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A Novel Triangular Silver Nanoprisms-Based Surface Plasmon Resonance Assay for Free Chlorine

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In this study, a novel assay for the detection of free chlorine was proposed for the first time. It is based on a redox reaction that occurs between triangular silver nanoprisms and free chlorine which results in a morphological transformation and a change of the localized surface plasmon resonance (SPR) of the triangular silver nanoprisms. In the assay, the presence of free chlorine would etch triangular silver nanoprisms from triangle to round, leading to a significant blue-shift SPR absorption band of triangular silver nanoprisms. The wavelength shift was used for facile and reliable free chlorine quantification in the range of 0.1 - 20 μM. The obtained detection limit was as low as 0.07 μM, which was about one and half order of magnitude lower than that of the most widely used N-N-diethyl-p-phenylenediamine (DPD) colorimetric methods. Moreover, this assay was employed to determine the free residual chlorine in local tap water samples. The obtained results were well accorded with that by the DPD colorimetric method.

Introduction

Chlorine as a powerful oxidizing agent has been widely used for the treatment of water and various manufacturing processes.[1-3] The sum of dissolved chlorine (Cl_2), hypochlorous acid (HClO), and hypochlorite (ClO^-) in water is defined as free residual chlorine. In water trement process, the strict control of the free residual chlorine concentration is necessary. The concentration of free residual chlorine with too low of a level can not kill pathogenic bacteria and viruses in water effectively. It will cause many hazards of an insufficient disinfection. Meanwhile, the concentration of free residual chlorine with too high of a level may produce adverse effects. For example, the intensification of taste and odor characteristics of phenols, and undesirable byproducts may exist in water, especially trihalomethane that has been reported to be potentially harmful to human beings and animals.[4,5] Therefore, the ability to detect concentrations of free residual chlorine in water is important by using simple and low-cost assays. In the past decade, several analytical methods, such as colorimetric methods, electrochemical methods, fluorescencent methods, chemiluminescence methods, and liquid chromatographic methods, have been extensively employed to determine free residual chlorine in water.[4,6-9] However, most of these approaches suffer from many drawbacks, such as the requirement for various reagents and expensive instrument that may produce strong toxicity and high cost, complex sample preparation protocols, low detection sensitivity, and poor selectivity. Thus, design and development of a novel detection method overcoming all these obstacles for free residual chlorine still remains a great challenge.

The emergence and recent advance of nanoscience and nanotechnology provide an exciting avenue that could significantly lower the detection limit of various analytes, simplify experimental process, improve detection sensitivity and selectivity.[10,11] For example, noble metal nanomaterials such as silver and gold nanomaterials exhibit strong surface plasmon resonance (SPR) absorption with ultrahigh extinction coefficients from the visible to near-infrared region, which offer a good opportunity to construct assays with unparalleled functionalities for highly sensitive target analysis. Moreover, the SPR absorption of nanomaterials are sensitive to their structural parameters, including shape, size, composition, distance, and the surrounding media, making them the basis for sensing and detection.[12] Among these nanomaterials, silver-based nanomaterials are now gaining increasing attention owing to their shape-dependent optical properties and low cost compared with gold. In particular, among other shapes, triangular silver nanoprisms show exquisite features in the localized SPR due to an extreme degree of anisotropy.[13] Meanwhile, triangular silver nanoprisms possess a much stronger SPR. It can increase the slope of the calibration curve and lead to a better sensitivity. Furthermore, triangular silver nanoprisms are easy to oxide thanks to their relatively active physicochemical properties.[14] This property may be utilized for the fabrication of SPR assays based on a redox reaction. Therefore, triangular silver nanoprisms can serve as building blocks for the construction of assays when their SPR shifts in response to a specific chemical event.

