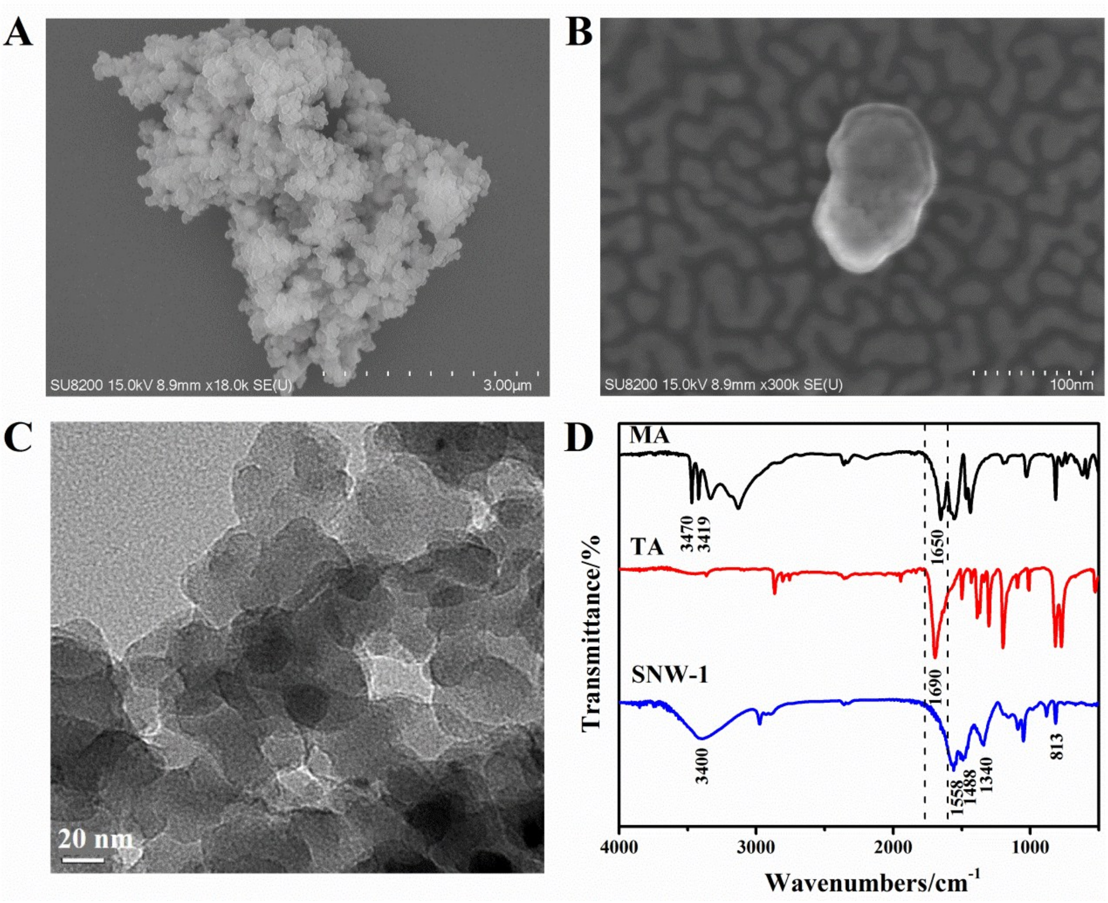


Figure S1 SEM (A&B) and TEM (C) image of SNW-1 NPs; (D) FT-IR spectra of MA, TA and SNW-1.

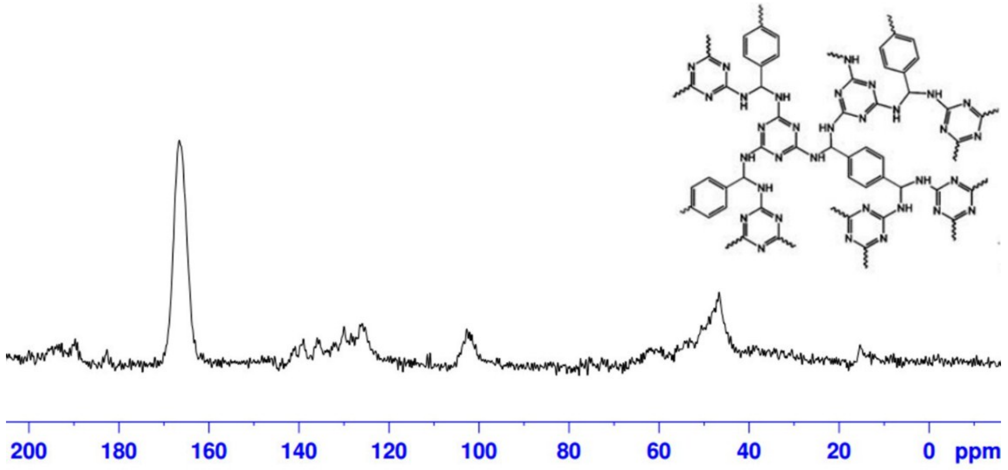


Figure S2 ^{13}C NMR spectrum of SNW-1 (inset: molecular structure of SNW-1 framework)

