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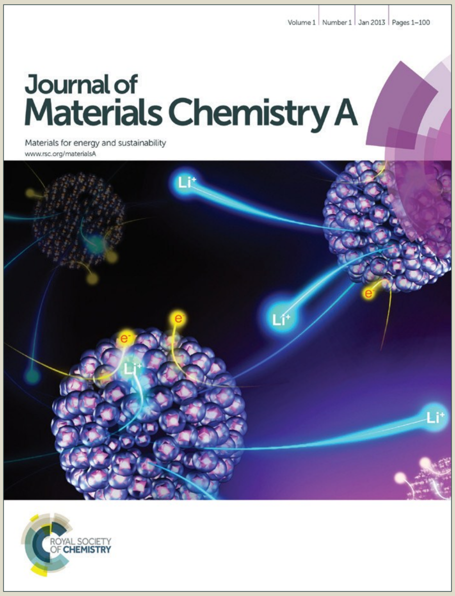

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Current status and challenges of ion imprinting

Junqing Fu,[ab] Lingxin Chen,*[ab] Jinhua Li[a] and Zhong Zhang[ac]

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Ion imprinting technology (IIT) aims to recognize ions while retain the unique virtues of molecular imprinting technology (MIT), namely structure predictability, recognition specificity and application universality. Owing to the special coordination or electrostatic interaction, ion imprinted polymers (IIPs) are generally compatible with aqueous media advantageous over most molecularly imprinted polymers (MIPs), and can achieve effective identification of water-soluble ions, especially heavy metals and radioactive elements, leading to increasing concerns. The purpose of this review is to summarize recent advances of ion imprinting, focusing on the current status and challenges in fundamentals and applications, involving almost all types of ions and ion-related molecular imprinting. Besides, various smart strategies are highlighted, such as surface imprinting, stimuli-responsive imprinting, dual/multiple components imprinting, click chemistry, and microwave-assisted heating. In this review, elemental periodic table is firstly utilized as template ion classification standard to introduce various IIPs, including main group, transition, actinide, rare earth, metalloid, anion imprinting and secondary imprinting. Finally, the challenges and possible solution strategies, and future trends are also proposed (302 references).

1. Introduction

Molecular imprinting technology (MIT)[1] has been increasingly developed to provide versatile receptors efficiently and economically.[2] In general, molecularly imprinted polymers (MIPs) based on MIT are prepared by the copolymerization of functional monomers and cross-linkers in the presence of the target analytes (the imprinted molecules) that act as template molecules.[2] By contrast, ion imprinted polymers (IIPs) are similar to MIPs and retain all virtues of MIPs, but they recognize ions.[3–6]

Fig. 1 schematically illustrates a brief view of imprinting technology history. In 1931, the concept of molecular imprinting first germinated as “unusual adsorption properties of silica particles prepared using a novel synthesis procedure” proposed by Polyakov.[1] These “unusual adsorption properties” have been displayed by numerous polymers, which has paved the way for the original concept of MIPs.[7] In 1949, Dickey[8] proposed the concept of molecular imprinting but not bring to the extensive attention. Patrikeev *et al.*[9] resorted to bacteria as templates in 1960. As pioneers, Wulff, Sarhan and Klotz[10–12] had further introduced the concept of MIPs in early 1970s and since then they had developed several approaches that come under the broad category of covalent and non-covalent imprinting. In this period of time, MIT started to large-scale blossom. More excitingly, IIPs were first proposed by Nishide *et al.*[3] using a metal ion (Cu(II), Fe(III), Co(II), Zn(II), Ni(II), and Hg(II)) as template via cross-linking poly(4-vinylpyridine) with 1,4-dibromobutane in 1976, which has been considered as the most promising branch of MIPs. Then, surface imprinting, a method of imprinting on the surface, was first developed by Sagiv[13] in 1979 using silica particles with polymerized siloxane as surface modifier. In 1993,[14] theophylline imprinted polymer was synthesized and reported in *Nature*, after which unprecedented enthusiasm for the study of MIT was formed. In 1994, Whitcombe[15] proposed and developed semi-covalent approach. In 1999, Sreenivasan *et al.*[16] discussed the possibility of simultaneously imprinting two different template molecules in poly(2-hydroxy ethyl methacrylate), namely, salicylic acid and hydrocortisone, which provided a convincing strategy. Nowadays, MIT and ion imprinting technique (IIT) have extended in many fields rapidly, while at the same time they are accompanied by many challenges.

Figure 1

IIPs are of remarkable attraction because of their ease of synthesis, high environmental stability and high ability to be reused, as well as broad applicability and high selectivity towards the target ion due to a memory effect resulting from their preparation process. Firstly, the force of metal complexes in IIPs is much larger than that of hydrogen bond (usually present in MIPs) especially in the aqueous phase, and thereby IIPs can achieve effective identification of water-soluble ions and metal ions. Because the molecular recognition of life system is closely related to the metal ions and the multitudinous courses of natural world occur in aqueous phases, the development of IIT and IIPs has important scientific significances and application values. Secondly, some transition metals, such as Co(II),[17,18] Pt(II)[19,20] and Fe(II),[21] not only can be used as part of the imprinting, but also as intrinsic catalytic center for complexes conversion. With the aid of ions catalysis, molecularly imprinted microreactors can be built. The last but not least, IIPs can reach thermodynamics and kinetics equilibrium rapidly and simultaneously compared with MIPs, owing to the interaction between central metal ions.

Recently, some reviews on imprinting have summarized rapid development and wide applications of imprinting technologies and materials.[2,22–26] Our group[2] gave a panoramic review on MIT and Whitcombe *et al.*[22] presented the survey to review 3779 references over the years 2004–2011, but neither of them focused on ion imprinting. Rao *et al.*[23] paid more attention to some applications of IIPs for solid-phase extraction (SPE), sensors and membrane separations. Branger *et al.*[24] concerned metal ion IIPs primarily, especially related approaches and techniques. Mafu *et al.*[25] reviewed environmental monitoring of inorganic pollutants using IIPs and Wu[26] focused on anion IIPs. All of the reviews mentioned above don't comprehensively involve the full development status, applications and trends of IIT and IIPs. Lately, more and more IIPs and synthetic techniques have been proposed, for instance, proton imprinting[27] reported in 2014, which further push forwards the development of ion imprinting. Hitherto, various IIPs for the majority of the elements from the first to the seventh period of the elemental periodic table have been prepared, except for some elements in metalloid, alkali metals, rare earth metals and transition regions, as seen in Fig. 2.

Figure 2

Herein, we review the progresses of ion imprinting, addressing the design and synthesis strategies, summarizing the current status and challenges, mentioning almost all types of ions even metal ion-related macromolecule imprinting, and emphasizing publications from 2008-2015. Various smart technologies are highlighted, including surface imprinting technology, stimuli-responsive imprinting technology, dual/multiple components imprinting strategy, click chemistry technology, and microwave-assisted heating technology. The challenges and possible solution strategies, and future perspectives are cautiously proposed.

2. Fundamentals of IIPs preparation

Similar to MIT, IIT targets ion as template mostly and combines the ligands or functional monomers to form chelates or composites by coordinate bond, metal bonding, hydrogen bonding and other effects, followed by the elution of template ions. Finally, the IIPs corresponding to the three-dimensional structure of pores with the target ion are obtained, which can realize the separation and concentration of ions. However, the completion of IIPs depends on various factors,[24] including sound choice of preparation components and techniques, which may become critical points to obtain ideal IIPs.

