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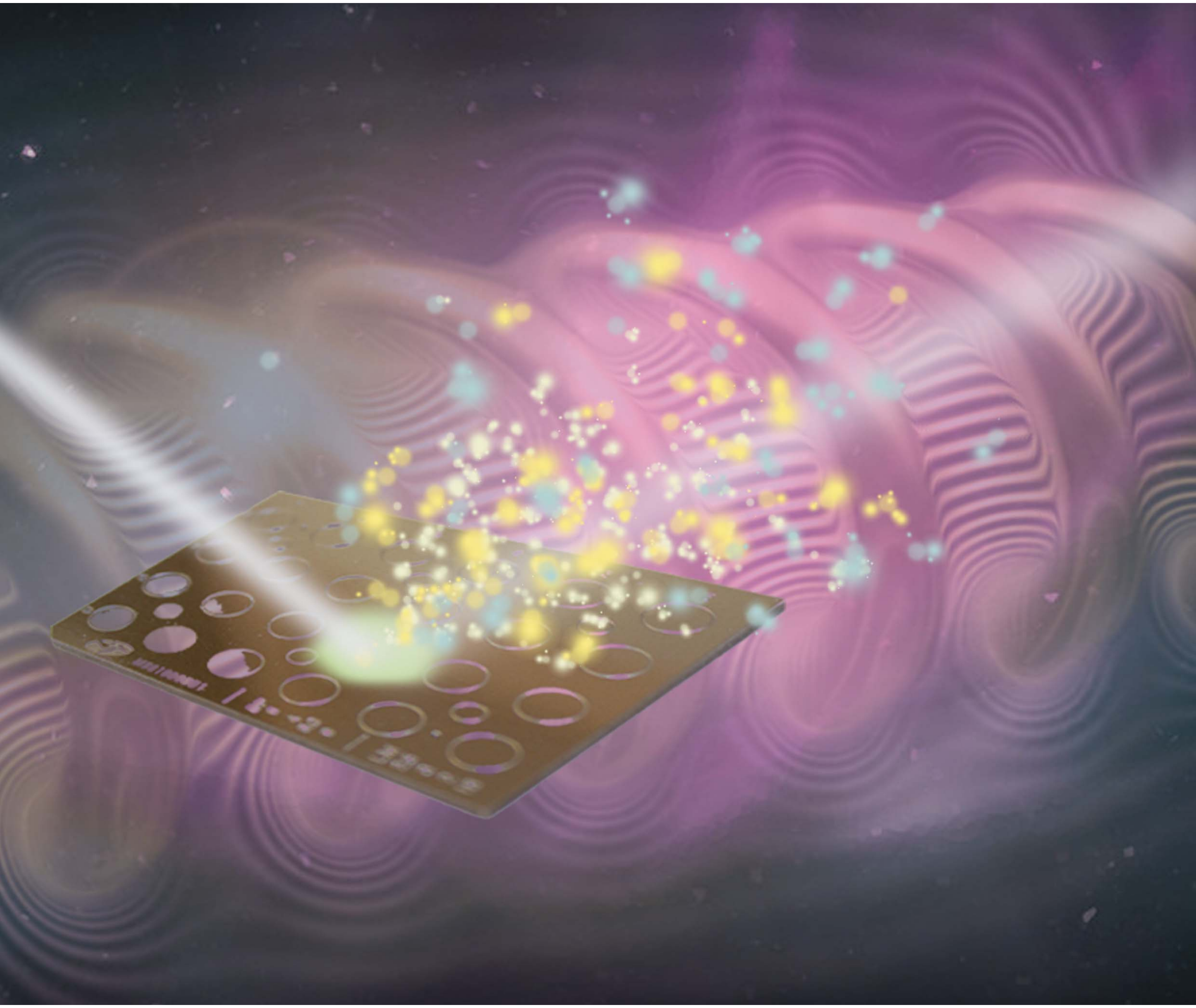