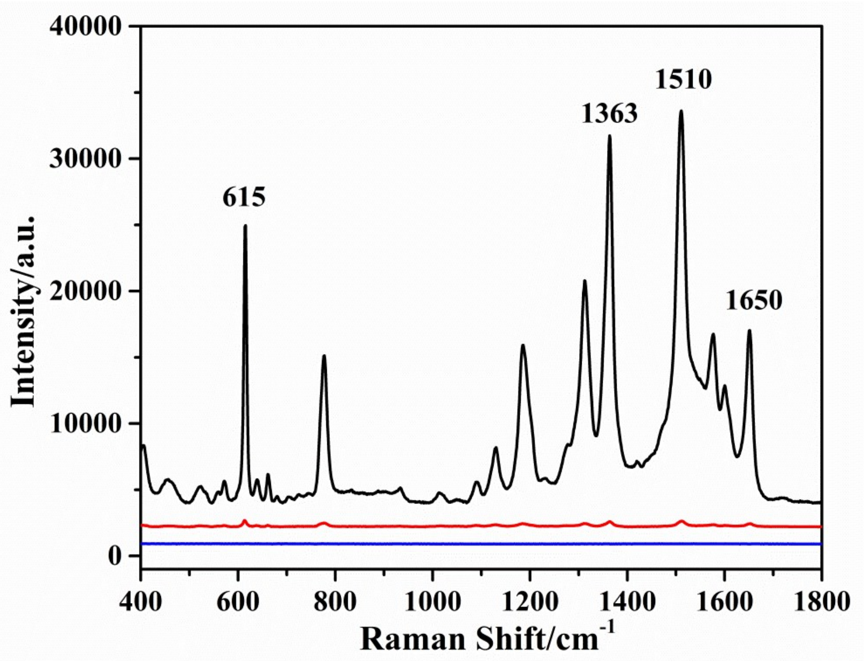


Figure S3. Raman spectra of R6G (10^{-5} M) obtained by using SNW-1 (blue), Au NPs (red) and AuNPs/SNW-1 (black) as SERS substrate, respectively.

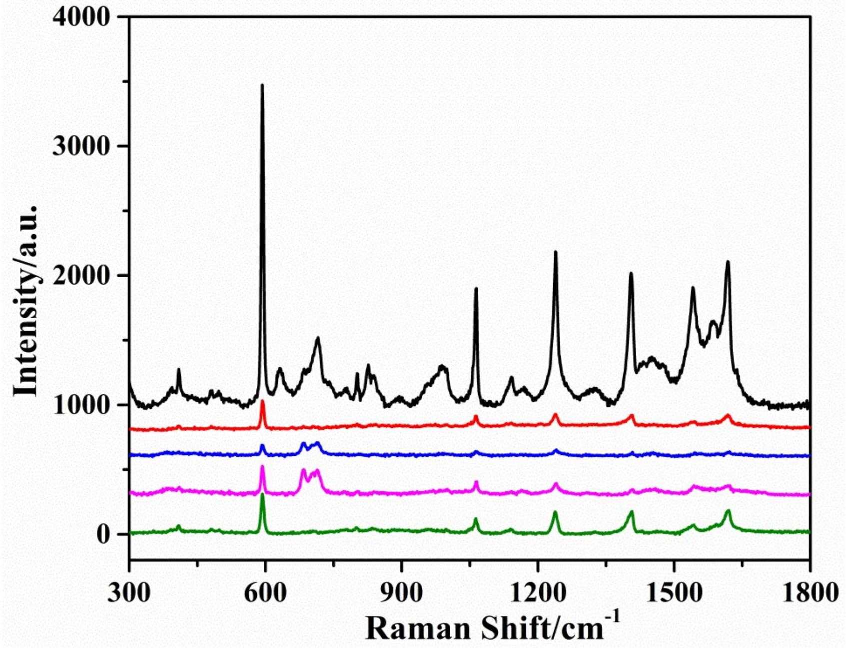


Figure S4 Raman spectra of PYR (10^{-5} M) using AuNPs/SNW-1 (black), AuNPs/TA (red), AuNPs/MA (blue), AuNPs/TA-MA (pink) and Au NPs (green) as SERS substrate, respectively.

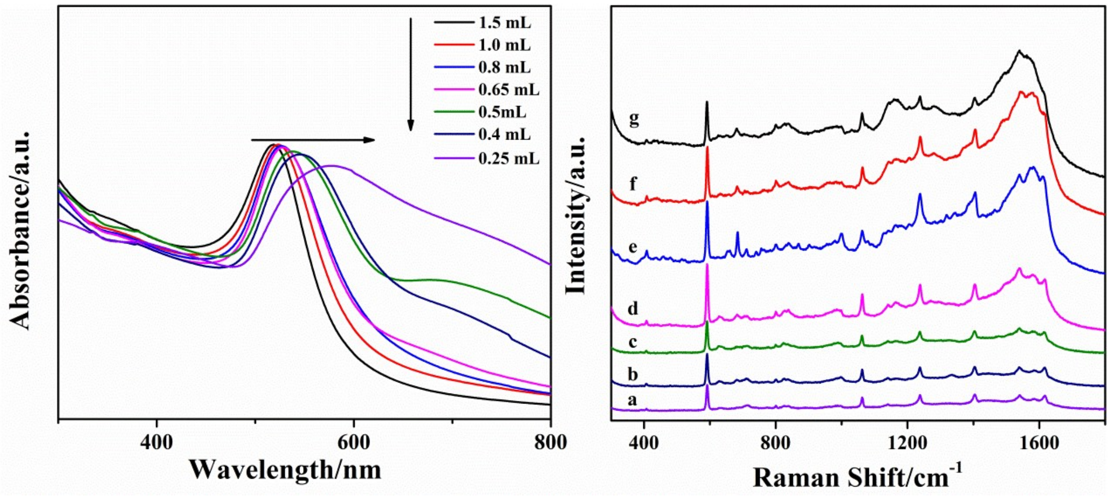


Figure S5 (A) UV-Vis spectra of Au NPs prepared with the solution of sodium citrate (0.1%, w/v) with different volumes; (B) Raman spectra of 10^{-5} M PYR obtained by using the AuNPs/SNW-1 as substrate fabricated with Au NPs prepared with the solution of sodium citrate (0.1%, w/v) with different volumes (a-g: 0.25, 0.4, 0.5, 0.65, 0.8, 1.0 and 1.5 mL).