2.1. Principles of IIPs preparation

IIPs can be divided into two main types at present. One, according to the coordination role between functional/ligand monomers and ions (as template ions), ions as target ions can achieve their own imprinting. The other, ions as a part of the functional monomer can contribute to the imprinting of macromolecules (especially biological macromolecules), which is able to solve the challenge of macromolecules imprinting in aqueous systems. Both of the imprinting processes are generally similar, which is composed of three steps: pre-polymerization, polymerization and removal.[28] On the basis of various binding forces in the first step, three synthesis techniques are presented: covalent imprinting,[10,28] non-covalent imprinting[28,29] and semi-covalent imprinting.[15,28] The principles of the three techniques for preparing IIPs are similar to that for preparing MIPs, which have been explained in detail in the publications.[2,28]

2.2. Components of IIPs preparation

In order to attain perfect IIPs, various components and reagents should be optimized, mainly including functional monomer and ligand, cross-linker, initiator and porogen. Their types and relative proportions can affect the recognition selectivity and binding capacities. Some general characteristics of the IIPs will be briefly introduced as follows.

2.2.1. Functional monomer and ligand

The purpose of selecting the appropriate functional monomer is to provide functional group that can covalently or non-covalently bind with template ions, and is to ensure it has end groups to link with cross-linkers in order to obtain the three-dimensional pore structured polymers. The force or molar ratio between monomer and template has a direct impact on the affinity of IIPs,[30,31] and determines the accuracy and selectivity of recognition sites.[32] Structures of several typical functional monomers such as acrylic acid (AA), methacrylic acid (MAA), vinyl pyridine (VP) are displayed in Fig. 3. However, many functional monomers cannot reach the requirements of imprinting or the bonding force is not strong enough. In recent years, a lot of efforts have been made on novel, self-synthetic monomers such as thymine-3-isocyanatopropyl-triethoxysilane (T-IPTS),[33] ethylenediaminetetra-N-(3-pyrrole-1-yl)propylacetamide (monomer L),[34] (4-ethenylphenyl)-4-

formate-6-phenyl-2,2-bipyridine,[35] (2Z)-N,N-bis(2-aminoethylic) but-2-enediamide,[36] 8-HQ-APTES,[37] N-(o-carboxyphenyl) maleamic acid (CPMA),[38] and 2,4-dioxopentan-3-yl methacrylate.[39] Karim *et al.*[40] have reviewed on different strategies utilized in optimizing MIP design, which can be a good reference.

As for ligand, some similarities and differences exist compared to monomer. The role of the ligand is specific and fundamental since ion chelation is involved in the recognition process.[24] The coordination interaction between ion and the polymer is due to electron donating of heteroatoms based on its unfilled orbitals of the outer sphere. Relatively speaking, commonly used monomers often possess universality to form immobilized covalent or non-covalent bonds for many ions, which may limit its selectivity. However, chelation is specific for certain target. As far as we know, there are three kinds of modes related to monomers and ligands for IIPs preparation, which are shown in Fig. 4. In the first type, ligand acts as an assistant monomer which contains prominent chelate groups without end groups to link with cross-linker. And a functional monomer is required to constitute cross-linked structure. In this case, ligand and monomer may form composite monomer, which is likely to gain better effect and often used for IIPs preparation. In the second type, just a monomer is needed and can meet the imprinting conditions, which is most commonly used for imprinting. Some ligands simultaneously conduct monomer and specific chelation roles, as displayed in the third type, which is uncommon but valuable.

Figure 4

2.2.2. Cross-linker, initiator and porogen

Apart from stabilizing the molecular recognition site, cross-linker also plays a major role in delivering mechanical stability and controlling the porosity of the polymer.[41] Some widely used ones to date including ethylene glycol dimethacrylate (EGDMA), divinylbenzene (DVB), tetraethoxysilane (TEOS),[42,43] trimethylolpropane trimethacrylate (TMPTM),[44,45] epichlorohydrin (ECH)[46,47] and pentaerythritol triacrylate (PETRA)[36,48] are listed in Fig. 3. Besides, the dosage of cross-linker determines the particle size and uniformity of IIPs. Many studies[49,50] have shown that finding an optimum ratio is very important to improve polymer's properties.

In order to select suitable initiators, their effects on polymer properties, polymerization method and temperature, storage and transportation security and other aspects should be considered seriously. Polymerization methods, for instance, oil-soluble initiator may be a good option to bulk, solution and suspension polymerization, while water-soluble one may fit for emulsion and aqueous solution polymerization. The typical and commonly used initiators for IIPs preparation include azobisisobutyronitrile (AIBN), benzoylperoxide (BPO) and persulfate, are shown in Fig. 3.

Porogen also plays an important role in polymerization, since it acts as both a porogen and a solvent in preparation process. The hydrogen bond parameter, dielectric constant, polarity and solubility of porogen make a difference on the polymer usability.[51–53] In addition, the dosage and polarity of porogen influence the bonding strength between functional monomers and templates as well as the property and morphology of polymers.[2] Aprotic and low polar organic solvents, such as toluene, acetonitrile, dichloromethane and chloroform show a high imprinting efficiency, especially in non-covalent interaction system.

Figure 3

2.3. Preparation technologies of IIPs

For IIPs, general polymerization technologies usually include sol-gel process and radical polymerization based on stepwise polymerization mechanism and chain polymerization mechanism, respectively. Radical reaction is composed of bulk,[54,55] suspension,[56] emulsion[57,58] and solution[59] polymerization. Bulk polymerization will provide monolithic morphology materials, while heterogeneous (suspension or emulsion) or homogeneous (precipitation, dispersion or sol-gel[60]) polymerization can produce regular-shaped polymers. All the general polymerization technologies have been dealt with in many reviews[2,24,60] and in book chapters[28] and will not be much described here.

Apart from them, many smart preparation techniques have appeared in order to seek better solutions for attractive and delicate well-designed IIPs. Among them, surface imprinting, stimuli-responsive imprinting and dual/multiple components imprinting strategies have been increasingly developed, while click chemistry and microwave-assisted heating techniques have been little reported. Related smart techniques are briefly illustrated in Fig. 5.

Figure 5

Surface imprinting. IIPs obtained by traditional synthesis methods may lead to the deficiencies of poor accessibility, slow dynamic identification and incomplete template ion removal, while a burgeoning method, surface imprinting,[13] to some extent, can solve the above problems. Core-shell structured microspheres can establish binding sites on the shell uniformly which is advantageous to the template ions elution and diffusion. Furthermore, various carriers are required to play a role of auxiliary supporting in the imprinting process. Amongst them, modified silica particles[45] are the most commonly used, and others such as active polystyrene,[61] chitosan (CTS),[62] quantum dots (QDs)[63–65] and magnetic nanoparticles (NPs)[57,66–69] are also favored.

Stimuli-responsive imprinting. Stimuli-responsive polymers, also called smart polymers, belonging to functional polymers, will produce the corresponding specific responses when the aggregates are subjected to some external environmental stimuli,[70] such as magnetic,[71] pH,[72,73] temperature,[74–76] light[77–79] and chirality.[80] For example, using N-isopropyl acrylamide (NIPAM) as a thermo-responsive element and AA as an interactive element, Ida *et al.*[76] synthesized a straight-chained thermo-responsive adsorbent with a wide range of chelating group content for the recovery of Cu(II). The end-product of poly (NIPAM-co-AA) exhibited considerably higher adsorption capacity (1 order higher) due to higher introduction amount of the interactive element compared to the previously reported cross-linked thermo-responsive adsorbents. Zhang and his team[81] designed and synthesized a temperature sensitive imprinted polymer hydrogels for lysozyme through metal coordinate interaction. N-(4-vinyl)-benzyl iminodiacetic acid (VBIDA) via Cu(II) formed a coordinate complex with the surface-exposed histidine of the template. At 28°C, the imprinting cavity was in a swollen state and the monomer chelated with the Cu(II), which was easily accessible for the protein, leading to the maximum adsorption capacity.[81] When the temperature increased to 43°C, the cavity was in a collapsed state and the Cu(II) was blocked, resulting in a lower adsorption of the protein.[81]

However, dual/multi-stimuli responsive imprinted polymers are relatively less explored for ions than molecules. For instance, using 4-[(4-methacryloyloxy) phenylazo]benzoic acid (MPABA) as a photoresponsive functional monomer and Fe_3O_4 as magnetic substrate, our group[82] prepared magnetic and photonic dual responsive-MIPs (DR-MIPs) by suspension polymerization. The simple, rapid and reliable DR-MIPs based method proved potentially applicable for trace caffeine analysis in complicated samples.[82] More details on stimuli-responsive MIPs can refer to our recent review article.[70] Based on the development of dual/multi-responsive MIPs, related stimuli-IIPs deserve expectation.