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PAPER

Mollica and Charles *et al.*

Towards the rationalization of the MALDI process: a combined mass spectrometry/solid-state NMR approach

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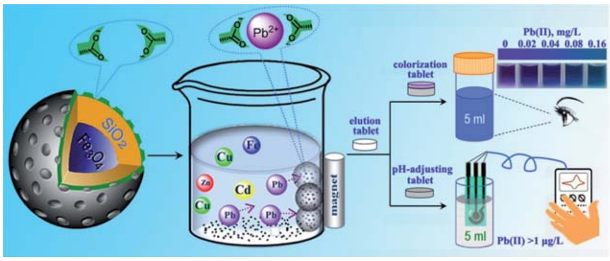
3095

Well-defined surface ion-imprinted magnetic microspheres for facile onsite monitoring of lead ions at trace level in water

Yang Cui, Jia-Qi Liu, Zhang-Jun Hu,* Xia-Wei Xu
and Hong-Wen Gao

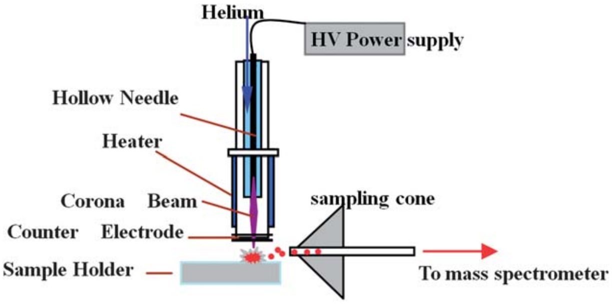


Pb(II)-imprinted polymer shell is chemically fabricated on the surface of $Fe_3O_4@SiO_2$ core, the microspheres capture Pb(II) rapidly and selectively from aqueous solution.

3098

Detection of intermediates in Leuckart reaction by desorption corona beam ionization ambient mass spectrometry

Guangming Xu, Bo Chen,* Hua Wang, Yinzhuang Chen,
Li Ding and Shouzhuo Yao*

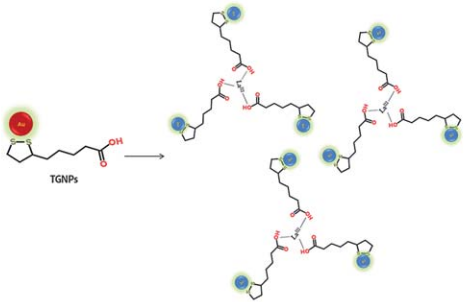


A new ingenious application of desorption corona beam ionization mass spectrometry for detection of intermediates in Leuckart reactions.

3102

Thioctic acid modified gold nanoparticles for highly specific and ultrasensitive detection of lanthanum in soil and water

Alok Pandya, Kuldeep V. Joshi, Pinkesh G. Sutariya
and Shobhana K. Menon*

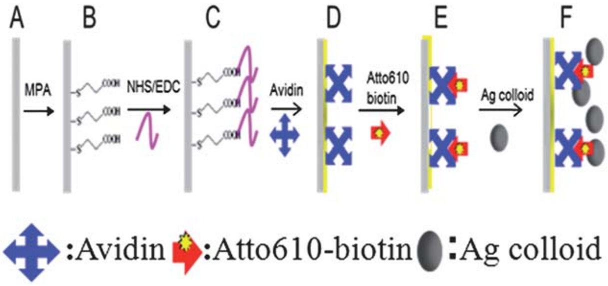


We report ultrasensitive ligand to metal charge transfer (LMCT) based thioctic acid modified gold nanoparticles for the detection of lanthanum ion with excellent sensitivity (50 nM) and selectivity over other cations.