In the present study, we propose a cheap, facile, sensitive, and selective assay for the detection of free residual chlorine for the first time. The assay utilizes the redox reaction of unmodified triangular silver nanoprisms and free chlorine, inducing the distinct morphological transformation from triangle to round (Scheme 1) and the change of localized SPR of triangular silver nanoprisms. The obtained detection limit (0.07 uM) is about one and half order of magnitude lower than that of the widely used N-N-diethyl-p-phenylenediamine (DPD)

colorimetric methods. More importantly, the proposed assay can be used to detect free chlorine in tap water. This study not only opens a novel avenue for the detection of free chlorine, but also further extends the application of silver nanomaterials in sensing, food safety, and environmental monitoring.

Experimental details

Chemicals and apparatus

Silver nitrate ($AgNO_3$), trisodium citrate, sodium borohydride ($NaBH_4$), hydrogen peroxide, sodium hypochlorite, hydrochloric acid, phosphoric acid, sodium hydroxide, sodium dodecyl sulfate, L-tryptophane, and DPD were purchased from Shanghai Reagent (Shanghai, China). Other reagents were of analytical grade and used as received. Ultrapure water (18.2 MΩ cm^{-1}) was prepared by a Millipore Milli-Q system and used throughout.

SPR absorption spectra were carried out on a UV-Vis spectrophotometer (Shimadzu UV-1800, Japan). Scanning electron microscopy (SEM) analysis was conducted with an Ultra-55 field emission scanning electron microscope.

Preparation of triangular silver nanoprisms

The triangular silver nanoprisms were synthesized according to the reported procedure.[15] Typically, 600 μL sodium citrate, 400 μL 0.01 M $AgNO_3$, and 96 μL hydrogen peroxide (30%) were mixed with ultrapure water at room temperature and vigorously stirred for 10 min. The final volume of the mixture solution was 40 mL. Then 400 μL 0.1 M $NaBH_4$ aqueous solution was quickly added to the mixture solution above, and the color of the solution changed gradually from colorless to yellow, red, and blue, indicating the formation of triangular silver nanoprisms. The obtained triangular nanoprism solution was kept at 4 °C before use.

Procedures for free chlorine assay

A 1.35 mL of crude triangular silver nanoprisms was added to a 5 mL calibrated test tube and diluted to 2.7 mL with Britton-Robinson (B-R) buffer solution (pH 5.0). Then a certain amount of NaClO standard solutions with different concentrations was sequentially injected and reacted for 30 min. Then the absorption was measured on the UV-Vis spectrophotometer at room temperature.

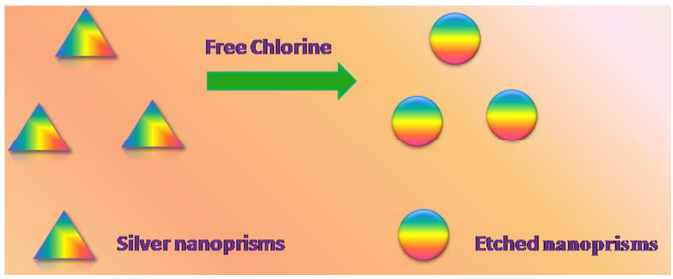
Analysis of real sample

A local tap water sample was collected and used in this study. The tap water was diluted two fold with B-R buffer solution (pH 5.0) before use. The diluted tap water was spiked with standard sodium hypochlorite solutions of different concentrations. Then, the spiked samples were analyzed for free residual chlorine by the DPD colorimetric method and the proposed assay, respectively.

Results and Discussion

Principle of free chlorine based on triangular silver nanoprisms

Triangular silver nanoprisms were prepared by previously reported method.[15] The side length of the nanoprisms is about 70 nm (Fig. S1). It should be noted that triangular silver nanoprisms not only endow a large surface-to-volume ratio but produce many highly reactive sharp edges/tips. The SPR absorption spectrum of the as-prepared triangular silver nanoprisms has three characteristic absorption peaks at 334 nm, 448 nm, and 657 nm as shown in Fig. 1 (red curve). According to the reported reference,[16] the absorption bands at 334 nm and 657 nm are ascribed to out-of plane quadrupole resonance and in-plane dipole plasmon resonance, respectively, and the in-plane quadrupole resonance and out-of-plane dipole resonance band are sufficiently weak and overlap together that it is barely discernible as a shoulder of 657 nm band at 448 nm.[16]



Scheme 1. Schematic illustration of the triangular silver nanoprism-based SPR assay for detection of free chlorine.

