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Coffee-ring effect-based simultaneous SERS substrate fabrication and analyte enrichment for trace analysis†

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Based on the “coffee-ring effect”, we developed a highly efficient SERS platform which integrates the fabrication of SERS-active substrates and the preconcentration of analytes into one step. The high sensitivity, robustness, reproducibility and simplicity make this platform ideal for on-site analysis of small volume samples at low concentrations in complex matrices.

Since its invention in the 1970s,^{1,2} surface-enhanced Raman spectroscopy (SERS) has been receiving growing interest in a variety of areas due to its inherent merits such as a high signal-to-noise ratio, non-photobleaching features and the use of single photoexcitation.³ These features make SERS one of the most powerful techniques for non-destructive, on-site and *in vivo* analysis of chemical and biological substances.⁴ However, the utilization of SERS in determination of trace analytes is restricted by the sophisticated and expensive nanofabrication of highly SERS-active substrates, as well as its limited sensitivity and selectivity for trace substances in complex matrices due to the swamping of the analyte signal in background molecule signals. For example, while the concentrations of PAHs in the environment are commonly in the range of 10^{-12} to 10^{-9} g L⁻¹, the lowest detection limits available with a well-designed SERS substrate are in the range of 3×10^{-6} to 1.78×10^{-4} g L⁻¹.⁵ To meet the requirements for analysis of trace analytes in complex matrices, metallic substrates were tailored to increase the signal strength, and analytes were preconcentrated before SERS analysis. As these two approaches are very complicated and time-consuming, it is highly desired to develop a fast, simple and robust approach to simultaneously perform the self-assembling of SERS substrates and preconcentration of trace analytes.

One technique that holds great promise in this regard is the “coffee-ring effect”, which refers to the accumulation of a ring-like dense array on the border by evaporating a droplet of aqueous solution containing nonvolatile solutes such as organic small molecules, biomacromolecules, polymers, and nanoparticle microspheres on solid surfaces. In this process, the three-phase contact line among the atmosphere, droplet and solid substrate is pinned, and a remarkable capillary flow happens because of the evaporation of solvents, driving solutes to move outward from the inner side to the rim of the droplet. Consequently, solutes are highly concentrated along the original droplet edge. It was found that the coffee-ring effect is applicable for enriching both chemical and biological substances.^{6–11} One example is its application in normal Raman spectrometry that is termed as drop coating deposition Raman (DCDR).¹⁰ In recent years, the coffee-ring effect has become a powerful tool for self-structuring of nanomaterials.^{12–15}

Herein, we report the development of a novel SERS platform by integrating the generation of SERS substrates and the enrichment of analytes into one step. We demonstrate the benefits of the coffee-ring effect in construction of SERS substrates and preconcentration of analytes, through the evaporation of an aqueous droplet containing both silver nanoparticles (AgNPs) and analytes. The formed SERS substrates are a self-ordered ring (SOR) of closely packed AgNPs, with uniformly distributed hotspots and captured analyte molecules that ensure sensitive and precise SERS detection. Malachite green (MG) and arsenate (As(v)) were adopted as representatives of organic and inorganic analytes, respectively, to evaluate the analytical merits of the platform.

This work aimed towards the development of a practical and on-site SERS platform. With this in mind, we made the SERS platform using simple, cost-effective and sensitive methods that require no specialized equipment and personnel. Scheme 1 shows the scheme of the coffee-ring effect-based self-assembly of AgNPs and enrichment of analytes. Samples with analytes, AgNPs and polyvinyl alcohol (PVA) were vortex mixed, and then a droplet of this mixture was dripped onto the silicon wafer.

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Scheme 1 Schematic of the simultaneous fabrication of SERS-active substrates and preconcentration of analytes via the coffee-ring effect. (a) Dropping a drop of water sample on the hydrophobic surface of the silicon wafer. (b) Evaporative self-assembly of AgNPs and analytes based on the coffee-ring effect; (c) deposition of AgNPs and analytes on the three-phase contact line to form the SOR structure. (d) Detection of analytes by confocal Raman spectroscopy.