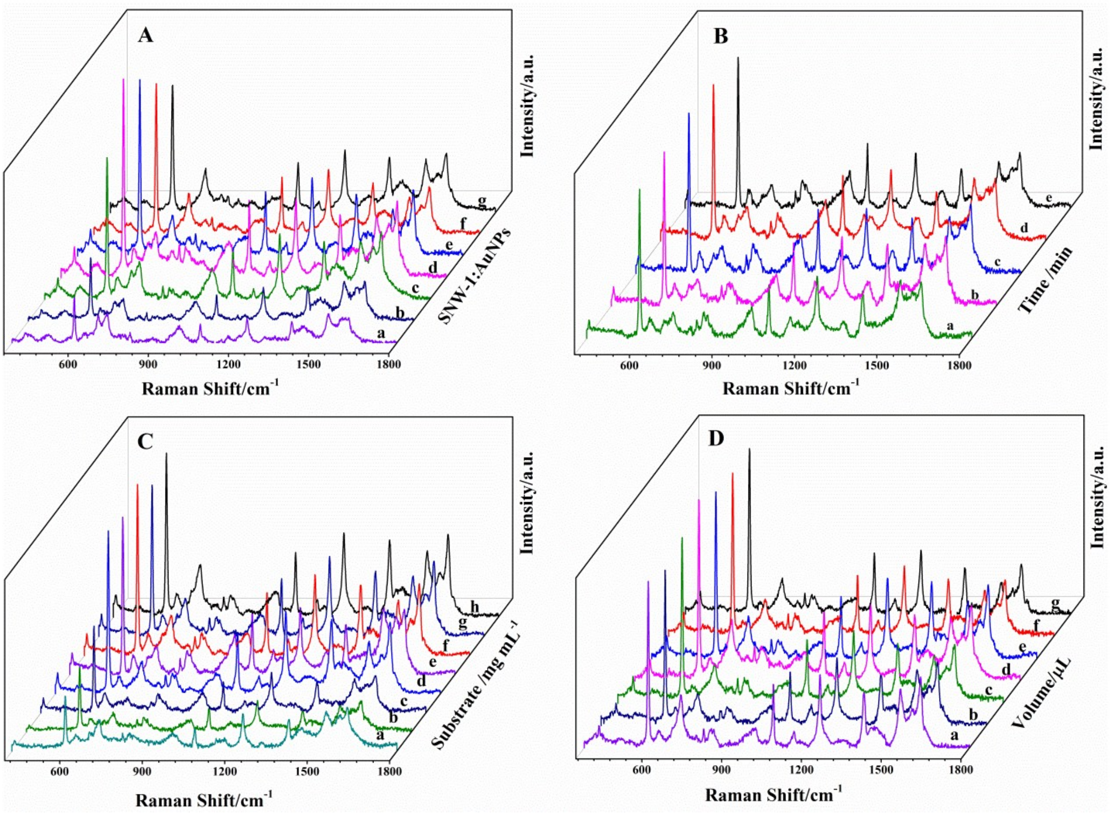
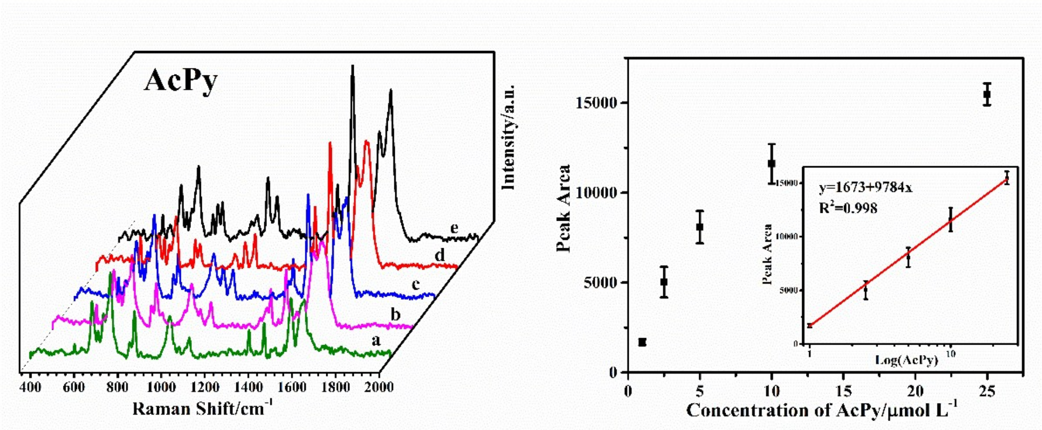
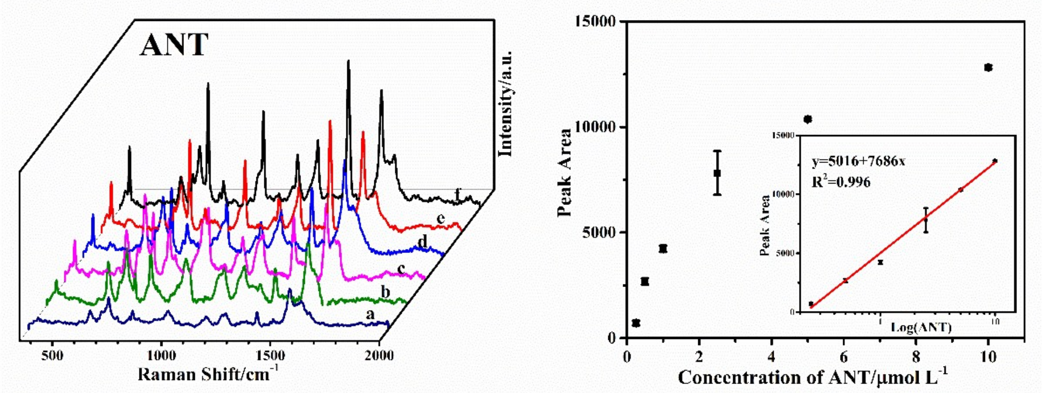
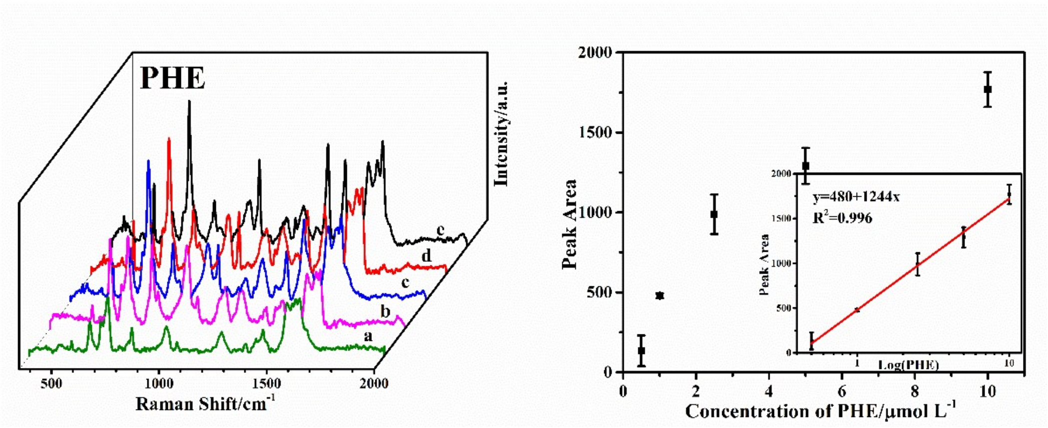


