Au nanoparticles grafted on Fe₃O₄ as effective SERS substrates for label-free detection of the 16 EPA priority polycyclic aromatic hydrocarbons

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HIGHLIGHTS

- SERS detection of the 16 EPA priority PAHs was conducted.
- The satellite-core structure lead to high SERS enhancement by confined hotspots.
- The approach does not require expensive instrumentation or large sample volumes.
- The effective protocol is useful for the identification of hydrophobic molecules.

GRAPHICAL ABSTRACT

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ABSTRACT

Several methods and materials have been explored for the sensitive and practicable detection of polycyclic aromatic hydrocarbons (PAHs). However, it is still a challenge to develop simple and cost-effective sensing techniques for PAHs. Herein we report the synthesis and construction of Fe₃O₄@Au SERS substrate. This magnetic substrate was composed by Fe₃O₄ microspheres and Au NPs. The size, morphology, and surface composition of Fe₃O₄@Au were characterized by multiple complimentary techniques including scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray powder diffraction. The spatial distributions of electro-magnetic field enhancement around Fe₃O₄@Au was calculated using finite difference time domain (FDTD) simulations. As a result of its remarkable sensitivity, the Fe₃O₄@Au-based SERS assay has been applied to detect the 16 EPA priority PAHs. The LODs achieved by our method (100–5 nM, 16.6–1.01 µg L⁻¹) make it promising for the rapid screening of highly contaminated cases. As a proof-of-concept study, the substrate was applied in SERS sensing of PAHs in river matrix. The 16 PAHs could be differentiated based upon their characteristic SERS peaks. Most importantly, the detection was successfully conducted using a portable Raman spectrometer, which could be used for on-site monitoring of PAHs.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the products of incomplete combustion of fossil fuels and other carbon-containing fuels such as wood and charcoal. Due to their mutagenic and

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carcinogenic properties, PAHs have attracted the attention of regulators [1,2]. The U.S. EPA has designated 16 priority PAHs based on their toxicity and potential for human exposure (Table 1). The current standard analytical methods for PAHs include liquid chromatography using fluorescence detectors (LC/FLDs) or gas chromatography coupled with mass spectrometry (GC/MS) [1]. A lengthy and laborious pre-concentration step is often required for GC or LC methods, which hinders their use in field analysis. Therefore, alternative techniques have been proposed for the *in situ* PAH identification, including electrochemical methods [3], and spectroscopic methods such as surface-enhanced Raman spectroscopy (SERS) [4,5].

SERS, with its potential for extremely high enhancement levels, transforms Raman spectroscopy from a structural analytical tool to a structurally sensitive single-molecule probe [6]. The SERS signal decays exponentially with distance from the metal surface, and the surface plasmon resonance prompts strong Raman scattering of a target species within an optimum spatial zone of 0–4 nm, where the electromagnetic fields are localized [7]. For molecules possessing high hydrophobicity such as PAHs, great efforts must be made to facilitate their affinity towards SERS substrates. Therefore, the adsorption of PAHs onto functionalized Ag or Au SERS substrates has been extensively investigated. The functional entities include thiol groups [4,8], calixarenes [9], cyclodextrin derivatives [10], dicarbamates [11], viologen [12], and humic acids [13]. Low detection LODs can be achieved on these chemically functionalized substrates. However, during the substrate modification, the intrinsic SERS fingerprints of PAHs can easily be distorted.

In recent years, substrates with specific geometries have been of particular interest for researchers working with PAHs. Novel SERS substrates with ultra-high enhancement factors, such as Au coffee ring [14], Au on nickel 3D foam [15], Au on TiO₂ nanotube arrays [16], Au NPs on porous polymer [17], Ag nanoparticle islands with a SiO₂ spacer layer [18], and Au NPs on alginate gel [19], have been proposed for PAH detection. In most previous reports, a stringent and complicated protocol is a prerequisite for the successful synthesis of substrates, and the substrates were tailored for detecting a specific class of PAHs. However, in real cases such as field assays and real-time analysis, the composition and content of PAHs change from sample to sample, thus the great challenge involves how to efficiently identify multiple PAH molecules with one SERS substrate. On the other hand, as most PAHs are soluble in organic

solvents, but have low solubility in water, it is important to separate and enrich them before SERS detection. From the practical perspective, immobilizing Ag or Au onto the surface of magnetic nano- or micro-particles has become a trend because they can be easily separated from the solution by an applied magnetic field [4,20–22].