During the evaporation of water, AgNPs and analytes migrated from the inner solution to the edge of three-phase contact line among the droplet, silicon surface and air. After several minutes, densely packed AgNPs and concentrated analytes were deposited on the contact line to form the SOR structure, which was ready for SERS detection.

As a feasibility study, the toxic pollutants As(v) and MG were used as the target analytes. Inorganic As contamination is a pressing environmental issue that causes a serious threat to human health.¹⁶ MG is a cationic dye that is widely used as an antiseptic in the aquaculture industry, but it is suspected of being genotoxic and carcinogenic.^{17,18} Recent studies showed that SERS is a promising technique for rapid detection of MG^{19–22} and As(v),^{23–26} but the method sensitivity and selectivity require further improvement, and a fast, highly efficient and low-cost procedure for preparation of SERS substrates is urgently needed.

In order to select the characteristic peaks for the identification and quantification of As(v) and MG, their SERS spectra were recorded (Fig. S1 in the ESI†) and analyzed with the major peak assignments listed in Table S1.† While As(v) shows two predominant peaks, namely the major peak at 790 cm^{-1} which corresponds to the ν_1 (A_1) symmetric As–O stretch and the minor peak at 423 cm^{-1} which is a superposition of ν_2 (A_1) and ν_5 (E) stretching modes of the arsenate molecule, MG has a few predominant peaks at different Raman shifts (Table S1†). In the following studies, the highest peaks at 790 cm^{-1} and 1625 cm^{-1} are chosen as the diagnostic peaks for As(v) and MG, respectively, unless otherwise noted.

The metal and capping agent species, as well as the morphology and size of the nanomaterials significantly influence the SERS signals of the target analytes. It is reported that the sphere particles benefit the formation of SOR;¹² moreover, it is generally believed that silver nanomaterials show higher

SERS activity than the gold nanomaterials,²⁷ and the size and morphology of AgNPs significantly influence the SERS activity.^{28–30} Therefore, PVA-capped sphere AgNPs with different sizes (20, 40, and 60 nm, see Fig. S2†) were prepared according to previously reported methods^{23,31,32} with slight modification, and used for the detection of As(v) and MG, respectively. Results (Fig. S3†) showed that the highest SERS intensity of As(v) and MG was obtained by using 20 nm and 40 nm AgNPs, respectively.

The AgNP concentration in the droplet mixture of sample and reagents also affects the SOR formation and therefore the SERS activity.³³ For both As(v) and MG, the SERS signal increased and then decreased with the increase of AgNP concentration (Fig. S4†). The maximum SERS intensity was obtained at 40 mg L^{-1} AgNPs for As(v) and 56 mg L^{-1} AgNPs for MG, respectively.

In this protocol, PVA is a dual-functional reagent which effectively assists the preconcentration of analytes during the course of SOR formation,⁸ and induces the self-assembly of AgNPs into dimers or larger or nanochains that provide active sites, *i.e.* “hot spots”, for enhancing the SERS intensity.³⁴ Our results showed that the SERS intensity initially increased with PVA concentration up to 0.08% (m/v) and 0.2% (m/v) for As(v) and MG, respectively, and then decreased rapidly (Fig. S5†). If the PVA concentration was not high enough, the contact line of the drying sessile droplet could not be pinned, which prohibited the formation of a ring-shaped deposit on the hydrophobic substrate. The reduction of SERS intensity at higher PVA concentration was ascribed to the increased sample viscosity, which reduced mobility of analytes and AgNPs during the SOR formation,³⁵ and therefore lessened the concentrated analytes and AgNPs in the SOR.