Figure S6 The Raman spectra of 10^{-5} M PYR obtained by using AuNPs/SNW-1 as SERS substrate (A) fabricated by mixing the stock solution of SNW-1 and Au NPs by different volumetric ratios (a-g: 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5); (B) fabricated for varied time (a-e: 1, 5, 10, 15, 30 min); (C) with different densities (a-h: 0.05, 0.1, 0.25, 0.5, 1, 2, 3, 5 mg mL^{-1}); and (D) mixed with PYR samples (v:v, 1:1) with different ultimate volumes (a-g: 10, 20, 50, 100, 200, 500, 1000 μL).


AcPy
Intensity/a.u.
a
b
c
d
e
400
600
800
1000
1200
1400
1600
1800
2000
Raman Shift/cm-1
Peak Area
0
5000
10000
15000
0
5
10
15
20
25
Concentration of AcPy/μmol L-1
y=1673+9784x
R2=0.998
Peak Area
5000
10000
15000
1
10
Log(AcPy)


ANT
Intensity/a.u.
a
b
c
d
e
f
500
1000
1500
2000
Raman Shift/cm-1
Peak Area
0
5000
10000
15000
0
2
4
6
8
10
Concentration of ANT/μmol L-1
y=5016+7686x
R2=0.996
Peak Area
0
5000
10000
15000
1
10
Log(ANT)


PHE
Intensity/a.u.
a
b
c
d
e
500
1000
1500
2000
Raman Shift/cm-1
Peak Area
0
500
1000
1500
2000
0
2
4
6
8
10
Concentration of PHE/μmol L-1
y=480+1244x
R2=0.996
Peak Area
0
500
1000
1500
2000
1
10
Log(PHE)