Inspired by the above facts, the objective of this study is to provide a facile SERS platform for on-site screening of the 16 EPA priority PAHs. Herein, we present a versatile SERS substrate composed by Fe₃O₄ magnetic microspheres and Au NPs. The Au NPs were homogeneously grafted onto the Fe₃O₄ surface. The magnetic structure of the substrate is beneficial to efficient adsorption of PAHs, fast separation from complex matrixes, and high SERS sensitivity. The characteristic SERS spectra can be seen as fingerprints, making it easy to recognizably identify a single PAH. Consequently, the active substrate can be used for label-free SERS sensing of the 16 EPA priority PAHs. Quantitative determination of PAHs was achieved using a portable Raman spectrometer. This quick and reliable platform opens a new avenue for the *in situ* identification of hydrophobic pollutants.

2. Experimental

2.1. Materials

All reagents were of analytical reagent grade and used without further purification. Ferric chloride, ferrous chloride, and absolute ethanol were obtained from Beijing Chemicals Corporation (China). Chloroauric acid tetrahydrate (HAuCl₄·4H₂O) and trisodium citrate dehydrate were purchased from Sinopharm Chemical Reagent Co., Ltd (China). PAHs were purchased from J&K Scientific Ltd. (China). 3-aminopropyltrimethoxysilane (APTMS, 97%) was from Aldrich Chemicals Corporation (USA). Milli-Q water was used in all experiments.

2.2. Apparatus

The size, morphology, and surface composition of Fe₃O₄@Au were characterized by scanning electron microscopy (SEM-EDX, HITACHI S-3000N SEM with an Oxford energy dispersive X-ray analyzer). X-ray photoelectron spectroscopy (XPS, ESCALab 220i-XL electron spectrometer from VG Scientific) was used to investigate

Table 1
The abbreviations, K_{ow} and lowest detection limits (LOD) of the 16 EPA priority PAHs.

PAHs	Abbreviation	logK _{ow}	EF ^a	LOD (M)	Reported LOD (M)
naphthalene	NAP	3.32	1 × 10 ⁵	1 × 10 ⁻⁷	2 × 10 ⁻⁷ [34]
acenaphthene	ACN	4.07	1 × 10 ⁵	1 × 10 ⁻⁷	—
acenaphthylene	ACL	3.98	1 × 10 ⁵	1 × 10 ⁻⁷	—
fluorene	FLU	4.18	1 × 10 ⁵	1 × 10 ⁻⁷	—
anthracene	ANT	4.45	8 × 10 ⁵	5 × 10 ⁻⁸	1 × 10 ⁻⁷ [17]
phenanthrene	PHE	4.45	2 × 10 ⁶	5 × 10 ⁻⁸	5 × 10 ⁻⁷ [17]
fluoranthene	FLA	5.20	6 × 10 ⁵	5 × 10 ⁻⁸	4 × 10 ⁻⁹ [35]
pyrene	PYR	5.20	3 × 10 ⁶	5 × 10 ⁻⁸	1 × 10 ⁻⁸ [36]
chrysene	CHR	5.63	6 × 10 ⁶	5 × 10 ⁻⁹	1 × 10 ⁻⁷ [5]
benzo[a]anthracene	BaA	5.90	2 × 10 ⁷	5 × 10 ⁻⁹	4 × 10 ⁻⁴ [27]
benzo[b]fluoranthene	BbF	6.06	3 × 10 ⁶	5 × 10 ⁻⁹	—
benzo[k]fluoranthene	BkF	6.06	7 × 10 ⁶	5 × 10 ⁻⁹	—
dibenzo[a,h]anthracene	DaA	6.57	2 × 10 ⁶	1 × 10 ⁻⁸	—
benzo[a]pyrene	BaP	6.06	1 × 10 ⁷	5 × 10 ⁻⁹	5 × 10 ⁻¹⁰ [19]
indeno[1,2,3-cd]pyrene	InP	6.58	7 × 10 ⁶	5 × 10 ⁻⁹	3 × 10 ⁻⁷ [14]
benzo[g,h,i]perylene	BgP	6.50	3 × 10 ⁶	5 × 10 ⁻⁹	3 × 10 ⁻⁷ [14]

*I*_{SERS}: Peak Intensity of the selected Raman band.

*I*_{RS}: The corresponding band intensity of the PAHs neat.

*C*_{RS}/*C*_{SERS}: The concentration ratio of the PAHs in neat solution and SERS sample.