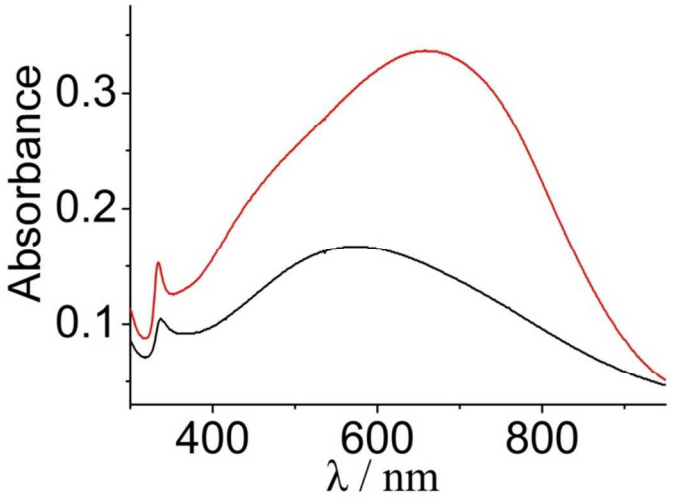


Fig. 1. SPR absorption spectra of triangular silver nanoprisms in the absence (red line) and presence of 20 μM free chlorine (black line).

After addition of free chlorine into triangular silver nanoprisms solution and reaction for 30 min, the in-plane dipole band of nanoprisms gradually shifted from 657 nm to 558 nm. As it well known, the plasmon band of silver nanoprisms is highly dependent on the tip sharpness and aspect ratio, and the blue shift of the in-plane plasmon band usually originates from the reduction of tip sharpness and aspect ratio of nanoprisms. SEM results confirm that silver nanomaterials change from triangle to round. Additionally, the size of reacted nanoprisms was evidently smaller than that of the original ones, leading to the decrease of extinction coefficient of the particles (Fig. S1). Thus the blue shift of in-plane dipole band followed a decrease in the absorbance. The results indicated that strongly oxidizing free chlorine can etch the surface of silver nanoprisms, resulting in the distinct morphological transformation from triangle to round (Scheme 1) and a blue-shift of the plasmon band as shown in Fig. 1 (black curve). To further prove this mechanism, effects of other commonly used oxidants on the SPR absorption spectra of triangular silver nanoprisms are also investigated as shown in Fig. S2. The results show the oxidant with stronger oxidation capability than

free chlorine such as potassium permanganate ($KMnO_4$) can etch silver nanoprisms, resulting in the disappearance of their plasmon band, while the oxidant with weaker capability than free chlorine such as hydrogen peroxide (H_2O_2) has no effect on the SPR absorption spectra of triangular silver nanoprisms. These experimental results further identify that the shape transformation and corresponding SPR blue shift was caused by the etching effect of free chlorine.

Optimization of detection conditions

In order to understand the response rate of the surface plasmon band of triangular silver nanoprisms to free chlorine, the time-dependent evolution of the SPR absorption spectra was monitored. As shown in Fig. 2a, the plasmon band of triangular silver nanoprisms at 657 nm was gradually blue-shifted to 558 nm. It is found that in-plane dipole band shift is very fast in first 2 min and the gradually decreases and levels off to a saturation value after about 20 min. The evolution behavior can be explained as follows. The tips/edges of triangular silver nanoprisms were highly active, which were preferentially etched and led to the shape transformation from triangle to round; then the SPR band shift decreased because the round products were less active and there was a decreased shape change of the round nanoplates. According to Fig. 2b, free chlorine could be well-detected after 20-30 min of reaction time. However, in order to get a better quantification, 30 min of reaction time was chosen in the following experiments.