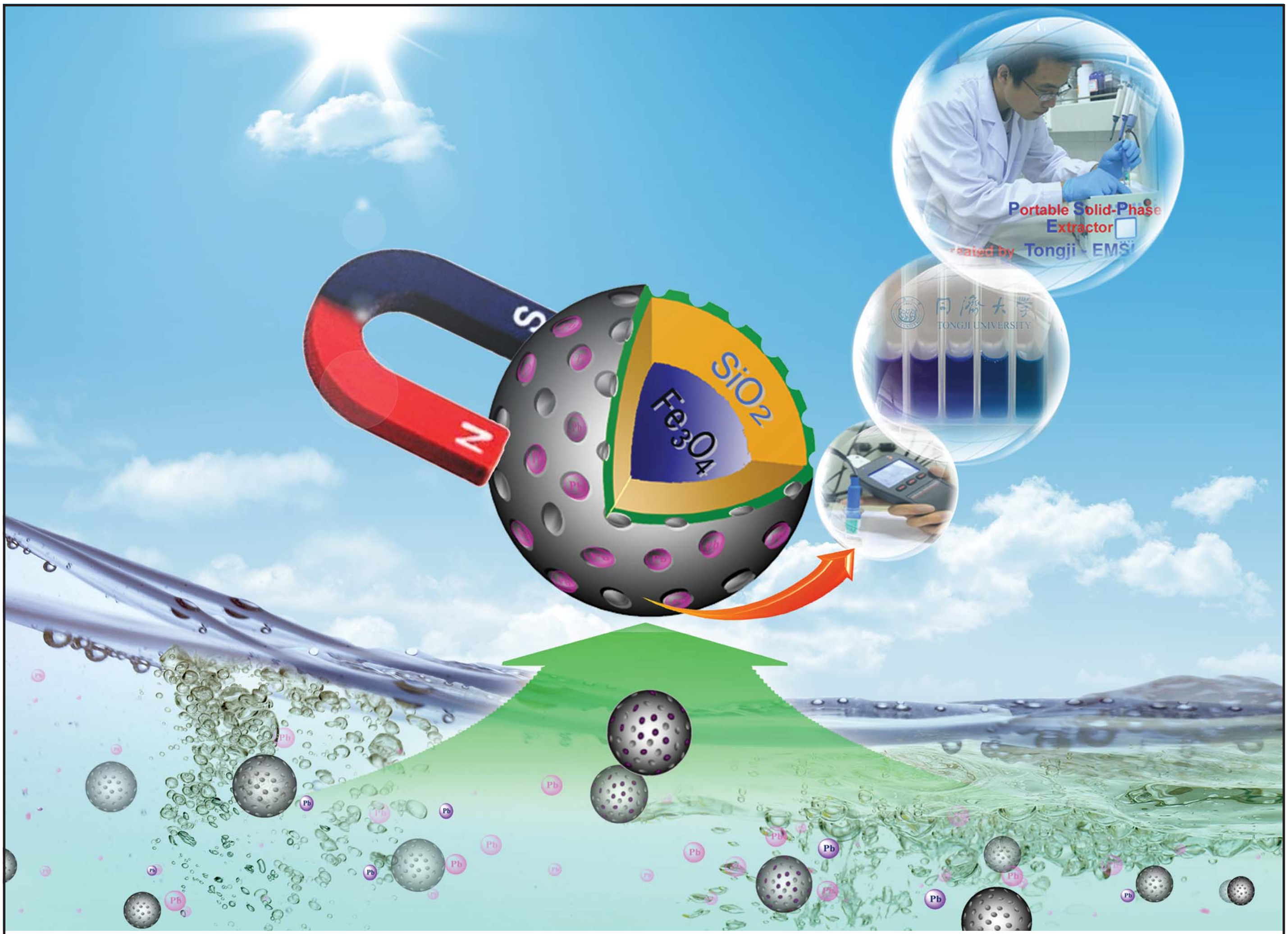
3107

Bioidentification of biotin/avidin using surface plasmon resonance and surface-enhanced Raman scattering (SPR-SERS) spectroscopy

Cuicui Fu, Chengxu Hu, Yu Liu, Shuping Xu
and Weiqing Xu*



A detection method for the bioidentification of avidin/biotin, based on SPR-SERS and a dye labeling technique.