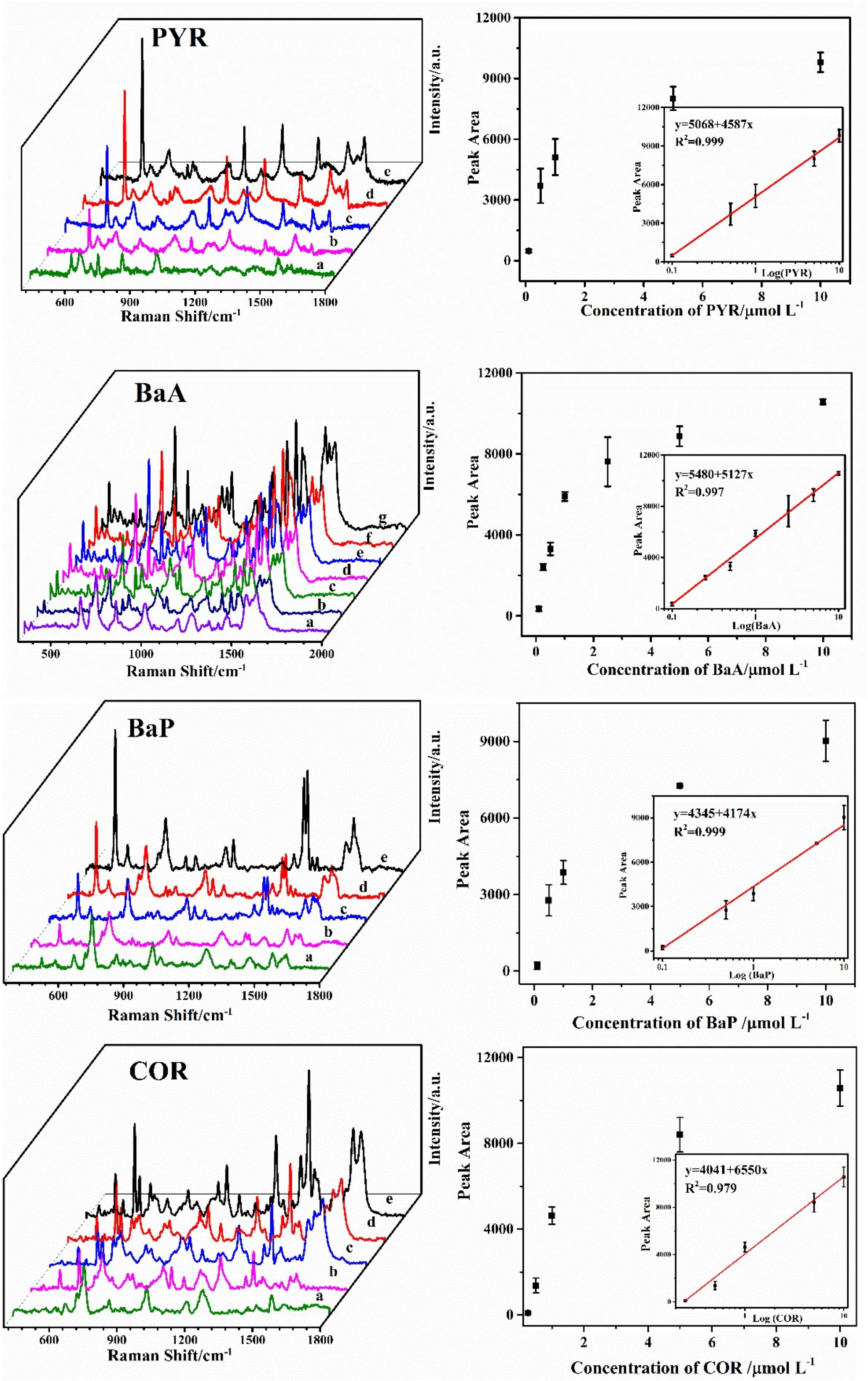


Figure S7 Left: Raman spectra by using the AuNPs/SNW-1 as the SERS substrate obtained from: AcPy of 1.0, 2.5, 5.0, 10, and 25.0 μM (a-e); ANT of 0.25, 0.5, 1.0, 2.5, 5.0 and 10.0 μM (a-f); PHE of 0.5, 1.0, 2.5, 5.0 and 10.0 μM (a-e); PYR of 0.1, 0.5, 1.0, 5.0,10.0 and 50.0 μM (a-f); BaA of 0.1, 0.25, 0.5, 1.0, 2.5, 5.0 and 10.0 μM (a-g); BaP of 0.1, 0.5, 1.0, 5.0 and 10.0 μM (a-e); COR of 0.25, 0.5, 1.0, 5.0 and 10.0 μM (a-e). Right: scatter plots of peak area of Raman spectra versus concentrations of: AcPy at 1421 cm^{-1}; ANT at 1398 cm^{-1}; PHE at 545 cm^{-1}; PYR at 591 cm^{-1}; BaA at 1392 cm^{-1}; BaP at 1383 cm^{-1}; COR at 482 cm^{-1}. Inset: calibration curve of the peak area of Raman spectra versus logarithm of the concentration of each according PAHs. Each data point was obtained from the average value ± standard deviation for 5 randomly chosen spots on the same substrate.