The performance of this coffee-ring effect-based SERS platform showed strong dependence on the pH value. This was ascribed to the fact that pH determines both the properties and the structure of AgNPs including existing speciation,^{36,37} surface charge and aggregation.³⁸ Furthermore, the pH could influence the interaction between the analyte molecule and the SERS substrate and therefore the SERS enhancement efficiency. It has been reported that the close interactions of As(v) and MG with noble metal nanoparticles (Ag and Au) could enhance the SERS signal through the chemical enhancement, which was likely affected by the solution pH.^{26,39} The impact of solution pH was evaluated in the range of 1.45–11.78, and results indicated that both As(v) and MG were sensitive to pH, with Raman intensities peaked at pH 10.22 for As(v) and pH 5.97 for MG, respectively (Fig. S6†). For MG, higher chemical enhancement was observed at pH 6, as the rich π -electronic structure of MG at acidic or neutral conditions facilitates the anchoring of MG to the surface of the SERS substrate.³⁹ However, a lower pH environment could accelerate the oxidative dissolution of AgNPs,^{36,37} leading to the loss of the SERS enhancement effect. The decline of SERS intensity at pH <10.22 in As(v) detection was probably owing to the transformation of the arsenate anion. Palmer *et al.* demonstrated that As(v) in the form of HAsO_4^{2-} or H_2AsO_4^- reduced the number of As–O[–] symmetric vibrations, which weakened the Raman intensity of As–O[–] symmetric vibrational

mode.⁴⁰ At pH > 10.22, the SERS intensity markedly declined as the SOR structure was hardly formed (Fig. S7†), which might be the dominant factor for the significant decline of SERS intensity of As(v) at pH 11.78.

Temperature influences various SOR related parameters such as the rate of evaporation solvent and analyte diffusion, solution viscosity, and PVA solubility. This in turn affects the SOR structure and the enrichment factors of analytes in the SOR, and therefore the Raman intensities of target analytes. It was proved that the formed SOR structure based on the coffee-ring effect was not satisfied unless the evaporation process was conducted at a temperature higher than 60 °C.⁸ In this present work, although the optimum temperature was 70 °C and 80 °C for As(v) and MG, respectively (Fig. S8†), the SOR structure was observed even at room temperature. The SERS intensity decreased as the temperature increased ulteriorly, which might be ascribed to the spoiled SOR and the enhanced dissolution of AgNPs in the form of Ag⁺ at high temperature,³⁷ resulting in the loss of AgNPs as the enhancement substrate.

The droplet size affects the morphology of the deposited drop, and the SOR formation occurs at a critical diameter which depends on the initial solute concentration.^{8,41} Therefore, the droplet size could influence the analyte enrichment factor and the assembled AgNP nanostructure in the SOR, which strongly affected the SERS enhancement factor. The effects of droplet volume were studied in the range of 0.5–2.5 μL, and results showed that 1 μL droplet provided the best ring-like shape deposited on the periphery (Fig. S9†). The SOR structure could hardly form at droplet volume < 1 μL, while the SOR structure became unstable when the droplet volumes were above 1 μL. Further studies indicated that although the SERS intensity of As(v) was dependent on the droplet volume, the SERS intensity of MG was fairly independent of the droplet volume (Fig. S10†). Therefore, 1 μL droplet was adopted as it provided the best results in consideration of SERS intensity and precision for both As(v) and MG.

Fig. 1 shows the SEM images of the fabricated SOR and the SERS signal of As(v) under the above optimized conditions. SEM

images showed that AgNPs were concentrated in the SOR area, and it was only in the SOR area that the Raman signal of As(v) could be detected. To further understand the function of the coffee-ring effect, we recorded the profile of Raman intensity of As(v) at the droplet edge during the process of SOR formation (Fig. 2). As time went on, the Raman intensity of As(v) at the droplet edge increased sharply and then leveled off, indicating the preconcentration of analytes and the formation of SOR.