^a Enhance factor, calculated by the following equation. $EF = (I_{SERS}/I_{RS})(C_{RS}/C_{SERS})$

the chemical properties of $\text{Fe}_3\text{O}_4/\text{Au}$. XPS data processing and peak fitting were performed using the XPSpeak software package. X-ray powder diffraction (XRPD) data was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA using a Cu-target tube and a graphite monochromator. Scans were made in the 2θ range of 10° – 90° with a step size of 0.01° and a count time of 2 s per step. Analyses of the XRPD patterns were performed using the PDF-2 reference database from the International Center for Diffraction Data database. High-performance liquid chromatography analysis was performed with Shimadzu HPLC-20A system equipped with a RF-20A xs fluorescence detector (HPLC-FLD). Raman and SERS spectra were obtained using a portable Raman spectrometer (Enwave Optronics, Inc. USA) with 4 cm^{-1} resolution at 785 nm excitation energy, and adjustable power with maximum at 300 mW.

2.3. Synthesis of $\text{Fe}_3\text{O}_4/\text{Au}$ particles

Fe_3O_4 particles were prepared following our previous work [20]. About 0.1 g of the as-prepared Fe_3O_4 particles were washed by ethanol three times and dispersed in 100 mL ethanol in a three neck flask. With constant stirring, 1 mL APTMS was slowly added to the above solution. The mixture was sonicated for 30 min, and stirred at room temperature for 3 h. The product was washed with ethanol and water several times to remove the excess APTMS. The APTMS-coated Fe_3O_4 was dispersed in 23 mL water in a three neck flask under mechanical agitation, and then 1 mL $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (2%wt.) solution was added. The mixture was heated to 100°C in an oil bath. Then, 1 mL of 50 mg mL^{-1} sodium citrate was added to the above solution and reacted for 20 min. The mixture was allowed to cool to room temperature and the final product was washed with DI water ($18.2\ \Omega\text{M}$) until the supernatant turned clear. The final $\text{Fe}_3\text{O}_4/\text{Au}$ particles were stored in 20 mL DI water before use.

2.4. Sample preparation for SERS analysis

The PAH stock solutions ($1 \times 10^{-3}\text{ M}$) were prepared in acetone for BgP and in ethanol for other PAHs, and the PAH working solutions were obtained by diluting the stock solutions in water. Water from the Qing River was passed through a $0.45\text{-}\mu\text{m}$ membrane before use to prepare river water samples containing the 16 PAHs. About $500\ \mu\text{L}$ $\text{Fe}_3\text{O}_4/\text{Au}$ suspension was immersed in a $500\ \mu\text{L}$ solution containing various concentrations of PAHs for 10 min. Then, the $\text{Fe}_3\text{O}_4/\text{Au}$ substrate was assembled by an applied magnetic field, and exposed to the laser for 5 s to measure the SERS signal.

2.5. Computational method

Geometry optimization and Raman frequencies were calculated using the Gaussian 09 program with B3PW91 hybrid density function theory (DFT). The vibrational frequencies of PAH-Au complexes were explored using Au clusters containing 4 Au atoms (Figure S1). The $6\text{-}31 + \text{G}^{**}$ basis set for C, H, and Au was used with a scale factor of 0.96. In all computations, no constraints were imposed on geometry. The interpretation of Raman spectra for BbF, BkF, and DaA was based on the DFT calculation results. The computations were performed on Deepcomp 7000 at the Computer Network Information Center of the Chinese Academy of Sciences.

2.6. FDTD calculations

The distribution of electromagnetic field intensity around $\text{Fe}_3\text{O}_4/\text{Au}$ was simulated using a three-dimensional finite difference time domain (FDTD) method. The FDTD Solutions software

package (Lumerical Solutions Inc, Vancouver Canada) was used to carry out the computational calculations and numerical analysis. The mesh size was 0.5 nm. The simulation time was 1000 fs. A Fe_3O_4 (2000 nm) core surrounded by varying satellite Au NPs (25 nm) was simulated. The distance between Au NPs was set to 10 nm. The distance between two $\text{Fe}_3\text{O}_4/\text{Au}$ was set to 5 nm. A 785 nm plane wave light source was used to calculate the electromagnetic field distribution.