Showcasing research into the onsite detection of lead ions by Prof. Hong-Wen Gao's group (http://www.ludist.com.cn/EMSL/) from the State Key Laboratory of Pollution Control and Resource Reuse (http://envirolab.tongji.edu.cn/), Tongji University, China.

Well-defined surface ion-imprinted magnetic microspheres for facile onsite monitoring of lead ions at trace level in water

Magnetic microspheres coated with a Pb(II)-imprinted polymer shell enable sensitive and selective isolation of Pb(II) ions and can be magnetically isolated from aqueous solution. Onsite monitoring of Pb(II) was established by means of colorimetric and hand-held electrochemical analysis for semiquantitative and quantitative determination, respectively.

As featured in:

See Hu *et al.*, *Anal. Methods*, 2012, **4**, 3095–3097.

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COMMUNICATION

Well-defined surface ion-imprinted magnetic microspheres for facile onsite monitoring of lead ions at trace level in water†

Yang Cui, Jia-Qi Liu, Zhang-Jun Hu,* Xia-Wei Xu and Hong-Wen Gao

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A Pb(II)-imprinted polymer shell is chemically fabricated on the surface of $Fe_3O_4@SiO_2$ core. The title magnetic microspheres capture lead ions rapidly and selectively from aqueous solution so that facile onsite preconcentration and monitoring of lead ions at trace level is possible.

During the last decade, heavy metals pollution has posed a risk for to humans and has become a grave concern worldwide.[1] The alarming state of affairs has promoted the development of onsite monitoring technologies.[2] A strategy involves the use of portable detection systems for controls of industrial discharge and surveys of temporal change of water quality.[3] However, most of those techniques still face challenges in portability and sensitivity due to trace level and matrix interference. An affiliated pretreatment is often indispensable. As well-known, the solid-phase extraction (SPE) has been proven as a highly efficient pre-treatment approach. Well-defined SPE extractants can achieve efficient preconcentration and enhanced anti-interference capacity in the further detection. A number of entity frameworks work as ideal host supports for constructing SPE extractants of heavy metals such as silicates,[4] chelating resin,[5] cross-linked polymers,[6] and carbon nanotubes.[7] These extractants not only exhibit high extraction performance on heavy metals but can also easily be combined with various detection techniques in on-line or off-line mode. In addition, to further enhance the anti-interference capacity, the imprinted technology has been successfully employed in developing highly selective SPE extractants.[8] Unfortunately, the separations using traditional SPE devices with low efficiency still hardly satisfy the requests for rapid onsite detections. Recently, silica-coated magnetic iron oxide nanoparticles ($Fe_3O_4@SiO_2$) have been technologically exploited as carrier to prepare rapidly separable SPE extractants.[9] Particularly noteworthy, the surface imprinting on magnetic cores results in higher extraction selectivity and efficiency.[10]

Predictably, such attributes would achieve faster and simpler analyte pretreatment, as well as higher efficiency and selectivity, which afford possible principles for onsite monitoring trace heavy metals. Consequently, well-defined magnetic ion-imprinted polymer microsphere ($Fe_3O_4@SiO_2@IIPs$) (Fig. 1e) was prepared by distillation–precipitation polymerization in acetonitrile (Fig. S1 in ESI†). For universality, the ubiquitous and toxic lead ion (Pb(II)) was arranged as the targeted analyte and subsequent polymerization was carried out by involving methacrylic acid lead chelate complex (MMA–Pb(II)) and ethylene glycol dimethacrylate (EGDMA) as monomer and cross-linker for the formation of imprinted layer outside magnetic cores. Furthermore, a novel application based on the title extractant for rapid onsite trace Pb(II) detection was proposed by assisting with a facile colorimetric and hand-held electrochemical analysis.