The SERS enhancement factors (EFs) of this proposed procedure for As(v) and MG were calculated based on eqn (1)³³

$$EF = \frac{I_{\text{SERS}}}{I_{\text{bulk}}} \frac{N_{\text{bulk}}}{N_{\text{SERS}}} \frac{P_{\text{bulk}}}{P_{\text{SERS}}} \frac{T_{\text{bulk}}}{T_{\text{SERS}}} = \frac{I_{\text{SERS}}(\text{normalized})}{I_{\text{NRS}}(\text{normalized})} \frac{N_{\text{NRS}}}{N_{\text{SERS}}} \quad (1)$$

where *I*, *N*, *P*, and *T* represent the Raman intensity, number of probe molecules, laser power, and acquisition time, respectively; while footnotes SERS, NRS and bulk represent surface-enhanced Raman spectroscopy, normal Raman scattering and bulk solution, respectively. Under the above optimized conditions, this platform provides high EF values of $>5.0 \times 10^8$ and 2.6×10^{10} for As(v) and MG, respectively.

We also evaluated the EF contributed from the Raman intensity enhancement factor (EF_R) by the SERS “hotspot” of the SOR structure and the enrichment factor of analytes (EF_A) by SOR, respectively. EF_R was calculated by the ratio of Raman intensity of an analyte determined after the formation of the SOR structure to that before the formation of the SOR structure, while EF_A was the ratio of Raman intensity of an analyte determined after the formation of the SOR structure to that determined by loading the same concentration of analyte to the SOR structure pre-formed with a blank sample.

The results showed that the SERS enhancement efficiency for As(v) ($>1.4 \times 10^6$) was lower than that for MG (3.1×10^7), which was ascribed to the fact that Raman scattering of inorganic ions was generally weaker than that of organic molecules. The different EF_A of As(v) (350) and MG (850) were ascribed to the different surface tensions of their aqueous solutions (Fig. S11†). Compared to pure water, aqueous solutions of As(v) showed an increased surface tension and contact angle on a hydrophobic surface, leading to an inward-moving trend in the aqueous

Fig. 1 SEM images of the SOR formed by the coffee-ring effect and the SERS signal of arsenate. (a) FESEM of the whole SOR. (b) FESEM of the border on the SOR. (c) FESEM of AgNPs in the SOR structure. (d) SERS signal of arsenate at the contact line of SOR.

Fig. 2 SERS spectra of As(v) at the SOR border recorded during the course of SOR formation. A 1 μL droplet of a mixture (pH 10.22) containing 10 μg L⁻¹ As(v), 30.6 mg L⁻¹ of 20 nm AgNPs, and 0.08% (m/v) PVA was dripped onto the silicon wafer, and recorded at room temperature with a 785 nm laser line.

droplet, which partly counteracted the enrichment factor resulting from the coffee-ring effect. In contrast, the aqueous solutions of MG showed decreased surface tension and contact angle on the hydrophobic surface, thus MG would enhance the coffee-ring effect by its outward-moving trend and therefore the enrichment factor. To further verify this, we measured the surface tension and contact angle of mixtures under the optimized detection conditions for As(v) (Mixture 1, containing 40 mg L⁻¹ of 20 nm AgNPs, 0.08% (m/v) PVA, and 1000 µg L⁻¹ As(v)) and MG (Mixture 2, containing 56 mg L⁻¹ of 40 nm AgNPs, 0.2% (m/v) PVA, and 8 × 10⁻⁸ M MG), respectively. Mixture 1 showed larger surface tension and contact angle than that of Mixture 2 (Fig. S12†), which agreed well with the EF_A values of As(v) and MG.