3. Results and discussion

3.1. Characterization

The morphology and structure of $\text{Fe}_3\text{O}_4/\text{Au}$ were characterized by scanning electron microscopy (SEM), and the average diameter and inter-particle gap distance of Au NPs were obtained with Gaussian fitting (Fig. 1). The substrate was composed of Fe_3O_4 particles with an average diameter of $20\ \mu\text{m}$. Compared with nanoparticles, the Fe_3O_4 microparticles with a high order of roughness could provide an inhomogeneous distribution of local plasmon resonance, resulting in a local increase in the electromagnetic field density [17,23]. As shown in Fig. 1, homogenous Au nanoparticles with an average diameter of 25 nm were grafted on Fe_3O_4 . The inter-particle gap between Au NPs was 5–10 nm, which is beneficial for enhancing SERS signals.

Energy dispersive X-ray spectrometry (EDX) confirmed the presence of atomic Au on the Fe_3O_4 particles (Fig. 2(b)). The mapping analysis exhibited the well-distributed Au over the $\text{Fe}_3\text{O}_4/\text{Au}$ substrate (Fig. 2(c)). The XRD patterns for $\text{Fe}_3\text{O}_4/\text{Au}$ (Fig. 2(d)) showed prominent Fe_3O_4 peaks at 2θ values of 30.2° , 35.7° , 43.3° , 53.7° , 57.2° , and 62.8° [20]. Peaks centered at 38.2° , 44.4° and 64.6° indicated the existence of 111, 200, and 220 Bragg reflections of metallic Au [24]. The XPS analysis of Ag 3d for $\text{Fe}_3\text{O}_4/\text{Au}$ is presented in Fig. 2(e). The $4f_{7/2}$ level located at 84.05 eV and the $4f_{5/2}$ level at 87.75 eV demonstrated the successful formation of zero-valent Au [24].

3.2. DFT-calculated Raman spectra of PAHs

Fig. 3 presents the molecular structures of the 16 PAHs. The DFT-calculated Raman spectra are shown in Figure S2. The theoretically derived Raman shifts correlated well with the experimental frequencies. Although Raman frequencies of PAHs have been reported [25–27], no comprehensive assignments have been made. Tables S1–S16 summarize the peak positions and assignments of Raman shifts for the 16 PAHs. Due to the linked aromatic ring structure of PAHs, the majority of the bending modes are restrained within the plane. The intense Raman peaks in the range $1200\text{--}1600\text{ cm}^{-1}$ were mainly recognized as the C–H bending modes. Peaks appearing at $300\text{--}1000\text{ cm}^{-1}$ with lower intensities are mainly attributed to the C–C bending modes coupling with the C–H bending modes [27]. It should be noted that the vibrational mode assignments only convey the most dominant oscillations, whereas in most cases, the predicted peaks are a result of the combined vibrations of multiple atoms and bonds within the molecule. The combination of various vibrations resulted in different wavenumbers for similar vibrational modes for PAHs compounds. This leads to a unique Raman fingerprint for each PAH.

3.3. SERS detection of PAHs

Fig. 4 exhibits the SERS spectra of the 16 PAHs on the surface of $\text{Fe}_3\text{O}_4/\text{Au}$. Normal Raman spectra for the solid PAHs are also presented for comparison. The major features of the SERS spectra for the 16 PAHs could be well reproduced by the DFT calculations

Fig. 1. SEM image of Fe₃O₄@Au (a, b), SEM image of Au NPs on the surface of a single Fe₃O₄@Au particle (c, d), Histograms of inter-particle gap distance (e) and particle size (f) of Au NPs.

Fig. 2. SEM image (a) and EDX spectra (b) of Fe₃O₄@Au. EDX mapping of O, Fe, Au on surface of Fe₃O₄@Au (c). XRPD pattern of Fe₃O₄@Au (d). The XPS spectra of Au 4f peaks of Fe₃O₄@Au (e).

(Figure S2, Tables S1–S16). The lack of change in SERS peaks from the normal Raman spectra implies that the SERS enhancement may be primarily due to the electromagnetic mechanism [28]. Compared with the C–C bending modes, the C–H bending modes have a higher polarizability [27]. Consequently, the PAHs with a larger number of C–H groups, such as InP, BaP, and BgP, tend to have a higher SERS activity compared with PAHs with fewer C–H groups (i.e. NAP and ANT). Furthermore, PAHs with more complex and asymmetric structures, such as BaA and BbF, tend to yield more Raman peaks that are closely packed within a narrow spectral

range, while fewer and more resolved peaks are found in similar but more symmetric molecules like PYR and DaA.