The transmission electron microscope (TEM) and scanning electron microscope (SEM) images of the magnetic microspheres are presented in Fig. 1a–d. As shown in Fig. 1a and c, the $Fe_3O_4@SiO_2$ microspheres are found to be approximately 250–280 nm in diameter

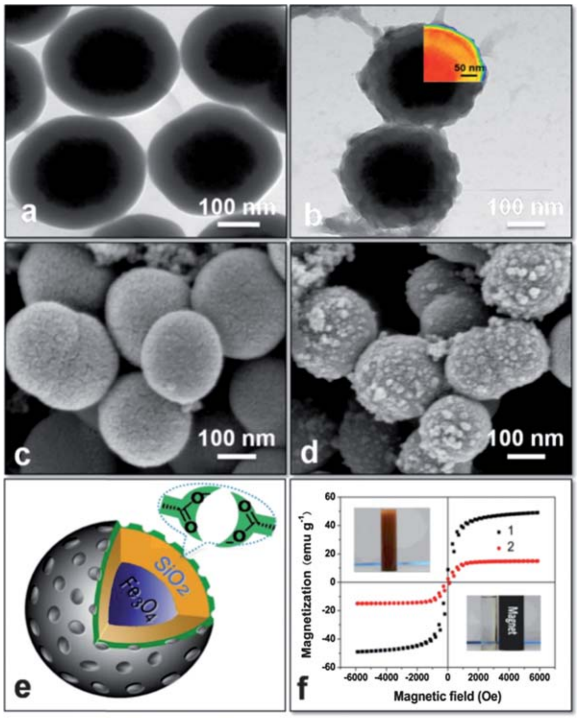

Fig. 1 TEM and SEM images of $Fe_3O_4@SiO_2$ (a and c), $Fe_3O_4@SiO_2IIPs$ (b and d), cartoon illustration of microsphere (e), and magnetization curves of Fe_3O_4 (1) and $Fe_3O_4@SiO_2@IIPs$ (2) (f), and digital photographs of the solutions containing $Fe_3O_4@SiO_2@IIPs$ before and after magnetic separation with the help of an external magnetic field (inset).

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with uniform spherical morphology. A further functionalization using a monolayer of 3-(trimethoxysilyl)propylmethacrylate (MPS) was carried out for the formation of terminal C=C bonds on particle surface (Fe_3O_4@SiO_2@MPS). This step was essential and the final magnetic microspheres were achieved by copolymerization of surface vinyl groups with MMA–Pb(II) and EGDMA. As the generated oligomers of P(MAA-Pb-*co*-EGDMA) in the polymerization are not soluble in acetonitrile, the oligomers will continuously precipitate from the solution and promote the copolymerization on the surface of magnetic particles. Therefore, the robust shells formed with simultaneous distillation of acetonitrile (Fig. 1b and d).[11] Fourier transform infrared (FT-IR) spectroscopy was employed to further investigate the fabrication (Fig. 2). Firstly, the nature of the coordination between MMA and Pb(II) was studied to control the imprint accurately. As shown in Fig. 2b, the antisymmetric ($\nu_{asym}(CO_2^-)$) and symmetric ($\nu_{sym}(CO_2^-)$) bands of the carboxylate of MMA–Pb(II) complex locate at 1517 and 1386 cm^{-1}, respectively. The separation ($\Delta = 131\ cm^{-1}$) between the $\nu(CO_2^-)$ of the coordination is less than the value for the free carboxylate group in MMA monomers (Fig. 2a). It indicates that MMA and Pb(II) coordinate in a chelation mode,[12] which is significantly favourable to guarantee further imprinting polymerization. In subsequent polymerization, the external vinyl groups of Fe_3O_4@SiO_2@MPS (Fig. 2c) gradually copolymerize with the stable chelate and cross-linker. The strong peaks at 1725 and 2950 cm^{-1} are clearly observed after polymerization, which can be assigned to the ester C=O and C–H bonds of MMA and EGDMA (Fig. 2d). The new peaks between 1200 and 1500 cm^{-1} correspond with the spectra of the MMA–Pb(II) (Fig. 2b) which indicates that the imprinted shell has been coated outside the magnetic core successfully (Fig. 1f).[13]