Fig. 3 illustrates the SERS spectra of standard solutions with different analyte concentrations. The SERS intensity increased with the analyte concentration, with squared correlation coefficients between 0.9828 and 0.9882, and the linear range was 4 and 5 orders of magnitude for As(v) and MG, respectively. The limit of detection (LOD) estimated from the signal-to-noise ratio of three ($S/N = 3$) was 0.03 µg L⁻¹ As(v) and 0.1 ng L⁻¹ MG, which was about 330 times lower than the U.S. Environmental Protection Agency limit of As for drinkable water (10 µg L⁻¹)⁴² and 20 000 times lower than the method performance limit (2 µg L⁻¹) for MG determination required by the European

Commission and the U.S. Food & Drug Administration.²² The precision was evaluated by measuring the intra-day and inter-day relative standard deviations (RSDs) in analyzing 6 standard solutions over one day and over 6 days, respectively. Results showed that the inter-day RSDs were 12% for 10 µg L⁻¹ As(v) and 6.1% for 1 × 10⁻⁹ mol L⁻¹ MG, and the intra-day RSDs were 9.2% for 10 µg L⁻¹ As(v) and 12% for 1 × 10⁻⁹ mol L⁻¹ MG (Fig. S13†).

The absence of As(v) and MG signals in SERS spectra of blank samples demonstrated that reagents like PVA used in this assay did not disturb the quantitative detection of the target compounds (Fig. S14†). This was ascribed to the specific interactions of As(v) and MG with noble nanoparticles,^{26,39} leading to stronger adsorption of As(v) and MG to the SERS substrate of AgNPs than the coexisted competing reagents. This result agreed with literature,⁴³ in which it was reported that the substrate based on the PVA dried gel with AuNPs has a clean background in the SERS spectrum.

Thanks to the low response to coexisting reagents, the Raman spectrum is still discriminable even in the MG concentration down to 10⁻¹² mol L⁻¹ (Fig. 3). Assuming all the MG molecules (10⁻⁶ L of 10⁻¹² mol L⁻¹ MG sample solution) are evenly adsorbed on the surface of the SOR (2 mm OD and 1.9 mm ID), the MG molecule density is about 2 µm⁻². As the laser spot size is about 4 µm in diameter, the number of MG being probed per laser shot is about 25. Considering that in fact only part of these MG molecules were adsorbed on the surface of the SOR, the number of MG probed per laser shot should be much less than 25. Thus we can safely conclude that this proposed platform is applicable for single-molecule detection of MG.

Since this proposed SERS procedure has no response to As(III), the speciation analysis of As(III) and As(v) was performed by the following protocol: As(v) in samples was at first determined by the above described procedure, then the total inorganic arsenic was determined after oxidizing As(III) with H₂O₂ (0.03%, v/v), and As(III) was obtained from the difference between the total inorganic As and As(v). To verify this protocol, 10 µg L⁻¹ of As(III) was determined by the proposed SERS method before and after oxidation with H₂O₂ (0.03%, v/v), respectively, and compared with that of 10 µg L⁻¹ As(v) (Fig. S15†). The comparable response of oxidized As(III) with that of As(v) demonstrated the validity of the protocol. The proposed method was validated by analyzing real environmental water samples (Fig. 4a). For the 2 groundwater samples, the total inorganic As content determined by this SERS procedure (371 and 1.03 µg L⁻¹) agreed well with that determined by ICP-MS (396 and 0.93 µg L⁻¹). SERS analysis results also showed that the As(v) contents were very close to those of the total inorganic As, indicating the As(III) in these samples was negligible.

For all 8 waters collected from aquafarms, the MG contents are below the LOD of the proposed method, thus spiked recovery was tested. The good recoveries of 97.8% and 109.3% at spiked levels of 0.5 and 5 µg L⁻¹ (Fig. 4b) demonstrated the applicability of the proposed method for analysis of real water samples.

It is noteworthy that the proposed method provides excellent specificity for As(v) and MG in real environmental waters, which

Fig. 3 SERS spectra of series standard solutions of As(v) (a) and MG (b). The insets are the enlarged signals of the lowest concentration standard solution, and the profiles of signal intensity (peak area) plotted against the analyte concentration. The 785 nm and 633 nm laser lines were adopted as the excitation source for Raman detection of As(v) and MG respectively.