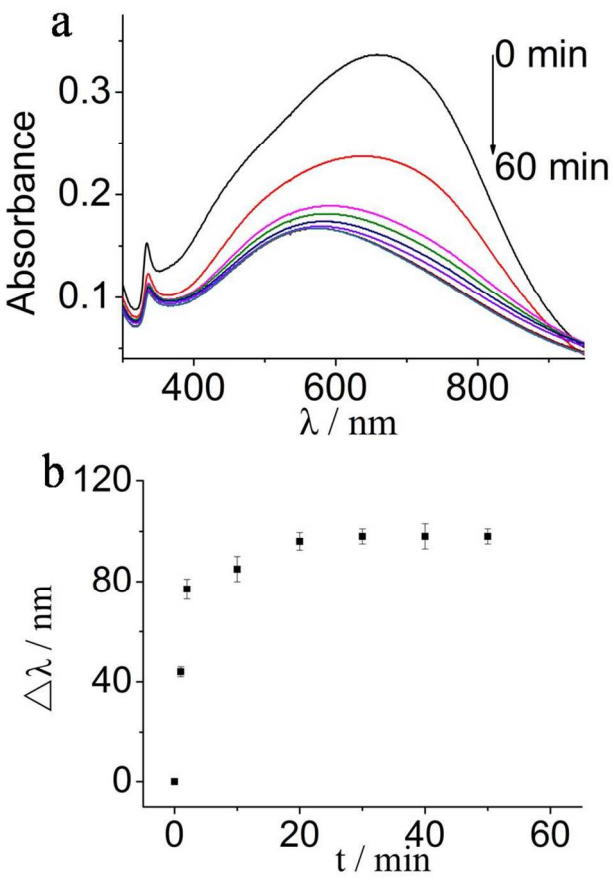


Fig. 2. (a) Time-dependent SPR absorption spectra of the triangular silver nanoprisms upon reacting with free chlorine (20 μM) (0, 1, 2, 10, 20, 30, 40, 50 min, respectively). (b) Plots of SPR peak shift (Δλ) vs incubation time.

The pH value of solution is a key factor for the assay. To choose a suitable pH value, the relationship between pH value of solution and SPR response of triangular silver nanoprisms was studied as shown in Fig. 3. It can be seen that the maximum SPR peak shift (Δλ) of triangular silver nanoprisms was observed at pH 5.0. This observation was related to the forms of free chlorine in water. Most of free chlorine was in the form of dissolved gas (Cl_2) at pH vaules lower than 3.0. Free chlorine mainly existed as hypochloric acid (HClO) at pH vaules around 5.0, and was coverted to hypochlorite anion (ClO^-) if the pH was increased to 9.0 or higher.[1] The ClO^- exhibited a weak oxidation capability than the HClO, which was a disadvantage in etching the triangular silver nanoprisms. Therefore, the oxidation capability of free chlorine achieved a high value at pH 5.0, and weakly acidic condition was suitable for this assay. And the pH of buffer solution was controlled at pH 5.0.

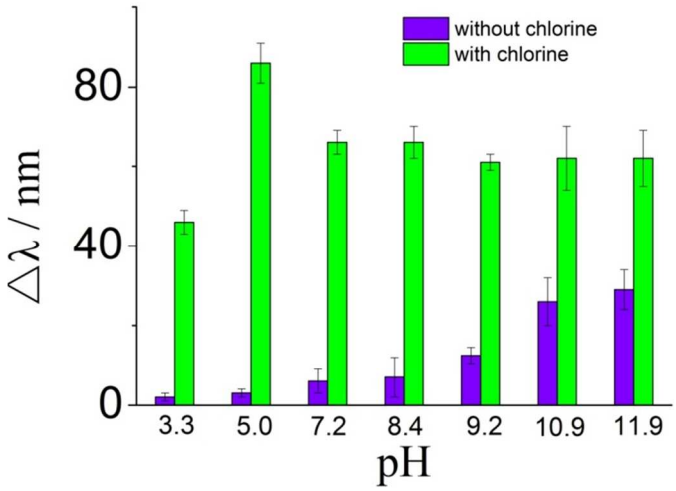


Fig. 3. SPR peak shift (Δλ) of triangular silver nanoprisms in the absence and presence of 20 μM free chlorine at different pH values.