Normally, the thickness of the imprinted shell influences not only their adsorption behavior but also the saturation magnetization of the surface imprinted magnetic materials. By adjusting the concentration of monomer and crosslinker, the shell can be controllably synthesized from 5 to 100 nm of thickness (Fig. S2c†). However, with the increase of the thickness, the microspheres crosslink together gradually and the removal of templates becomes incomplete in spite of eluting for many times, although it may favour maximum adsorption capacities. Ultimately, a 10–20 nm thickness of imprinted layer was established as appropriate for efficient extraction according to the eluting experiments (Table S2†). Compared to the thicker imprinted layer, the optimized imprinted layer could result in a higher adsorption–elution efficiency, as well as faster kinetics owing to easy accessibility (Fig. S6†). In addition, the magnetization was investigated to clarify magnetic separation capability of microspheres. As shown in Fig. 1f, the magnetization saturation of the microspheres approaches 18 emu g^{-1}, decreasing by 2/3 that of pure Fe_3O_4 particles. However, as shown in the inset of Fig. 1f, enough magnetization still remains for fast separation.

Actually, pH of the aqueous solution affects the adsorption of heavy metal ions during the adsorption process. As shown in Fig. S3a,† the adsorption amount of Pb(II) onto the Fe_3O_4@SiO_2@IIPs microspheres increases with increasing pH. It is found that the adsorption rates of Pb(II) are more than 90% when pH > 5.0. It is known that the hydrolysis degree of the metal ions increases along with increasing pH. In order to avoid hydrolyzing at higher pH, pH 5 was chosen for further studies. In a Pb(II) solution containing Cd(II), Ni(II), Cr(III), Cu(II), Mn(II), As(III) and Zn(II), the adsorption selectivity measurement within only 15 min indicated that the co-existing metal ions do not interfere with the adsorption of Pb(II) (Fig. S4†). Therefore, the magnetic Pb(II)-imprinted microspheres are proven to be selective, sensitive and rapid to adsorb Pb(II). The detailed experiments show that the co-existence of 500-fold of K(I) and Na(I), 200-fold Ca(II) and Mg(II), 50-fold of As(III), Cr(III), Zn(II), Ni(II), Mn(II), Fe(III) and Cd(II) and 25-fold of Cu(II) ions almost do not affect the preconcentration of Pb(II) (errors < 10%). According to the proposed procedure (Fig. 3), 40 mg of Fe_3O_4@SiO_2@IIPs adsorb over 90% Pb(II) from 200 mL of aqueous solution with 20 μg L^{-1} Pb(II) (Fig. S6†). The influence on the elution of Pb(II) from microspheres indicates that all targets can be completely eluted by using 5 mL of 2 M nitric acid or 2 g of sulfamic acid (Table S1†); and the enrichment factor of Pb(II) approaches 40.

In fact, the above adsorption–elution procedure has simultaneously removed most of chemical substances from samples within Pb(II) preconcentration, which possibly interfere with further detections. It facilitates the further detection of Pb(II) and makes the onsite detection possible. In order to onsite monitor Pb(II) in the eluate, portable devices, *e.g.*, facile colorimetric and hand-hold electrochemical analysis were proposed. Into a 5 mL colorimetric tube filling with the acidic