Fig. 4 Typical Raman spectra of As(v) and MG in environmental water samples. (a) Raman spectra of As(v) in two ground waters, note sample 1 was diluted 100 times with water. (b) Raman spectra of surface water from an aqua farm spiked with 0, 0.5 and 5 $\mu\text{g L}^{-1}$ MG, respectively. The 785 nm and 633 nm laser lines were adopted as the excitation source for Raman detection of As(v) and MG respectively.

was mainly attributed to the extremely high signal ratio of analytes to matrices, especially in the detection of MG (Fig. S16†). This can be ascribed to the intrinsic advantages of the proposed SOR-based SERS methodology, which provides a high Raman intensity enhancement factor by the SERS “hot-spot” of the SOR structure, and high enrichment factors for the target analytes As(v) and MG through SOR based on the coffee-ring effect.

In summary, we have demonstrated that the coffee-ring effect is a promising platform for practical on-site SERS detection, which integrates the preconcentration of analytes and the fabrication of SERS-active substrates into one-step. The platform is simple, cost-effective, sensitive, and requires no specialized equipment. Both inorganic ions and organic molecules can be determined by this SERS platform with high sensitivity, thanks to the dual enhancement from the enrichment of analytes and the SERS enhancement of the assembled AgNPs. The proposed platform has been successfully applied to determine ultra-trace pollutants in environmental waters.

Competing financial interests

The authors declare no competing financial interests.

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Notes and references

- 1 M. Fleischm, P. J. Hendra and A. J. Mcquilla, *Chem. Phys. Lett.*, 1974, **26**, 163.
- 2 D. L. Jeanmaire and R. P. Vanduyne, *J. Electroanal. Chem.*, 1977, **84**, 1.