Dual/multiple components imprinting strategies. Although IIPs are suitable to separate and remove heavy metal ions, the selectivity is still urgently required to improve. Besides the novel, self-synthetic monomers, the strategies of dual/multiple functional monomers and dual/multiple template ions have gradually aroused increasing attention. The widely and generally used functional monomers such as MAA and VP can offer coordination to some metal ions, such as Cu(II)-IIPs[83] and Pb(II)-IIPs.[84] Two functional monomers can provide an excellent synergy effect to achieve fast adsorption kinetics and high binding capacity. Dual/multiple template ions imprinting is also a meaningful strategy, since multiple ions can be removed simultaneously. For example, Cu(II) and Cd(II) dual-template IIPs[85] as well as Cd(II) and Pb(II) dual-template IIPs[86] have been attained and demonstrated excellent imprinting performances. More interestingly, Zhu and his team[87] synthesized a mixed As(V)-Cr(III) dual-template IIP using two functional monomers. The resultant IIPs could provide a potential material to treat the mixed pollutions of Cr(III) and As(V) in a contaminated water environment.

Click chemistry. Click chemistry is an approach to a set of powerful, highly reliable, and selective reactions for the rapid synthesis of useful new compounds and combinatorial libraries through heteroatom links (C-X-C),[88] which was proposed firstly in 2001 by Sharplessk,[88] the winner of the Nobel Prize in Chemistry. Shortly thereafter, this smart technique was applied to the fields of drug discovery,[89] organic synthesis and polymer chemistries[90,91] and others.[92–95] However, reports on click chemistry applied in imprinting are rare.[96–102] With the aid of Cu(I) catalysis, Li *et al.*[92] have constructed new azo-chromophore-containing hyperbranched polymers (HP1 and HP2) from AB_2 monomers through click chemistry reactions. However, the utilization of click chemistry in IIPs is few. Naeimi *et al.*[102] obtained Cu(II)-imprinted mesoporous organosilica nanocomposites as a recyclable catalyst by using click synthesis of 1,2,3-triazole derivatives. Performing related studies is imperative and will further push forwards the development of IIPs and click chemistry.

Microwave-assisted heating. Microwave-assisted heating technique has been widely applied in synthesis, sintering, sterilization and other areas,[2] due to the property of heating speed, selectivity and efficiency, resulting from the rapid energy transfer and the high energy efficiency of microwave irradiation. So far, the microwave-assisted synthetic method has been applied to almost all types of polymerization, including bulk,[103] emulsion,[104–106] suspension,[107] solution polymerization[108] and sol-gel synthesis.[109] Taking suspension polymerization as an example, a kind of magnetic MIP beads was prepared using microwave-assisted method for the analysis of trace triazines in complicated samples.[107] The resultant products exhibited good characteristics, such as narrow size distribution, uniform morphology, and superior selectivity for analyte, and offered rather high imprinted efficiency factors, which proved the bright prospects of microwave-assisted imprinting. However, by now, to the best of our knowledge, no studies have been reported related to the synthesis of IIPs by microwave-assisted heating technique. The technique for IIPs preparation will be a promising direction.

3. Applications of various IIPs

The majority of the IIPs involves the metal elements, some actinide and rare earth elements from the first to the seventh period in the periodic table, and even metalloid, anion imprinting and secondary imprinting have also been successfully prepared now, as shown in Fig. 2. We present an overview of various IIPs as below.

3.1. Main group elements IIPs

Groups 1, 2 (s-block) and 13 to 18 (p-block) in the elemental periodic table constitute the main group, including Pb, Sr, Al, Bi, Ca, Cs, Ga, H, Sn, Tl, *etc*.

3.1.1. Lead ion imprinted polymers (Pb-IIPs)

Lead (Pb), one of the five heavy metals, with environmental and toxicological significances, has become a research hotspot and received wide concerns. Various methods are available for the determination and removal of Pb(II), especially Pb-IIPs attract much attention. Table 1 summarizes the preparation of Pb-IIPs by various polymerization techniques and their related performances.[43,68,84,110–116]

Table 1

Aboufazeli *et al.*[68] have synthesized IIP magnetic mesoporous silica NPs for selective separation and determination of Pb(II) in food samples simply, rapidly and stably. Li *et al.*[110] have added nano-TiO$_2$ to Pb-IIPs to form covalently bound surface monolayers of the metal alkoxide in order to connect monomer and cross-linker with excellent chemical stability. Yang *et al.*[111] have employed CTS modified multi-walled carbon nanotubes (MWCNTs) as matrix materials to prepare a polymer layer of 15 to 20 nm successfully. Atomic absorption method has been used to study the adsorption properties of the Pb-IIPs, which can be applied to the separation and determination of Pb(II) in waste water.[111] By using microporous polypropylene membrane (MPPM) as support material, Zheng *et al.*[112] have prepared Pb(II) ion-imprinted composite membrane according to three-steps reaction: grafting polymerization of AA, CTS covalent immobilized and ion imprinting reaction. Based on inverse emulsion polymerization, Luo *et al.*[113] prepared Pb(II)-IIPs using crown ether as functional monomer to get higher capacity and selectivity in real environmental water samples. Based on semi-interpenetrating polymer network (s-IPN) technique, Chen *et al.*[114] prepared an innovative Pb(II)-imprinted polyvinyl alcohol (PVA)/polyacrylic acid (PAA) membrane (Pb-IM), as shown in Fig. 6. The analyses indicated that the adsorption of Pb(II) was mainly due to the complexation between carboxyl groups of PAA and hydroxyl groups of PVA and lead ions. The material may be powerful for the selective removal of lead from contaminated water and the s-IPN technique can be a potential tool.[114]

Figure 6

Pb-IIPs are commonly applied to solid-phase extraction (SPE).[43,84,115,116] Tarley *et al.*[43] have synthesized a ion imprinted polyvinylimidazole-silica hybrid copolymer (IIHC), which was used as a selective solid sorbent forpreconcentration of Pb(II) by an on-line SPE system coupled to thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). Our group[84] has made a successful attempt on Pb-IIPs based on ionic interaction via synergy of dual functional monomers (MAA and VP) for selective SPE of Pb(II) in water samples. Compared to single monomer, this strategy provides high selectivity and reliability, obvious anti-interference ability and high extraction efficiency.[84]

3.1.2. Strontium ion imprinted polymers (Sr-IIPs)

Strontium (Sr), a soft silver-white or yellowish metallic element of the alkali metal group, has the minimum abundance and active chemical properties, which commonly exists in mineral water and is essential trace element for human health to prevent arteriosclerosis and thrombosis. IIT is a strong pre-processing mean to concentrate Sr.

Thanks to the large specific surface area, palygorskite has strong adsorption capability to metal ions, inorganic and organic species. Sr-IIPs has been synthesized by surface imprinting with palygorskite as a sacrificial support.[117] The monolayer adsorption capacity of Sr-IIPs is 45.0 mg/g at 298 K, 53.5 mg/g at 308 K and 58.5 mg/g at 318 K. Kalal et al.[118] have synthesized Sr-IIPs based on aniline-formaldehyde for extraction of Sr by SPE from tap water samples. Hrdina et al.[119] synthesized crown ether modified cation exchange IIPs particles, attaining 86±2% ^{90}Sr uptake at pH=9 when applied in urinalysis. Based on graphene oxide, Liu et al.[120] synthesized thermal-responsive magnetic imprinted polymer based on mesoporous silica SBA-15 for the removal of Sr(II) in aquatic environments. In the same year,[121] they successfully synthesized hydrophilic surface IIP by reversible addition–fragmentation chain transfer (RAFT) polymerization, as displayed in Fig. 7. The results showed that the polymers were homogeneous thin layers and they exhibited excellent imprinting efficiency and adsorption capacity.[121]

Figure 7

3.1.3. Other main group ion IIPs

Besides Pb and Sr, some main group ions based IIPs have also been synthesized.[27,122–135]

Alkaline-earth metal. Willner and his group[122] synthesized gold nanoparticles (AuNPs) functionalized with electropolymerizable thioaniline units and dithiothreitol ligands for alkaline-earth metal imprinting, presenting ultrasensitive and selective detection of Mg(II), Ca(II), Sr(II) and Ba(II) using surface plasma on resonance spectroscopy (SPRS). The atomic force microscopy (AFM) image showing the morphology of the electropolymerized Au aggregated composite and related schematic presentations for the electropolymerization are displayed in Fig. 8A and Fig. 8C, respectively. Taking Ba(II) as an example, Fig. 8B reveals that the association of the ions and their dissociation to from the imprinted sites are reversible processes. And then, other main ions for IIPs are briefly introduced as follows.