Sensitivity and reproducibility of the proposed assay

The sensitivity of the proposed assay was further investigated. A series of free chlorine with different concentrations were added to the triangular silver nanoprisms solution and reacted with 30 min. As shown in Fig. 4a, the in-plane dipole band of triangular silver nanoprisms was gradually blue-shifted as the concentration of free chlorine increases. Moreover, the linear relationship between Δλ and free chlorine concentration was obtained in the range of 0.1- 20 μM (Fig. 4b), which followed a linear equation: $\Delta\lambda = 7.3 + 4.4\ C$ with a correlation coefficient of 0.9949, where C was the concentration of free chlorine. The detection limit was calculated to be 0.07 μM based on three times the standard deviation of the control. This sensitivity was about one and half order of magnitude lower than that of the most widely used DPD colorimetric methods (1.40 μM) and was also comparable to fluorescent methods (0.05 μM)[4] and chemiluminescent methods (0.08 μM).[8] The reproducibility of this assay was estimated by a series of five repetitive measurements of 0.1 μM, 5 μM, and 10 μM free chlorine, which corresponded to a relative standard deviation (RSD) of 1.3%, 5.2%, and 8.5%, respectively. These results demonstrated that the developed assay had good linearity and relatively high sensitivity and precision.

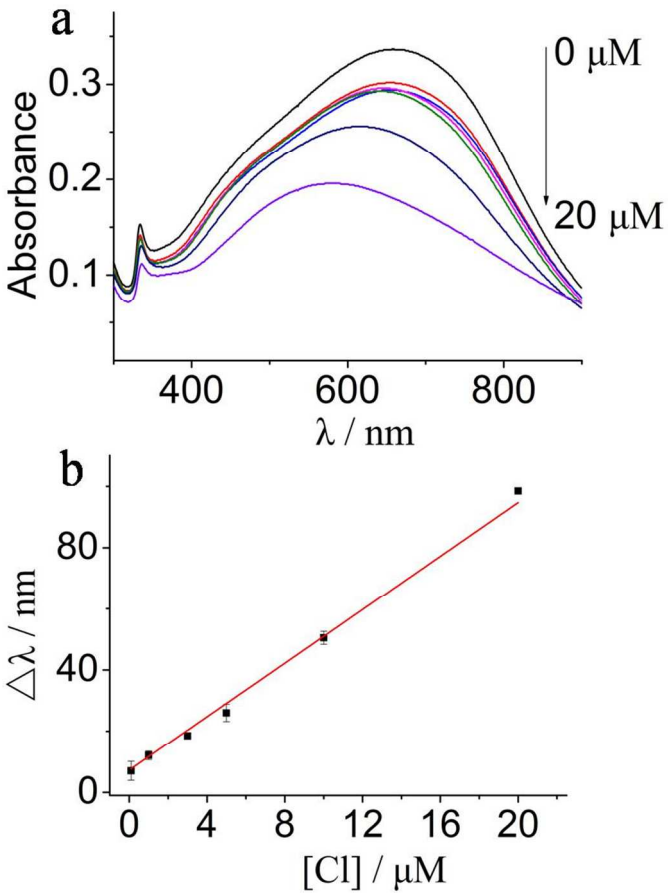


Fig. 4. (a) SPR absorption spectra of the triangular silver nanoprisms for free chlorine concentrations of 0, 0.1, 1, 3, 5, 10, 20 μM . (b) The linearity for the detection of free chlorine.