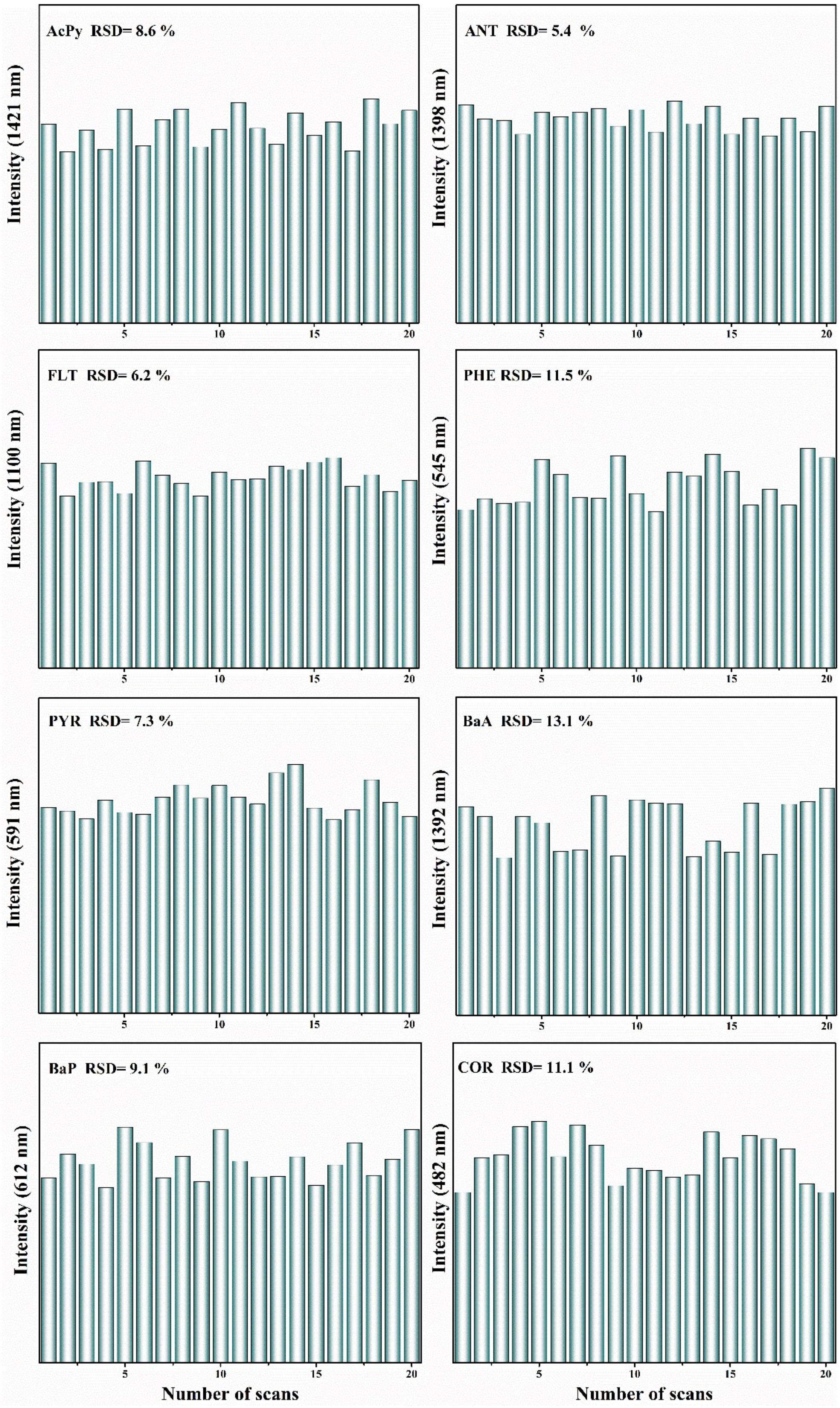


Figure S8 The intensity of one characteristic Raman peak (for demonstration) of each PAHs collected from 20 randomly selected spots on the same AuNPs/SNW-1 substrate (inset: calculated relative standard deviation of the intensity).

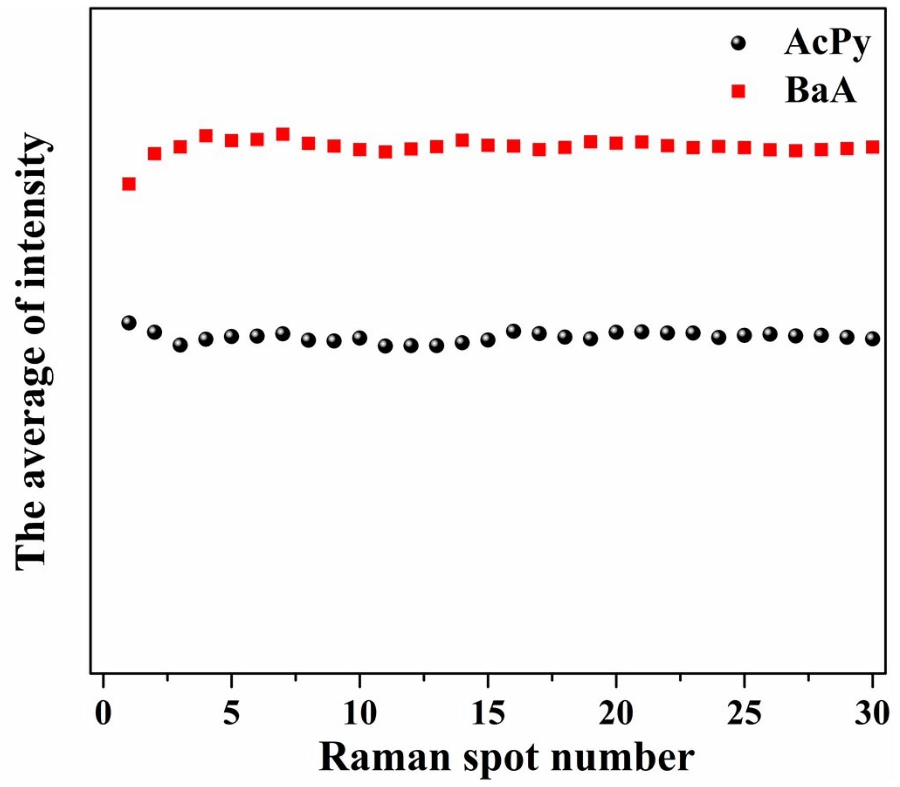


Figure S9 Averaged intensity of Raman signals obtained from randomly selected spots on the same substrate of AuNPs/SNW-1.

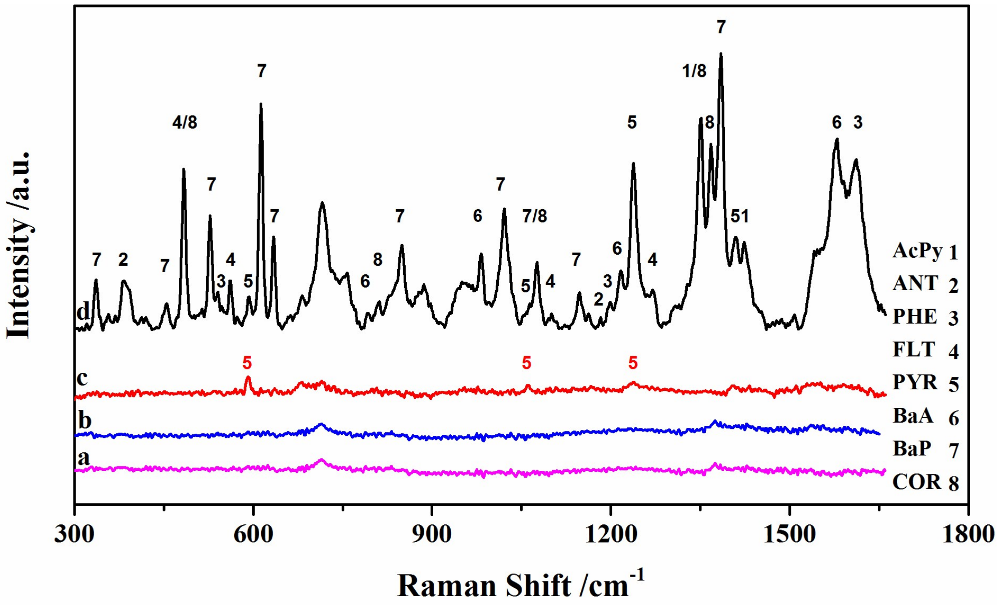


Figure S10 Raman spectra by using the AuNPs/SNW-1 as the SERS substrate obtained from blank (a), tap water sample (b), pond water sample (c) and mixture of the eight PAHs with each PAHs at a concentration of 5×10^{-6} M.