Figure 8

Al. Aluminium (Al) is an element in the boron group with atomic number 13, which is a known neurotoxicant element contributed to some neurodegenerative diseases,[136] and its positively charged aqua and hydroxy monomeric forms have been found to be the most toxic species to living organisms.[137] So, the selective removal of Al(III) is worth studying. In addition, some metal impurities have great influence on the properties of rare earth material. Gao *et al.*[123] prepared surface imprinted polymers for selective removal of Al(III) from Pr(III) and Nd(III) rare earth solutions. The adsorption capacity could reach 1.98 mmol/g, and relative selectivity coefficients relative to Pr(III) and Nd(III) were 23.47 and 22.85, respectively. N-methacryloyl-L- glutamic acid (MAGA) chosen as the complexed monomer, Denizli and his copartners[124] prepared Al(III)-imprinted poly(hydroxyethylmethacrylate-N-methacryloyl-L-glutamic acid) beads to be used for the selective removal of Al(III) from aqueous solutions. After then, they prepared Al(III)-free PHEMAGA-Al(III) beads for selective separation of Al(III) out of human plasma, applying them for a continuous system by packing the beads into a separation column.[125]

Bi. Bismuth (Bi), with atomic number 83, resembles arsenic (As) and antimony (Sb) chemically and possesses strong polarization effect. The outermost electronic structure is $6s^2\ 6p^3$, but the second outer electronic structure of the atom is $5s^2\ 5p^6\ 5d^{10}$ which is 18 electronic structure. By forming 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex via bulk polymerization, Bi(III) imprinted polymer was prepared for selective preconcentration of ultra-trace amounts of Bi(III) in environmental and biological samples followed by electrothermal atomic absorption spectrometry (ETAAS) detection.[126]

Ca. Calcium (Ca) is essential for living organisms and the fifth-most-abundant dissolved ion in seawater by both molarity and mass, after sodium, chloride, magnesium and sulfate. To design a green material with Ca(II) and to take advantage of its abundance may find out a good imprinting idea. For example, Ca(II) imprinted CTS microspheres with uniform size and morphology were synthesized[127] as an effective and green absorbent in packed column for Pb(II), Cu(II) and Cd(II) removal. Ca(II) was valid for tuning the cross-linking degree of CTS by a weak NH_2-Ca(II) complex.

Cs. Cesium (Cs) is one of only five elemental metals that are liquid at near room temperature with a melting point of 28°C (82°F). Due to its large size, Cs(I) usually adopts coordination numbers greater than six. Zhang *et al.*[128] prepared a surface whisker-supported IIPs to selectively separate trace Cs in different water samples with satisfactory results. CTS incorporated sol-gel process was applied to the synthesis. Rajabi *et al.*[129] used dibenzo-24-crown-8 ether as a selective crown ether and prepared Cs IIP NPs by a precipitation polymerization strategy, followed by flame photometry determination.

Ga. Gallium (Ga) is a soft, silvery metal with atomic number 31. Exposure to airborne particulates of GaP, GaAs and AlGaAs may result in potential health hazards and toxicity.[138] Using MWCNTs as supporting materials, Zhang and his copartners[130,131] have synthesized Ga(III) imprinted composite sorbent[130] and electrochemical sensor,[131] respectively. After removal of template Ga(III)-8-hydroxyquinoline complex, Ga(III)-imprinted materials were used for SPE and preconcentration of Ga(III) in fly ash samples.[130] And electrochemical sensor was stepwise modified by a gold electrode with β-cyclodextrin (β-CD) incorporated MWCNTs and imprinted sol-gel composite film, presenting the detection limit of 7.6×10^{-9} mol/L.[131]

H. Hydrogen or proton (H), is the lightest element from the periodic table and the most abundant chemical substance in the universe but has quite difficult to be imprinted. Excitedly, lately in 2014, Hoshino and his team[27] have designed proton imprinted stimuli-responsive nanogel particles. The schematic illustration of preparation, reversible pKa shift and proposed mechanism of the IIP NPs is shown in Fig. 9.[27] As seen, the NPs exhibited a large reversible pKa shift with AA as monomer. When acidic monomers were protonated in the polymerization process, the protonated acids were easily incorporated into the less polar domains of growing collapsed-NPs and were subsequently stabilized by cross-linkers. As a result, high pKa acids were imprinted in the NPs. The rational design is expected to broadly apply to other stimuli-responsive materials and will be an integral step in the creation of active proton transporters that enable effective ion transport, gas separation, and catalytic reactions.[27]

Figure 9

Sn. The virulence of tin (Sn) metal, its oxides, and its salts are almost unknown. But certain organotin compounds are almost as toxic as cyanide. In terms of Sn-IIPs, speciation analysis, such as various organotin, has become an usual application branch[132,133]. Mercedes *et al.*[132] prepared several bulk polymers using organotin compounds (OTCs) such as monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT) and triphenyltin (TPhT) as templates following covalent and non-covalent strategies, used in SPE for OTCs screening in seawater. Low detection limits, not specific stationary phases, quantitative recovery and high enrichment factor results are responsible for its good application prospects.[132]

Tl. Thallium (Tl) is known to have mutagenic, carcinogenic and teratogenic effects.[139] Tl can be found in nature as Tl(I) and Tl(III); its monovalent state has higher stability, whereas its trivalent state forms complexes are of greater stability.[135] Darroudi and his team[134,135] prepared the ternary complex of Tl(III) at first with 5,7-dichloroquinoline-8-ol (DCQ) and 4-VP for the adsorption and preconcentration of the target Tl(III) in aqueous solution. Then, a "mini-column" SPE system was developed using Tl(III)-IIP particles as adsorbents followed by on-line FAAS detection.

Beyond that, other several elements of main group, especially alkali and alkaline-earth metals such as lithium (Li), sodium (Na) and potassium (K) have hardly been imprinted, as far as we are aware. Two reasons may be responsible for that as follows. (1) Difficult to imprint: because of the small atomic radius and low mass, some metal ions are not easy to be captured. In addition, it is hard to be fixed by appropriate chelating agents compared to transition ions, even the successful imprinting still cannot get a good selectivity. (2) Slight removal significance: they have low damage or even benefit to organism, that is to say, it is not necessary to remove these ions. What's more, Na, K and other ions existing in the seawater are able to be enriched by making salt from seawater with the superiorities of large output and low cost.

3.2. Transition elements IIPs

Transition element, also called transition metal, refers to the metal of d-block in the periodic table other than f-block element (Fig. 2), including Hg, Cu, Cd, Cr, *etc*. Significantly different properties exist based on the 18 electron rule compared to other elements. Some transition metals are easy to form complexes because valence d-orbits are not filled. So, the study of transition element is a hotspot in the field of ion imprinting. As a matter of fact, related researches to imprint transition elements have gradually reached maturity.

3.2.1. Mercury, methylmercury ion imprinted polymers (Hg-IIPs, MeHg-IIPs)

Mercury (Hg) is one of the most important but toxic elements in the environment, due to its high reactivity, extreme volatility and relative solubility in water and living tissues.[140,141] As is known, the toxicity of Hg depends on its chemical forms. Due to their strong lipophilic characteristics, organic Hg compounds are generally much more toxic than Hg(II), especially methylmercury (MeHg). Table 2 summarizes the preparation and applications of various Hg(II)-IIPs[33,34,45,141–147] and MeHg(I)-IIPs[35,148].