Specificity of the proposed assay

To investigate the selectivity of the proposed assay, different kinds of species that were considered to possibly interfere with free chlorine detection were tested before its application in a real sample. As shown in Fig. 5, the separate presence of each kind of some common ions including Cl^-, ClO_4^-, CO_3^{2-}, PO_4^{3-}, Mg^{2+}, Al^{3+}, Ba^{2+}, Mg^{2+}, and Fe^{3+} had no influence on the free chlorine detection. Moreover, some heavy metal ions, sulfur containing species, and organic substances such as Cu^{2+}, Ag^+, Mn^{2+}, S^{2-}, L-cysteine (L-Cys), carbon disulfide(CS_2), sodium dodecyl sulfate (SDS), and L-tryptophane (L-Try) were also investigated. These ions had nearly no interference to the in-plane dipole band of triangular silver nanoprisms (Fig. 5). Apparently, the proposed assay exhibited a high selectivity for the detection of free chlorine.

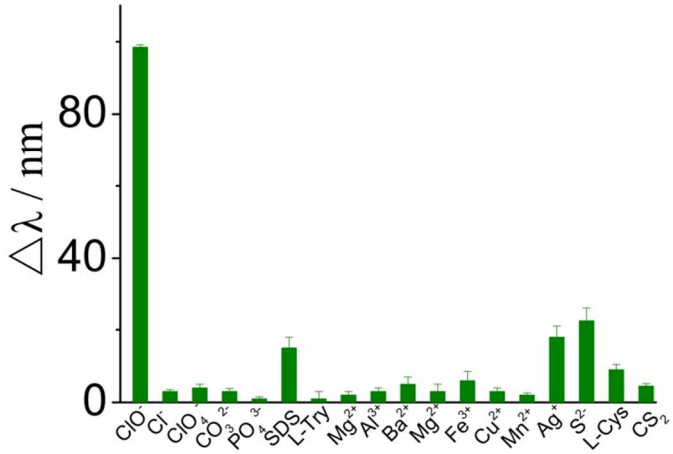


Fig. 5. Selectivity of triangular silver nanoprisms-based assay for free chlorine over other ions, sulfur containing species, and organic substances in pH 5.0 B-R buffer solution (all at a concentration of 20 μM).

Determination of free chlorine in real sample

Practical performances of the proposed assay for free chlorine detection in local tap water were investigated according to a standard addition method. The tested samples were firstly diluted two times for better avoiding the matrix interference. Subsequently, the samples were spiked with standard free chlorine concentrations with different concentrations. As described in Fig. 6, the spiked samples could cause a gradual blue-shift of in-plane dipole band of triangular silver nanoprisms with increasing the concentration of free chlorine. The results showed that the content of free chlorine in the sample was 5.91±0.36 μM , which was closed to the result obtained by DPD colorimetric method (6.01 ± 0.25μM), suggesting that the proposed assay had a capacity for free chlorine detection in tap water.

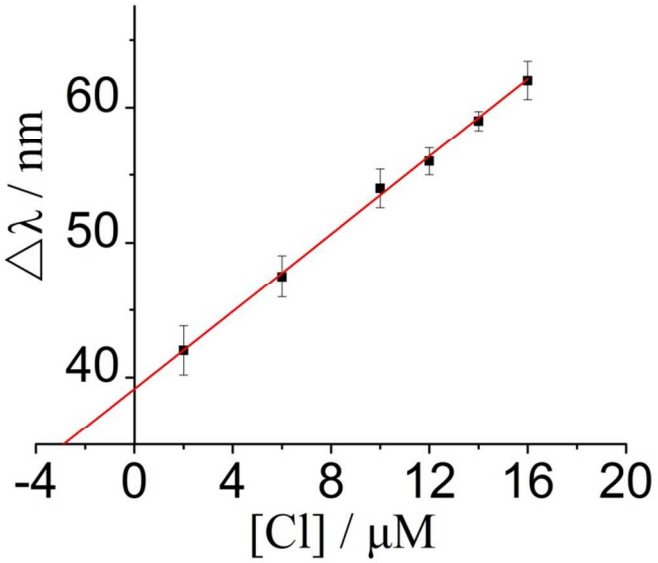


Fig. 6. The SPR peak shift (Δλ) of triangular silver nanoprisms upon addition of tap water and various concentrations of free chlorine in a pH 5.0 B-R buffer solution. The tap water was diluted two fold with pH 5.0 B-R buffer solution before use.