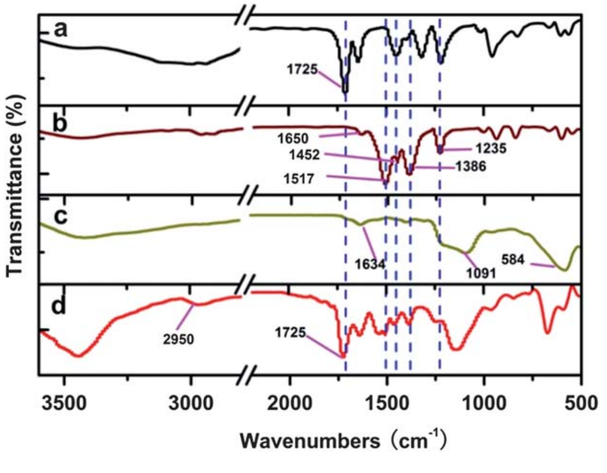

Fig. 2 FTIR spectra of MMA (a), MMA–Pb(II) (b), Fe_3O_4@SiO_2@MPS (c), Fe_3O_4@SiO_2@IIPs (d).

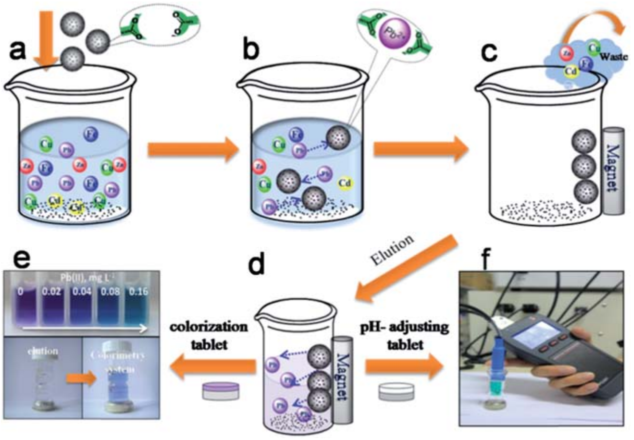

Fig. 3 Preconcentration and onsite monitoring of lead in water samples with Fe_3O_4@SiO_2@IIPs: adding the extractants (a), selective adsorption (b), magnetic separation (c), elution (d), onsite colorimetric determination (e) and onsite electrochemical determination (f).

eluate, a self-prepared colorization tablet was added and then mixed, which consists of chlorophosphonazo III (CPA-III, 0.1 mg), thiourea (0.1 g) and pH 4 adjusting reagent, *i.e.*, sodium bicarbonate (0.6 g)–sodium acetate (0.15 g) mixture (in ESI†). Thus, the concentrations of Pb(II) from 0.02 to 0.16 mg L^{-1} in water samples are rapidly acquired by comparison of the defined violet to blue color gradation (Fig. 3b and Fig. S7†). In addition, a highly quantitative detection of Pb(II) was introduced with a hand-held electrochemical analyzer combined with a commercial printed electrode. Prior to the measurement, an above tablet excluding CPA-III was added to adjust pH of the solutions. A linear calibration curve was obtained under the proposed experimental conditions (Fig. S8†). The electrochemical analysis is proven to be accurate and sensitive between 0 and 20 μg L^{-1} Pb(II), confirmed by ICP-OES. The limit of detection is calculated to be only 1 μg L^{-1} Pb(II). The proposed method was applied to determine Pb(II) in two kinds of water samples from municipal water supply system and factory sewage. The results are 1.17 mg L^{-1} in municipal water and 24.87 mg L^{-1} in factory sewage (Table S3†), which accord with those determined by ICP-OES. The relative standard deviation (R.S.D.s) is less than 2.4% and the recovery of Pb is more than 85%.

In conclusion, the magnetic Fe_3O_4@SiO_2 microspheres were coated with a optimized polymer-imprinted shell to yield the Fe_3O_4@SiO_2@IIPs microspheres. As SPE extractant, it is sensitive and selective to adsorb Pb(II) and easy to be magnetically isolated from aqueous solution. The onsite monitoring of Pb(II) was established by means of the facile colorimetric and hand-held electrochemical analysis for semiquantitative and quantitative determination, respectively. In addition, the self-prepared colorization tablet and the pH-adjusting tablet have greatly facilitated the onsite detection.

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