Table 2

Based on thymine-Hg(II)-thymine (T-Hg(II)-T) interaction, our group[33] has synthesized novel functional monomer T-IPTS to form Hg(II)-IIPs using sol-gel method for the detection of Hg(II) in water samples by SPE coupled with AFS. Preconcentration factor and detection limit were achieved of 200 and 0.03 μg/L, respectively. Moutet *et al.*[34] synthesized poly(EDTA-like) film in order to voltammetric sense Hg(II). This electrode material especially showed a great affinity towards Hg(II) against Cu(II) while being almost insensitive to Cd(II) and Pb(II). A simple and selective electrode modified with Hg(II) IIPs[141] provided an efficient and cheap voltammetric sensor for the determination of ultra-trace Hg(II) in tap, river and lake water. Also for sensors, Shamsipur *et al.*[142] used a carbon ionic liquid paste electrode (CILE) impregnated with Hg(II) imprinted polymeric nanobeads (IIP) based on dithizone. The voltammetric sensor got low level detection of Hg(II) in aqueous solutions. Wang and his group[145,146] have succeeded in making high selective adsorption materials with the combination of surface imprinting and dual templates imprinting.

Furthermore, Hg speciation analysis has been increasingly investigated. Hg(II) core-shell imprinted sorbents[45] have been completed and tested for speciation and determination of Hg(II) and MeHg(I) in wine samples. Dakova's group[143,144] have made related works for Hg speciation analysis. The microbeads[143] were prepared and applied in river and mineral waters: inorganic mercury has been determined selectively in nondigested sample, while total mercury has been determined in digested sample. A kind of nanoparticle[144] for mercury speciation in surface waters was synthesized and used to SPE. Limits of quantification was achieved, namely 0.015 μg L^{-1} for Hg(II) and 0.02 μg L^{-1} for methylmercury. In 2014,[147] we further presented speciation analysis of Hg by using dithizone-Hg(II) chelate as a template for Hg(II)-IIPs synthesis, as schematically shown in Fig. 10A, followed by SPE and atomic fluorescence spectroscopy (AFS) detection in environmental and biological samples. Satisfactory results have shown that the IIPs could readily discriminate Hg(II) from organic Hg (Fig. 10B and C) and get significant application perspectives for rapid and high-effective clean up, enrichment and determination of trace Hg species in complicated matrices.

Figure 10

MeHg(I) can be bonded to many organic ligand groups, such as -COOH, -SH, $-NH_2$, -OH, and -C-S-C-. For instance, methionine possesses three potential binding sites, -COOH, -NH_2 and -C-S-C-. Under strong acidic conditions of pH less than 2, MeHg(I) bonded the thioether group; under conditions of pH greater than 2, the carboxy group should be bonded; when the pH is greater than 8, the amino group is bonded. Therefore, it is easy for MeHg(I) to react with proteins and amino acids.

Liu *et al.*[35] prepared MeHg-IIPs with novel synthesized monomer of (4-ethenylphenyl)-4-formate-6-phenyl-2,2-bipyridine, by thermal polymerized for determination of MeHg(I) in certified human hair samples and certified soil reference materials using cold vapor atomic absorption spectrometry (CVAAS). The detection limit for MeHg(I) was 0.041 μg L^{-1} and adsorption capacity was 170 μmol g^{-1} of dry microbeads which was 22.6 times of Hg(II). Fu *et al.*[148] synthesized MeHg(I) imprinted fluorescence film with polyvinylidene fluoride (PVDF) films as supporting medium, 4-VP as a functional monomer and 8-mercaptoquinoline as both a complex-forming agent and a fluorescence tag. Using fluorescence microplate reader (FMR) for fluorescence detection, the MeHg-IIP sensor showed a high selectivity against other metal ions.

3.2.2. Copper ion imprinted polymers (Cu-IIPs)

Copper-containing wastewater is also a serious environmental pollution which exists widely in the processes of organic synthesis, electroplating, printed circuit board etching and metallurgy, etc. The study of how to recover the Cu(II) from the mixed metal ion solutions efficiently is a hot topic. Cu-IIPs strategy is particularly interesting which has been summarized in Table 3.[44,83,85,102,149–155]

Table 3

From the polymerization technique, solution and bulk polymerization seem to be more favored. Khajeh and his team[149–151] have conducted a series of experiments through solution polymerization, for example, Cu-IIPs have been prepared with 4-VP as a monomer for extraction, along with Cu(II) analysis via FAAS or ICP-OES etc. The optimization process was carried out using the Box-Behnken design (BBD) which may promote the development of imprinting technology in theoretical research. This method is suitable for analytical chemistry to optimize reaction conditions fast, reasonably and effectively. With the aid of BBD, Naeimi *et al.*[102] developed a convenient method for one-pot synthesis of b-hydroxy-1,2,3-triazoles over Cu-imprinted periodic mesoporous organosilica nanocomposites (Cu@PMO NCs) under ultrasound irradiation. Thanks to the model the catalytic synthesis, water as solvent, ultrasound irradiation, short reaction times and high yields, the work provided an economical and environmentally friendly method, which may be worth to study more. According to precipitation polymerization, core-shell Cu(II) imprinted polymethacrylate microspheres have been prepared[152] with low cost. As for bulk polymerization, a Cu(II) imprinted sorbent has been prepared[153] using 5-methyl-2-thiozylmethacrylamide (MTMAAm) for determination of Cu in sea, lake and tap water samples, hemodialysis concentrates and multivitamin/multielement supplements. In the case of suspension polymerization, a direct imprinting method was developed to prepare porous polymethacrylate micro-particles using a complex of two functional monomers, MAA and VP.[83] Tang *et al.*[154] prepared highly ordered Cu ion imprinted mesoporous silica (IIMS) using a co-condensation pathway. As shown in Fig. 11,[154] Cu(II) was imprinted in (not on) a 1 nm thick matrix wall. The IIMS combines the advantages of imprinting technology and typical mesoporous materials to effectively solve traditional IIP issues of low accessibility and highly heterogeneous binding sites and to improve selectivity of classic mesoporous materials. This approach is applicable for many metal ions during water pollution treatment.

Figure 11

From the aspect of application, the study mainly concentrates in SPE sample pretreatments. Dakova and his group[44,155] prepared a variety of imprinted materials by changing monomers and copper compound groups, using for SPE. More excitingly, Prasad and his team[85] developed a dual ion templates imprinted polymer embedded in sol-gel matrix for the ultra-trace simultaneous analysis of binary mixture of Cu(II) and Cd(II) in tablet, human blood serum, cow's milk and lake water samples. Such strategy has also been applied to preconcentrate and determine Cd(II) and Pb(II)[86] in different seafood samples, such as squid, hake, sardine, horse mackerel, grouper and gilthead bream successfully.