The lowest detection limit (LOD) and the octanol–water partition coefficient (K_{ow}) of each PAH are listed in Table 1. SERS spectra of the 16 PAHs at different concentrations on Fe₃O₄@Au substrate are illustrated in Figure S3–S4. As the concentration exceeds the LOD, the weak PAH peaks begin to emerge. The Fe₃O₄@Au magnetic substrate could concentrate the hydrophobic PAHs close to the closely spaced Au NPs to generate SERS enhancement. Therefore, the substrate shows an enhanced SERS sensitivity towards PAHs

Fig. 3. The optimized molecular structures of the 16 PAHs.

Fig. 4. Raman spectrum ((black line) and SERS spectrum (red line) of NAP, ACN, ACL, and FLU (a); Raman spectrum ((black line) and SERS spectrum (red line) of ANT, PHE, FLA, and PYR (b); Raman spectrum ((black line) and SERS spectrum (red line) of CHR, BaA, BbF, and BkF (c); Raman spectrum ((black line) and SERS spectrum (red line) of DaA, BaP, InP, and BgP (d). The concentration is 5×10^{-7} mol L⁻¹ for each PAH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compared with substrates such as functionalized silver and gold colloids (Table 1). Moreover, the clean background spectrum of the substrate would not interfere with detection of the 16 PAHs. The uniformity of the Fe₃O₄@Au substrate was evaluated by collecting SERS spectra at 25 points that were randomly chosen on the substrate. The relative standard deviations of the peak intensity for PAHs with different benzene rings were between 8.5 and 14.1% (Fig. 5). The results demonstrated our method can produce reliable SERS signals with practically minimum spatial variations.

To quantify the SERS response as a function of PAH concentration, the SERS intensity at the most intense PAH band was averaged from 50 randomly chosen points on one substrate, and the results

are listed in Figure S5. The signal intensity increased in response to increasing PAH concentration and then reached a plateau. The concentration–response curve followed the equation:

$$I/C = P + QI + R^2 \quad (1)$$

where I is the peak intensity of the SERS spectra of PAHs, c is the concentration of each PAH, and P , Q and R are fitting parameters. A similar relationship between the PAH concentration and SERS intensity was also observed in our previous reports [14].

Fig. 5. SERS intensity of 10^{-6} M NAP, ANT, CHR, BaP, and BgP collected at 25 randomly chosen spots on $\text{Fe}_3\text{O}_4/\text{Au}$. The average SERS intensity (AVG) and relative standard deviation (RSD) of 25 spots are also summarized.

3.4. SERS enhancement

The formation of plasmonic near-field hot spots of Ag or Au NPs has been usually achieved uncontrollably with inhomogeneous distribution, which severely restricts the SERS detection of hydrophobic PAHs. Our previous study indicated that citrate-reduced Au NP colloids cannot generate any SERS signals for PAHs [14]. In contrast, when the Au NPs were packed on the Fe_3O_4 , the $\text{Fe}_3\text{O}_4/\text{Au}$ is capable of efficient adsorption of PAHs. In our preliminary experiment, it was found that fast initial adsorption of 74% BaP occurred within 10 min, which followed pseudo-second-order kinetics (Figure S6). Once PAHs adsorbed on $\text{Fe}_3\text{O}_4/\text{Au}$, the closely packed Au NPs on a single Fe_3O_4 microsphere should lead to high SERS enhancement due to the plasmon resonance within them (1st hotspots, Fig. 6(a)). In this study, the area of the Raman laser spot was 0.0143 mm^2 [27], and the surface area for a single Fe_3O_4 hemisphere is estimated to be $\sim 0.0006 \text{ mm}^2$ ($2\pi R^2$, $R = 10 \mu\text{m}$). The $\text{Fe}_3\text{O}_4/\text{Au}$ microparticles were closely arranged in response to the external magnetic field. Therefore, in each scan, the SERS response was generated from more than 20 Fe_3O_4 micro-particles. The regular arrangement of Fe_3O_4 microspheres with magnetic self-assembly provides well defined rough grooves, resulting in

efficient generation of plasmonic hot spots between $\text{Fe}_3\text{O}_4/\text{Au}$ microparticles (2nd hotspots, Fig. 6(a)).

The FDTD method was employed to predict the optimal optical near-field enhancement factors for the hotspots of the plasmonic $\text{Fe}_3\text{O}_4/\text{Au}$ (Fig. 6, b-e). It is evident that the local electromagnetic field was greatly enhanced near the 1st and 2nd hotspots. The SERS enhancement factor (EF), as estimated from $E_{\text{local, max}}/E_0^4$ [29], was 0.8×10^7 , which is consistent with our experimental results (10^5 – 2×10^7 , Table 1). The FDTD simulations provided theoretical support for significant SERS enhancement of $\text{Fe}_3\text{O}_4/\text{Au}$ substrates.