Tables

Table S1 Summary of recently reported SERS substrates used for the analysis of PAHs

Substrate	Fabrication Methods	PAHs	LOD (M)	RSD(%)	Ref.
"Au NPs decorated GMA-EDMA"	Au colloids self-assembled with amino-functionalized polymer of glycidyl methacrylate-ethylene dimethacrylate for 10 h	ANT	10^{-8}	14.8 (5)	3
		PHE	10^{-7}	N. R.	
		PYR	10^{-7}	N. R.	
"CD-SH modified Au NPs"	Au colloids functionalized with per-6-deoxy-(6-thio)-β-cyclodextrin overnight	ANT	10^{-7}	N. R.	4
		PYR	10^{-8}	N. R.	
"Au NPs/Ni foam-1-octadecanethiol"	Ni foam soaked in $HAuCl_4$ to grow Au NPs on the surface, then modified with 1-octadecanethiol for 6 h	PYR only	10^{-8}	0.98 (3)	5
"Au-DS-$C_{10}H_{21}$"	Incubated Au nanorod arrays in 4-dodecylbenzenediazonium-tetrafluoroborate in H_2SO_4 at 40 °C for 12 h	BaP	10^{-7}	<5	6
		FLT	10^{-7}		
"Fe_3O_4@Au NPs"	Fe_3O_4 particles modified with APTMS, sonicated for 30 min and stirred for 3 h, followed by addition of $HAuCl_4$ and heated to 100 °C, and then followed by addition of sodium citrate and then reacted for 20 min.	AcPy	10^{-7}	N. R.	7
		ANT	10^{-8}	10.7 (25)	
		BaA	10^{-8}	N. R.	
		BaP	10^{-8}	8.5 (25)	
		FLT	10^{-8}	N. R.	
		PHE	10^{-8}	N. R.	
		PYR	10^{-8}	N. R.	
"bare Au NPs coupled film"	Silica slides soaked in APTMS for 10 h, coated with Au film via vapor deposition, functionalized with 1-hexanethiol for 12 h, and then loaded with Au colloids	BaA	10^{-8}	N. R.	8
		FLT	10^{-8}	N. R.	
		PYR	10^{-8}	N. R.	
"AgNP functionalized with LG"	Ag NPs functionalized with bis-acridinium dication lucigenin (time not reported)	ANT	10^{-6}	N. R.	9
		COR	10^{-8}	N. R.	
		PYR	10^{-7}	2.5 (3)	
"C5 functionalized Fe_3O_4@Ag NPs"	Fe_3O_4 NPs coated with Ag layers and then functionalized with 1-pentanethiol for 4 h	ANT	10^{-6}	N. R.	10
		BaP	10^{-7}	N. R.	
		PHE	10^{-5}	N. R.	
		PYR	10^{-6}	N. R.	
"metallic	Deposited carbon nanotubes on to	PYR	10^{-9}	N. R.	11

single-walled carbon nanotubes”	Ag colloids in acetone	only			
“Has-AgNPs”	Human acids reacted with $AgNO_3$ at 90 °C for 3 h	ANT	10^{-7}	6.5 (3)	12
		BaP	10^{-8}	7.8 (3)	
		FLT	10^{-7}	9.2 (3)	
		PYR	10^{-7}	9.0 (3)	
“β-CD dimer@Ag@ SiO_2 NPs”	*β*-cyclodextrin dimer mixed with assembled Ag embedded silica NPs and stirred for 12 h	PYR	10^{-7}	N. R.	13
AuNPs/SNW-1	Au NPs were loaded to SNW-1 *via* 1-min self-assembling at room temperature	AcPy	10^{-7}	8.6 (20)	This work
		ANT	10^{-7}	5.4 (20)	
		BaA	10^{-8}	13.1 (20)	
		BaP	10^{-8}	9.1 (20)	
		COR	10^{-7}	11.1 (20)	
		FLT	10^{-8}	6.2 (20)	
		PHE	10^{-7}	11.5 (20)	
		PYR	10^{-8}	7.3 (20)	

LOD: within the linear range the lowest concentration of PAHs from which characteristic Raman spectra were obtained and reported in the according reference; RSD(%): the relative standard deviations of the Raman peak intensity of each PAHs obtained by measuring certain number (in the bracket) of randomly selected spots on the same substrate; N.R.: not reported in the according reference.