3.2.3. Cadmium ion imprinted polymers (Cd-IIPs)

Cadmium (Cd), a soft and bluish-white metal, is chemically similar to the two other stable metals (Zn and Hg) in the 12th group, which is one of the highly toxic elements among the priority pollutants regulated by the U.S. Environmental Protection Agency (U.S. EPA).[156,157] Cd(II) is highly toxic at low concentrations and can accumulate in living organisms by smoking cigarettes, eating contaminated food, and drinking contaminated water.[157–159] Surface imprinting technology with support particles like silica gel is a common design for the synthesis of Cd-IIPs.[157,160,161] Table 4 summarizes the relevant studies about Cd-IIPs as below.[36,37,46,86,157,160–164]

Table 4

Based on sol-gel technique combining with a double-imprinting concept, Hu *et al.*[162] prepared Cd(II) imprinted 3-mercaptopropyltrimethoxysilane (MPTS)-silica coated stir bar for selective stir bar sorptive extraction (SBSE) of trace Cd(II) from environmental water samples via ICP-MS detection. Candan *et al.*[163] synthesized magnetic Fe_3O_4 porous microspheres in order to remove excessive Cd(II) in human plasma, which is expected to apply to the heavy metal detoxification in organism. Moreover, the commonly application of Cd(II)-IIPs is still SPE. Zhai *et al.*[36] designed a novel dual-ligand monomer (2Z)-N,N-bis(2-aminoethylic)but-2-enediamide for Cd(II)-IIPs preparation, which was used as SPE adsorbents followed by ICP-AES determination, presenting the detection limit of 0.14 μg L^{-1}. Chen *et al.*[46] developed thiourea-modified magnetic ion imprinted CTS/TiO_2 (MICT) for Cd(II) adsorption and 2,4-dichlorophenol (2,4-DCP) degradation simultaneously. 2,4-DCP was adsorbed onto the sorbents' surface and the degradation process occurred with the help of TiO_2 photocatalysis. The maximum adsorption capacity for Cd(II) was 256.41 mg g^{-1} and 2,4-DCP degradation efficiency was up to 98%. The results showed that the MICT composite was an ideal platform to accelerate the disposal of heavy metals and organic pollutants in wastewater. Pourali *et al.*[164] described a nanosized Cd(II)-imprinted polymer for selective SPE and preconcentration of Cd(II) in food and water samples. Besides above, Cd(II) imprinted materials also have certain development in sensor.[37] Yan *et al.*[37] reported fluorescent ion imprinted mesoporous silica combination with one-pot co-condensation method based on fluorescence turn-on sensor array for discrimination of Cd(II) and Zn(II). This work proved that using a simple fluorescent receptor can design a pattern based fluorescent sensing system by taking advantage of the imprinting effect.

3.2.4. Chrome ion imprinted polymers (Cr-IIPs)

Chromium (Cr) is the first element in Group 6 with the atomic number 24. Cr pollution commonly exists in two stable oxidation states in aqueous solutions, namely Cr(III) and Cr(VI). Right amount of water insoluble Cr(III) compounds are not considered as a health hazard, while the most toxic and carcinogenic valence is Cr(VI).[165] Cr(VI) is approximately 100–1000 times' toxicity than Cr(III).[166,167]

A one-step sol-gel reaction with surface imprinting technique on the support of mesoporous silica material (SBA-15) was utilized[168] to prepare Cr(III)-IIPs coupled with the determination of ICP-AES and UV spectrophotometry. The Cr(VI) content was calculated by subtracting the Cr(III) content from the total Cr content. Also via sol-gel process, Tavengwa *et al.*[169] used γ-methacryloxypropyltrimethoxysilane (γ-MPS) packaged Fe_3O_4 magnetic imprinted polymer adsorbent with Cr(VI) as template ion and 4-VP as monomer to remove Cr(VI) in water. In addition, Bayramoglu *et al.*[170] obtained bulk IIPs and applied to remove Cr(VI) anions in water phase. Ren *et al.*[171] prepared Cr(VI)-IIPs and investigated 8 functional monomers to achieve a fast adsorption rate (the adsorption equilibrium was reached within 3 min) and a high adsorption capacity (338.73 mg g^{-1}). The selectivity coefficient for Cr(VI)/Cu(II) and Cr(VI)/Cr(III) was up to 189.05 and 96.56, respectively. The optimized methodology is reliable and valuable, and the study of Cr(VI) and Cr(III) may be a successful case for speciation analysis.

3.2.5. Other transition ion IIPs

Besides Hg, Cu, Cd and Cr ions, other transition group ions have also been imprinted but with relatively few reports. A brief introduction is presented as follows.

Ag. Shawky *et al.*[172] synthesized an ion-imprinted CTS/PVA cross-linked membrane for selective removal and preconcentration of Ag(I) from aqueous solution. Su *et al.*[173] combined IIT with a photocatalytic reaction to deal with the effects of trace TiO_2 on Ag(I)-mycelium surface imprinted. TiO_2 loading improved the adsorption ability because TiO_2 bounded with adsorbents through hydrogen bonding and Ag(I) was reduced to Ag(0) on the adsorbents surface. Hou *et al.*[174] prepared four kinds of Ag-IIPs with different morphologies used for the removal and concentration of Ag^+ from wastewater, as shown in Fig. 12 (Upper). The adsorptivity of ion-imprinting single-hole hollow particles (Ag-IISHPs) was highest, as shown in Fig. 12 (Below). And they tried to elucidate the adsorption mechanism. The adsorption kinetics indicated that the inner surface adsorption process was generally associated with the formation and breaking of chemical bonds.

Figure 12

Au. Ebrahimzadeh and his team[175,176] have developed two Au-IIPs and applied them to aqueous samples and mine stone samples, which is reliable and fast to preconcentrate and determinate the Au(III). In addition, a novel chelating Au(III) imprinted resin has been prepared by Mbianda *et al.*[177], which is highly selective to Au(III) compared to Pb(II), Ni(II), Cu(II), Mn(II) and Fe(III), even at the optimum binding pH (pH=5~6) for the other metal ions.

Co. Co(II)-IIPs were prepared[178] by modifying the surface of ordered mesoporous silica SBA-15 with its surface area remained as much as 299.56 m^2 g^{-1}. Ha *et al.*[179] obtained ion-imprinted functional ligand derivative bearing periodic mesoporous organosilica (IIPMO) with a newly designed Co^{2+}-imprinted ligand core. High adsorption capacity, selectivity and recyclability were reached. Co(II) imprinted CTS was prepared by Bhaskarapillai and his group[180] for its potential application in the chemical decontamination of nuclear power plants. The synthesis of metal-complexing polymer microparticles were accomplished[181] with $[Co(C_2H_3O_2)_2(z\text{-Histidine})]$ molecule as template, which can potentially find application in the purification of histidine-tagged recombinant proteins.

Fe. Denizli and his team[182–184] aimed to synthesize the Fe(III)-imprinted poly(HEMA-MAGA) beads by suspension polymerization and imprinted poly(hydroxyethyl methacrylate-N-methacryloyl-(l)-cysteine methyl ester) [PHEMAC]cryogel by cryo-polymerization for the recognition of Fe from human plasma. What's more, a composite template (Fe and CTAB) imprinted sorbent[185] was prepared by sol-gel process.

Mn. Mn is often used as dope onto ZnS QD. Wang and his team[64,65] constructed the enhanced MIP-based room temperature phosphorescence (RTP) probe by combining the RTP of Mn-doped ZnS QDs, and the schematic illustration is shown in Fig. 13.[64] Hu *et al.*[186] synthesized Mn(II) imprinted MPTS-silica coated capillary by sol-gel technique combining with a double-imprinting concept employed for capillary microextraction (CME) of trace Mn(II) followed by on-line ICP-MS detection.

Figure 13

Mo. Ren *et al.*[187] prepared Mo(VI)-IIPs by the amino-silica surface imprinting technique with a sol-gel process. The isonicotinic acid (4-picolinic acid) was served as a functional monomer and a possible imprinting mechanism was put forward for the Mo(VI)-IIPs.

Ni. Based on inverse suspension polymerization, Branger *et al.*[49] reported the simple synthesis of Ni(II) imprinted polymers beads using mineral oil as the continuous phase for the first time. Because of the large porosity of the polymer, the template ions could be easily eluted. In 2015, they[188] synthesized highly porous particles with good nickel binding capacity and investigated the effect of the complex structure on IIPs selectivity. The good exploration made it possible to establish a desired complex structure by adjusting properly the metal/ligand ratio.[188] Bagheri *et al.*[189] prepared a nanostructured IIP by bulk polymerization applied to the selective extraction and determination of Ni in certified reference materials (soil and polymetallic gold ore), fish, vegetables, river sediments, and river water. Also applying bulk polymerization, Saraji *et al.*[190] synthesized a new IIP material used as sorbent in a SPE column in the presence of Ni-dithizone complex.