The SERS response was observed to increase with increasing log K_{ow} and molecular mass (Table 1). The substrate preference for larger PAHs may be attributable to increased van der Waals interaction. As a result, the PAHs-substrate interaction mainly came from the presumed hydrophobic interaction between the PAHs and $\text{Fe}_3\text{O}_4/\text{Au}$. Analyzing the SERS spectra of the 16 PAHs suggests that compared with conventional Raman spectra of solid standards, the ring stretching modes in the SERS spectra were slightly red shifted (i.e. 1262 cm^{-1} to 1252 cm^{-1} for ANT; 1003 cm^{-1} to 996 cm^{-1} for BbF; 1024 cm^{-1} to 1016 cm^{-1} for BaP). The results indicated that for most PAHs, weak interactions take place between the π orbitals of the ring and the valence orbitals of Au [26]. That is, an additional

Fig. 6. Schematic representation of the plasmonic hotspots formed on Fe₃O₄@Au (a). The 1st type is the gaps between Au NPs located on a single Fe₃O₄ sphere. The 2nd type is the gaps between Au NPs located on the surface of two neighboring Fe₃O₄ spheres. Calculated electric field intensity distribution induced by the LSPR on Fe₃O₄@Au system with 785 nm excitation (b–e).

charge-transfer (CT) effect might contribute to the overall SERS enhancement. The CT can further be validated with the energy state analysis of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The results in Fig. 7 show that the energy of the electronic transition states varied in the range 0.097–0.112 eV, which allowed the CT under the irradiation of 785 nm laser (1.66 eV) [30].

3.5. Identification of 16 PAHs in complex matrixes

Concentrations of PAHs reported in drinking water and river water in recent studies are listed in Table S17. Due to their high K_{ow} values and low Henry's constants, the PAHs concentration could accumulate up to mg L⁻¹ levels in drinking water [31]. High concentrations of PAHs in river water have also been reported, and

Fig. 7. Variation of frontier orbital energies for PAH-Au₄ clusters. The numbers in horizontal axis stand for the 16 PAHs, which follow the sequence in Table 1.

Fig. 8. SERS spectra of PAHs in Qing River water spiked with 16 PAHs at 1×10^{-7} mol L $^{-1}$ and 5×10^{-8} mol L $^{-1}$ concentration levels for each PAH.

could reach $\mu\text{g L}^{-1}$ levels [32]. Therefore, the LODs achieved by our method (100–5 nM) make it promising for the rapid on-site screening of highly contaminated cases. As a proof-of-concept study, the magnetic substrate was applied in SERS sensing of PAHs in complex mixtures. A standard sample containing the 16 PAHs was spiked into the water from a local river (Qing River, Beijing). The SERS spectra were collected as shown in Fig. 8. The 16 PAHs are labeled with different symbols. Three main peaks at approximately 1380 cm $^{-1}$, 1421 cm $^{-1}$, and 1601 cm $^{-1}$ indicated the presence of PAHs, which are composite signals and the result of in-plane ring-stretch vibrations of individual PAHs [33]. The discriminant peaks of most specific PAHs can be distinguished, where some of the key SERS peaks were overlapped. The overlap of peak positions prevented the accurate quantitative determination of PAHs with ≤ 4 benzene rings such as NAP, ACN, ACL, PHE, FLA, and PYR. For larger PAHs such as BaA, BaP, and InP, there was a significant increase in contribution to the total spectrum compared to smaller ones. These results are in general agreement with our previous findings, where the SERS substrate prefers less soluble PAHs [4,14]. The results proved that the Fe $_3\text{O}_4$ @Au SERS platform can be applied as a semi-quantitative sensor for PAHs in heavily polluted water matrixes.

4. Conclusions

The present work has proposed a facile method for SERS sensing of the EPA 16 priority PAHs. The Fe $_3\text{O}_4$ @Au SERS substrate can be simply and rapidly synthesized without a complicated modification process. The 16 PAHs could be differentiated based upon characteristic SERS peaks. Identification of PAHs with detection limit at the nmol L $^{-1}$ level was achieved. The present approach does not require expensive instrumentation or large sample volumes. The quick and cost-effective protocol is expected to be particularly useful for the identification of hydrophobic molecules with similar chemical structures, for which effective separation protocols may be difficult to develop. Higher enhancement of the currently restrained sensitivity by specific sampling design and laser adaptation is expected and is the object of our ongoing research.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.aca.2016.02.009>.

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