Table S2 Vibrational assignment of the wavenumbers (cm^{-1}) of PAHs and according n value

PAHs	SERS	n[a]	Assignment[b]
AcPy	550	1.8	Ring stretching
	1351	2.9	C-C stretching/ring stretching
	1421	7.2	C-C stretching
ANT	394	14.1	Ring stretching
	755	15.9	Ring C-C stretching
	1398	14.7	Ring C-C stretching/ring stretching
PHE	545	11.2	C-C-C bending
	708	16.6	skeletal deformation
	1438	16.3	C–C stretching/H-C-C bending
FLT	670	20.6	C-H stretching
	1100	16.2	C-H in-plane bending
	1421	27.0	C-C stretching
PYR	591	7.0	C-C breathing
	1239	8.7	C-C stretching/C-H in-plane bending
	1403	6.5	C-C stretching/Ring stretching
BaA	357	11.0	skeletal deformation
	722	17.5	C-H stretching
	1392	14.8	C-C stretching
BaP	612	28.0	C-H stretching
	1237	28.5	C-H in-plane bending
	1383	23.1	C-C stretching
COR	482	8.4	C-C breathing
	1350	5.2	C-C stretching
	1366	6.2	C-C stretching/δCH

[a] The ratio of the SERS signal intensity obtained by using the AuNPs/SNW-1 (I_{di}) and Au NPs (I_{ci}) as the substrate, respectively, calculated by the equation of $n=I_{di}/I_{ci}$[14];

[b] The assignment of the SERS bands for all eight PAHs are based on previously reported.[9, 10, 12]

Table S3 Particle size and max absorption of Au NPs prepared with citrate of different volumes

$V_{\text{sodium cirate}}$ (mL)	1.5	1.0	0.8	0.65	0.5	0.4	0.25
λ_{max} (nm)	518	521	526	528	538	546	578
X	18	21	26	28	38	46	78
d (nm)	11	15	33	38	59	73	113

The particle size (d) of prepared Au NPs was calculated by the following equation[2]:

$$d = \begin{cases} 3 + 7.5 \times 10^{-5} X^4, X < 23 \\ \dfrac{\sqrt{X - 17} - 1}{0.06}, \quad X \geq 23 \end{cases} \qquad X = \lambda max - 500$$

Table S4 SERS analysis of local tap and pond water or spiked with 1.0 μM PAHs using the substrate of AuNPs/SNW-1

Sample	**PAHs**	**Concentration (μM)**	**Found (μM)**	**Recovery[a] (%)**	**RSD (%) (n=3)**
Tap water	AcPy	nd[b]	0.94	94	4.2
	ANT	nd[b]	110	110	11
	PHE	nd[b]	0.95	95	10
	FLT	nd[b]	0.96	96	3.8
	PYR	nd[b]	0.92	92	2.8
	BaA	nd[b]	0.80	80	3.7
	BaP	nd[b]	1.07	107	2.3
	COR	nd[b]	0.82	82	8.1
Pond water	AcPy	nd[b]	1.07	107	4.9
	ANT	nd[b]	0.85	85	9.7
	PHE	nd[b]	1.14	114	4.5
	FLT	nd[b]	1.06	106	12.7
	PYR	0.05	0.96	91	8.3
	BaA	nd[b]	0.80	80	4.9
	BaP	nd[b]	0.83	83	5.8
	COR	nd[b]	0.85	85	14

[a]spiked with PAHs of 1.0 μM; [b]not detected.

References

1. W. Zhang, L.-G. Qiu, Y.-P. Yuan, A.-J. Xie, Y.-H. Shen and J.-F. Zhu, *Journal of Hazardous Materials*, 2012, **221–222**, 147-154.
2. X. Ji, X. Song, J. Li, Y. Bai, W. Yang and X. Peng, *Journal of the American Chemical Society*, 2007, **129**, 13939-13948.
3. X. Wang, W. Hao, H. Zhang, Y. Pan, Y. Kang, X. Zhang, M. Zou, P. Tong and Y. Du, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2015, **139**, 214-221.
4. Y. Xie, X. Wang, X. Han, W. Song, W. Ruan, J. Liu, B. Zhao and Y. Ozaki, *Journal of Raman Spectroscopy*, 2011, **42**, 945-950.
5. H. Zhao, J. Jin, W. Tian, R. Li, Z. Yu, W. Song, Q. Cong, B. Zhao and Y. Ozaki, *J. Mater. Chem. A*, 2015, **3**, 4330-4337.
6. I. Tijunelyte, S. Betelu, J. Moreau, I. Ignatiadis, C. Berho, N. Lidgi-Guigui, E. Guénin, C. David, S. Vergnole, E. Rinnert and M. Lamy de la Chapelle, *Sensors*, 2017, **17**, 1198.
7. J. Du, J. Xu, Z. Sun and C. Jing, *Analytica Chimica Acta*, 2016, **915**, 81-89.
8. H.-X. Gu, K. Hu, D.-W. Li and Y.-T. Long, *Analyst*, 2016, **141**, 4359-4365.
9. I. López-Tocón, J. C. Otero, J. F. Arenas, J. V. Garcia-Ramos and S. Sanchez-Cortes, *Analytical Chemistry*, 2011, **83**, 2518-2525.
10. J. Du and C. Jing, *The Journal of Physical Chemistry C*, 2011, **115**, 17829-17835.
11. P. Leyton, J. S. Gómez-Jeria, S. Sanchez-Cortes, C. Domingo and M. Campos-Vallette, *The Journal of Physical Chemistry B*, 2006, **110**, 6470-6474.
12. L.-L. Qu, Y.-T. Li, D.-W. Li, J.-Q. Xue, J. S. Fossey and Y.-T. Long, *Analyst*, 2013, **138**, 1523-1528.
13. E. Hahm, D. Jeong, M. G. Cha, J. M. Choi, X.-H. Pham, H.-M. Kim, H. Kim, Y.-S. Lee, D. H. Jeong, S. Jung and B.-H. Jun, *Scientific Reports*, 2016, **6**, 26082.
14. X. Liu, L. Cao, W. Song, K. Ai and L. Lu, *ACS Appl Mater Interfaces*, 2011, **3**, 2944-2952.