Pd. Baba and his group[191,192] synthesized Pd(II)-imprinted CTS derivative (PIPMC) using N-[pyridylmethyl]-CTS (PMC) in order to recover extremely low concentration precious metals from metal plating liquid wastes. By examining the adsorption selectivity and kinetics, the template effect of Pd(II) was studied. In 2011, they proceeded to examine quantitatively the template effect and investigate the mechanism of imprinting process. In addition, Beata *et al.*[193] synthesized three ternary ion imprinted complex (Pd-PDC-VP, Pd-DET-VP, Pd-DMG-VP) and imprinted them into a polymeric network with styrene as cross-linker. The developed materials were successfully applied to separate and concentrate trace amounts of Pd in tap and river water, grass, and certified platinum ore samples with high reproducibility (relative standard deviation below 6.5%).

Pt. Leśniewska *et al.*[194] obtained two Pt(II)-IIPs by acetaldehyde thiosemicarbazone (AcTSn) and benzaldehyde thiosemicarbazone (BnTSn) as chelators for SPE of Pt(II) and Pt(IV) from aqueous solution. And the method was applied to the determination of Pt(IV) by ETAAS in tap water, tunnel dust and anode slime samples.

Rh. A Rh(III)-imprinted amino-functionalised silica gel sorbent was achieved[195] by a surface imprinting technique and was applied to the determination of trace Rh(III) in geological samples with satisfactory results. The relatively selective factor values of Rh(III)/Ru(III), Rh(III)/Au(III), Rh(III)/Pt(IV), Rh(III)/Ir(IV) and Rh(III)/Pd(II) were 26.7, 39.0, 29.2, 28.1 and 43.7, respectively. Cao *et al.*[196] prepared Rh(III)-IIPs used into resonance light-scattering (RLS) method for the determination of Rh(III) based on the reaction among Rh(III), WO_4^{2-} and ethylrhodamine B.

Zr. Mizuki *et al.*[197] prepared an adsorbent Zr(IV)-immobilized resin to remove F^- from tap water and industrial wastewater. A F^-/Zr(IV)/dioleyl phosphoric acid complex with an ideal F:Zr:P mole ratio of 3:1:3 could be optimized by a model complex using computational chemistry. Silica was also usually used as a carrier[198,199] for surface immobilized Zr IIPs.

Furthermore, there are still some related works on imprinting of Ir[200], Lu[201], Ru[202–205] and Zn[206,207], which is not discussed here.

3.3. Actinide elements IIPs

Actinide elements have more lively chemical properties and most of them can form coordination compounds but present low annual output. They are dangerous with the high toxicity and radiation. As far as we are aware, only uranium and thorium IIPs have been reported.

3.3.1. Uranyl ion imprinted polymers (UO_2^{2+}-IIPs)

Uranium (U), weakly radioactive metal, reacts with almost all non-metal elements and the resultant compounds show an exception of the noble gases with temperature increasing. Li *et al.*[208] synthesized amidoximated magnetite/graphene oxide composites, which are potential and suitable candidates for the preconcentration and separation of U(VI). In addition, the most common and stable uranium oxide is UO_2^{2+}, and it has become a commonly used template in the ion imprinting. For helpful expounding UO_2^{2+}-IIPs, we selected some references to present in Table 5.

Table 5

Bulk polymerization[39,50,67,209,210] is most adopted in UO_2^{2+} imprinting. By using bulk polymerization, Tavengwa and his team[67] prepared highly selective γ-MPS coated magnetic IIPs for uranium and studied their binding properties and application to wastewater samples. Zhang *et al.*[39] synthesized UO_2^{2+} imprinted materials used for the extraction of U in sea-water with a high recover efficiency of approximate 93%.

Ion imprinting is often coupled with SPE[50,211–213]. Shamsipur *et al.*[211] grafted IIPs on the surface of silica gel particles. On-line SPE realized determination of subnanogram per milliliter level of UO_2^{2+} and increased sampling frequency of the method in analysis of complex aqueous samples. Also with the help of silica gel, Milja *et al.*[212] prepared imprinted polymer nanospheres, as schematically shown in Fig. 14, and applied them successfully in Sambhar salt lake and ground water for selective removal of uranium. The method can be extended to imprinted nano materials for other toxic metal ions and apply in pollution control processes.

Figure 14

Besides, chitosan/PVA cross-linked hydrogel,[214] anthraquinone based ion-imprinted copolymer[215] and magnetic ion-imprinted composites[216] also have been prepared, which may provide more orientations for the further study. Chen *et al.*[216] prepared magnetic ion-imprinted composite with a uniform core-shell structure. The maximum sorption capacity of MIIC for U(VI) was 354.85 mg g^{-1}.

3.3.2. Thorium ion imprinted polymers (Th-IIPs)

Thorium (Th) is a radioactive actinide metal with atomic number 90. Although +3, +2, and +1 states are also known, the most important oxidation state of thorium is +4. For all we know, only Th(IV)-IIP has been proposed. He *et al.*[38] synthesized new functional monomer N-(o-carboxyphenyl)maleamic acid (CPMA) for Th(IV) polymer adsorbent based on the surface coating of silica gel with a thin layer. The detection limit was 0.51 ng mL^{-1} and it showed superior selectivity, in particular for Zr(IV) at 433.8. Wang and his group carried out a series of work[69, 217–219] on Th(IV) imprinting: In 2011[218], using 3-methyl-1-phenyl-4-(cis-acylbutenoicacid)-2-pyrazolin-5-one as the functional reagent, a surface ion-imprinted composite polymer was prepared with high affinity, selectivity and fast kinetic process advantages. The method was rapid, sensitive and reliable, which could be applied for the preconcentration and determination of trace Th(IV) in real samples. In the same year,[219] it was reported that a surface-grafted technique with MAA as a functional monomer was used to prepare Th(IV)-imprinted polymers. The imprinted matrix for Th(IV)/U(VI), Th(IV)/Ce(III), Th(IV)/La(III) and Th(IV)/Zr(IV) was 58.8, 107, 106.4 and 151.7 times greater than non-imprinted matrix, respectively. In 2013,[69] magnetic Th(IV)-IIPs with salophen Schiff base (N,N'-bis(3-allyl salicylidene)o-phenylenediamine) was obtained for separation and recognition of Th(IV).

3.4. Rare earth elements IIPs

As defined by IUPAC, rare earth element (REE) or rare earth metal is one of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides plus scandium and yttrium.[220] For the past few years, a good deal of functional rare earth complexes have been developed along with the researches dug the rare earth compounds and their complexes in biology, medicine and materials science deeply, which is due to the high coordination number,[221] multiple coordination modes,[222,223] flexible coordination configuration[224] of rare earth ions. From the above, a good foundation is provided to rare earth IIPs.

3.4.1. Europium ion imprinted polymers (Eu-IIPs)

Europium (Eu), the rarest rare earth element but with the highest reactivity, is really important in industrial application, material science, electronics and life science.[225] Most applications of Eu exploit the phosphorescence of Eu compounds for luminescent materials.[226–229] For example, Murray and his team[226] combined the imprinting technique and sensitized lanthanide luminescence to create the basis for a fiber optic sensor that can selectively measure the hydrolysis product of the nerve agent Soman in water. Alizadeh *et al.*[230] synthesized Eu(III)-imprinted NPs using suspension polymerization in silicon oil. Carbon paste electrodes impregnated with IIP were incubated in the solutions containing Cu(II) and different kinds of lanthanide ions. The developed method exhibited low detection limit of 15 μmol L^{-1}.[230]