- 3 W. E. Doering, M. E. Piotti, M. J. Natan and R. G. Freeman, *Adv. Mater.*, 2000, **19**, 3100.
- 4 R. Liu, J. F. Liu, X. X. Zhou and G. B. Jiang, *TrAC, Trends Anal. Chem.*, 2011, **30**, 1462.
- 5 I. Lopez-Tocon, J. C. Otero, J. F. Arenas, J. V. Garcia-Ramos and S. Sanchez-Cortes, *Anal. Chem.*, 2011, **83**, 2518.
- 6 J. T. C. Wen, M. Ho and P. B. Lillehoj, *Langmuir*, 2013, **29**, 8440.
- 7 D. M. Zhang, Y. Xie, M. F. Mrozek, C. Ortiz, V. Jo Davisson and D. Ben-Amotz, *Anal. Chem.*, 2003, **75**, 5703.
- 8 Y. Liu, C. Z. Huang and Y. F. Li, *Anal. Chem.*, 2002, **74**, 5564.
- 9 T. S. Wong, T. H. Chen, X. Y. Shen and C. M. Ho, *Anal. Chem.*, 2011, **83**, 1871.
- 10 R. A. Halvorson and P. J. Vikesland, *Environ. Sci. Technol.*, 2011, **45**, 5644.
- 11 R. A. Halvorson, W. N. Leng and P. J. Vikesland, *Anal. Chem.*, 2011, **83**, 9273.
- 12 P. J. Yunker, T. Still, M. A. Lohr and A. G. Yodh, *Nature*, 2011, **476**, 308.
- 13 W. Han and Z. Q. Lin, *Angew. Chem., Int. Ed.*, 2012, **51**, 1534.
- 14 R. G. Larson, *Angew. Chem., Int. Ed.*, 2012, **51**, 2546.
- 15 H. M. Ma and J. C. Hao, *Chem. Soc. Rev.*, 2011, **40**, 5457.
- 16 Y. G. Wu, S. Zhan, F. Wang, L. He, W. Zhi and P. Zhou, *Chem. Commun.*, 2012, **48**, 4459.
- 17 V. Fessard, T. Godard, S. Huet, A. Mourot and J. M. Poul, *J. Appl. Toxicol.*, 1999, **19**, 421.
- 18 B. Bose, L. Motiwale and K. V. K. Rao, *Cancer Lett.*, 2005, **230**, 260.
- 19 S. Lee, J. Choi, L. Chen, B. Park, J. B. Kyong, G. H. Seong, J. Choo, Y. Lee, K. Shin, E. K. Lee, S. Joo and K. Lee, *Anal. Chim. Acta*, 2007, **590**, 139.
- 20 W. L. Fu, S. J. Zhen and C. Z. Huang, *Analyst*, 2013, **138**, 3075.
- 21 Y. Y. Zhang, K. Q. Lai, J. L. Zhou, X. C. Wang, B. A. Rasco and Y. Q. Huang, *J. Raman Spectrosc.*, 2012, **43**, 1208.
- 22 L. X. Quang, C. Lim, G. H. Seong, J. Choo, K. J. Do and S. K. Yoo, *Lab Chip*, 2008, **8**, 2214.
- 23 M. Mulvihill, A. Tao, K. Benjauthrit, J. Arnold and P. Yang, *Angew. Chem., Int. Ed.*, 2008, **47**, 6456.
- 24 M. J. Han, J. M. Hao, Z. H. Xu and X. G. Meng, *Anal. Chim. Acta*, 2011, **692**, 96.
- 25 J. L. Li, L. X. Chen, T. T. Lou and Y. Q. Wang, *ACS Appl. Mater. Interfaces*, 2011, **3**, 3936.
- 26 J. J. Du, J. L. Cui and C. Y. Jing, *Chem. Commun.*, 2014, **50**, 347.
- 27 I. Yoon, T. Kang, W. Choi, J. Kim, Y. Yoo, S. Joo, Q. Park, H. Ihee and B. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 758.
- 28 J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. Van Duyne, *Nat. Mater.*, 2008, **7**, 442.
- 29 B. Lim and Y. N. Xia, *Angew. Chem., Int. Ed.*, 2011, **50**, 76.
- 30 M. Rycenga, C. M. Cobley, J. Zeng, W. Li, C. H. Moran, Q. Zhang, D. Qin and Y. Xia, *Chem. Rev.*, 2011, **111**, 3669.
- 31 Q. A. Zhang, W. Li, C. Moran, J. Zeng, J. Chen, L. P. Wen and Y. Xia, *J. Am. Chem. Soc.*, 2010, **132**, 11372.
- 32 O. Choi and Z. Q. Hu, *Environ. Sci. Technol.*, 2008, **42**, 4583.
- 33 R. Liu, J. F. Liu, X. X. Zhou, M. T. Sun and G. B. Jiang, *Anal. Chem.*, 2011, **83**, 9131.

- 34 D. He, B. Hu, Q. F. Yao, K. Wang and S. H. Yu, *ACS Nano*, 2009, **3**, 3993.
- 35 M. K. Fan, C. Z. Huang and Y. F. Li, *Anal. Chim. Acta*, 2002, **453**, 97.
- 36 J. Y. Liu, Z. Y. Wang, F. D. Liu, A. B. Kane and R. H. Hurt, *ACS Nano*, 2012, **6**, 9887.
- 37 J. Y. Liu and R. H. Hurt, *Environ. Sci. Technol.*, 2010, **44**, 2169.
- 38 A. M. El Badawy, T. P. Luxton, R. G. Silva, K. G. Scheckel, M. T. Suidan and T. M. Tolaymat, *Environ. Sci. Technol.*, 2010, **44**, 1260.
- 39 X. M. Qian, S. R. Emory and S. M. Nie, *J. Am. Chem. Soc.*, 2012, **134**, 2000.
- 40 S. J. Palmer and R. L. J. Frost, *J. Raman Spectrosc.*, 2011, **42**, 224.
- 41 H. M. Gorr, J. M. Zueger and J. A. Barnard, *J. Phys. Chem. B*, 2012, **116**, 12213.
- 42 National Primary Drinking Water Regulations, EPA 816-F-09-0004, May 2009.
- 43 S. Yao, C. Zhou and D. Chen, *Chem. Commun.*, 2013, **49**, 6409.