Conclusions

In summary, by taking advantage of unique optical property of triangular silver nanoprisms and etching effect of free chlorine, a novel assay for the detection of free chlorine was proposed for the first time. The strongly oxidizing free chlorine could effectively etch the surface of triangular silver nanoprisms, resulting in the blue-shift of in-plane dipole band. The $\Delta\lambda$ were proportional to free chlorine concentration in the range of 0.1 – 20 μM with a detection limit of 0.07 μM. Moreover, the assay coud be used to determine free chlorine in tap water. The proposed assay had a number of advantages: 1) Contrary to conventional plasmonic assays, the proposed approach did not rely on any interparticle interaction, which improved the accuracy and reproducibility. 2) The preparation of triangular silver nanoprisms was very facile, and the whole operation process was conducted at room temperature. 3) The crude triangular silver nanoprisms were directly used for free chlorine detection without any purification processes. 4) The developed method had a high selectivity over common ions, heavy metal ions, sulfur containing species, and organic substances. Therefore, the proposed assay was envisioned to have great potential applications in food safety and environmental monitoring.

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Note and references

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1 M. Belz, W. J. Boyle, K. F. Klein and K. T. Grattan, *Sensor Actuat. B: Chem.*, 1997, **39**, 380.
2 J. D. Sivey and A. L. Roberts, *Environ. Sci. Technol.*, 2012, **46**, 2141
3 P. Wang, Y. L. He and C. H. Huang, *Water Res.*, 2011, **45**, 1838.
4 Y. Dong, G. Li, N. Zhou, R. Wang, Y. Chi and G. Chen, *Anal. Chem.*, 2012, **84**, 8378.
5 E. Pobozy, K. Pyrzynska, B. Szostek and M. Trojanowicz, *Microchem. J.*, 1995, **51**, 379.
6 F. Kodera, M. Umeda and A. Yamada, *Anal. Chim. Acta*, 2005, **537**, 293.
7 L. Moberg and B. Karlberg, *Anal. Chim. Acta*, 2000, **407**, 127.
8 Y. Tang, Y. Su, N. Yang, L. Zhang and Y. Lv, *Anal. Chem.*, 2014, **86**, 4528.
9 T. Watanabe, T. Idehara, Y. Yoshimura and H. Nakazawa, *J. Chromatogr. A*, 1998, **796**, 397.
10 C. M. Cobley, S. E. Skrabalak, D. J. Campbell and Y. Xia, *Plasmonics*, 2009, **4**, 171.
11 K. Saha, S. S. Agasti, C. Kim, X. Li and V. M. Rotello, *Chem. Rev.*, 2012, **112**, 2739.
12 L. M. Liz-Marzán, *Langmuir*, 2006, **22**, 32.
13 L. J. Sherry, R. Jin, C. A. Mirkin, G. C. Schatz and R. P. Van Duyne, *Nano Lett.*, 2006, **6**, 2060.
14 Y. Xia, J. Ye, K. Tan, J. Wang and G. Yang, *Anal. Chem.*, 2013, **85**, 6241.
15 X. Yang, Y. Yu and Z. Gao, *ACS Nano*, 2014, **8**, 4902.
16 X. H. Yang, J. Ling, J. Peng, Q. E. Cao, Z. T. Ding and L. C. Bian, *Anal. Chim. Acta*, 2013, **798**, 74.