3.4.2. Other rare earth IIPs

Using a microcolumn packed with scandium IIPs as SPE adsorbent, a new method[231] was developed for the selective separation and pre-enrichment of trace amounts of Sc(III) prior to the determination by ICP-MS, which was validated using certified reference materials and was applied to the determination of trace Sc(III) in geological samples and environmental water samples successfully. Froidevaux *et al.*[232] obtained imprinted polystyrene ion-exchange resin and described the synthesis and structural, thermodynamic and photophysical characterization of complexes for yttrium (Y) and lanthanides with two vinyl derivatives of dipicolinic acid, HL1 and L2. The resin displays high selectivity for Y(III) and lanthanide cations against alkali metals and alkaline earth metals, applying to the production of highly pure 90Y and radio lanthanides for medical applications and trace analysis of these radio chemicals in food and environment. Employing SPE method, Rao and his team have performed some imprinting jobs about rare earth ion. They synthesized IIP particles via single pot reaction for separation of Y(III) from selected lanthanides,[233] and Er(III) IIP particles via thermally copolymerizing[234] and photochemical polymerization,[235] respectively. What's more, Nd(III) IIP materials[236] were prepared as well and got a good result. Guo *et al.*[237] prepared Nd(III)-IIPs followed by ICP-AES determination with the largest selectivity coefficient over 110 for Nd(III) in the presence of competitive ions such as La(III), Ce(III), Pr(III) and Sm(III). As for terbium (Tb), Pb(II) templated thermosensitive heteropolymer gel for multiple-point adsorption of Tb(III)[238] has been synthesized and characterized. The imprinted gel showed strong binding ability to Tb(III). With respect to La(III),[239,240] Ce(III),[241] Gd(III),[242] Dy(III)[243] and Sm(III),[244] only a few studies are reported on their related IIPs.

3.5. Metalloid elements IIPs

Metalloid is the chemical element that has properties between those of metals and nonmetals. The six commonly recognized metalloids include boron, silicon, germanium, arsenic, antimony and tellurium, and even selenium is also regarded as a kind of metalloid in rare cases.

3.5.1. Arsenic ion imprinted polymers (As-IIPs)

Pentavalent or trivalent arsenic (As) exists mostly in the compounds. As(III), medium reduced state, is mainly from the groundwater while oxidation state As(V) is mainly present in the surface water. As for toxicity, As(III) is much stronger than As(V), which is 10~60 times.[245] The widely used arsenic removal method has been mature and arsenic contamination in water governance has made certain achievements.[246] But the development of imprinting technique has opened up new idea and direction for solving arsenic pollution.

Liu and his group prepared a bio-based α-Fe_2O_3 impregnated CTS bead (As-IFICB)[245] with As(III) using for selective removal of As(III) from aqueous solutions. In the same year, an As(III)-imprinted CTS resin (As-ICR)[247] was successfully synthesized to remove As(III) from Laminaria japonica Aresch juice. A As(V)-IIP[248] obtained by bulk polymerization with good reusability up to 20 cycles and the LOD down to 0.025 μmol L^{-1}. According to comparing three functional monomers of 1-vinylimidazole, 4-VP and styrene, 1-vinylimidazole was proved better selectivity and adsorption capacity of reinforced material.[248] Sun *et al.*[249] used surface ion-imprinted amine-functionalized silica gel sorbent to selectively remove As(V) from aqueous solution.

3.5.2. Other metalloid ions IIPs

Polymerization in a glass tube containing SeO_2, o-phenylenediamine, 2-VP, EGDMA and AIBN was achieved by Yamini *et al.*[54] And the IIPs were applied to the recovery and determination of selenium (Se) in different real samples. For the first time, Luccas and his group[250] put forward the concept of atomically imprinted polymers (AIPs) for Se. The proposed method was successfully applied to determine Se in Brazil nuts, apricot, white bean, rice flour and milk powder samples and it was possible to perform 12 analyzes per hour via HG-FAAS online. Fan *et al.*[251] developed a Sb(III)-imprinted iodole-functionalized organic-inorganic hybrid sorbent with sol-gel process. The experiments showed some encouraging results for adsorption capacity, selectivity, reusability and application. Combined with ETAAS, Dadfarnia *et al.*[252] developed SPE method using Sb(III)-IIP sorbent. If Sb(V) is reduced to Sb(III) firstly, this method could measure the total Sb of the juice.

Lack of study on metalloid ions imprinting may be due to the weaker valence bond force between metalloid ion and ligand or monomer relative to the metal.

3.6. Anion imprinting

Besides the increasing cationic ions imprinting, anionic imprinting has also gradually attracted concerns. Anionic species generally include spherical (F^-, Cl^-, Br^-, I^-), linear (OH^-, CN^- , SCN^-), triangular (NO_3^-, CO_3^{2-}), tetrahedral (PO_4^{3-}, SO_4^{2-}, VO_4^{3-}), square planar ($[PdCl_4]^{2-}$, $[Pt(CN)_4]^{2-}$), octahedral (PF_6^-, $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$), and complex shapes (DNA, nucleotides).[26] Nevertheless, not all the anionic species possess imprinting by now. The studies of anion imprinting are seldom reported, which may be caused by the following points. Some of anions are either too small or less functional than other species. The electrostatic interactions for anionic molecules are less effective compared to the smaller cationic species.[26] Anionic species are often not suitable for apolar media.[253] All in all, the significant hindrance is that it is generally difficult to create well-defined recognition sites. Following paragraphs summarize the relevant studies, which are divided into four sections: phosphate, carboxylated, sulfate or sulfonate template and other anionic template imprinted polymers.

Phosphate template. Powell *et al.*[254] chose cyclic adenosine 3':5'-monophosphate (cAMP) as template.[255] incorporated a fluorescent dye as an integral part of the recognition cavity to extra obtain a signal by the change of luminescence. For pinacolyl methylphosphonate (PMP), the hydrolysis product of Soman, used by Murray and his team,[225,256] was reversibly bounded to ligand-coordinated Eu(III) as a template in the preparation of an imprinted polymeric luminescent sensor. Wulff *et al.*[257] employed a phosphate-derived TSA template to present catalytic MIPs modelled on carboxypeptidase A. In the same year, Zhou *et al.*[258] reported a potentiometric chemosensor for the detection of methylphosphonic acid (MPA), degradation product of nerve agents. In addition, diphenyl phosphate (a flame retardant hydrolysis product),[259] p-nitrophenyl phosphate,[260,261] and phytic acid,[262] were also chosen as analytes.

Carboxylated template. Willner *et al.*[263] prepared molecular imprinted ultrathin TiO_2 films firstly by allowing titanium (Ti) butoxide to covalently complex with a carboxylated template molecule. Subsequently, molecular imprinted TiO_2 films were used for selective recognition of chiral carboxylic acids including amino acid derivatives,[264,265] and azobenzene carboxylic acids.[266] Penicillin G, a kind of β-lactam antibiotics, was developed as imprinted polymeric receptor, which was applied to SPE procedure for the selective preconcentration of BLAs from environmental samples.[267, 268] Schmitzer and coworkers[269] used self-synthetic monomer di(ureidoethylenemethacrylate)azobenzene and methotrexate analogue (bis(TBA)-N-Z-L-glutamate) as template to obtain good selective photoresponsive polymers. Photoinduced cis→trans isomerization of theazobenzene-containing polymer backbone is able to regulate the receptor sites' geometry and can regulate the release and uptake of a substrate, as shown in Fig. 15. This stimuli-responsive MIP may find applications in smart drug delivery systems. Prasad *et al.*[270] developed an folic acid imprinted polymer-carbon consolidated composite fibersensor by copolymerizing a novel tri-functional monomer and 2,4,6-trisacrylamido-1,3,5-triazine. Relevant graphic presentations are displayed in Fig. 16. The detection of folic acid with the MIP-fiber sensor was found to be specific and quantitative in aqueous, blood serum and pharmaceutical samples, without any problem of non-specific false-positive contribution and cross-reactivity. For carboxylate anions, bilirubin,[271] daminozide,[272] enrofloxacin,[273–275] dipicolinic acid[276] all have been reported as template ions for IIPs.

Figure 15
Figure 16

Sulfate or sulfonate template. Sevilla and his team[277] created piezoelectric quartz crystal sensor for monitoring of pollutant surfactants such as sodium dodecyl sulfate (SDS). The imprinted polypyrrole film was synthesized by electrodepositing a buffer solution of pyrrole. Ibrahim *et al.*[278] prepared an MIP for SPE of Cibacron reactive dyes, which got good adsorption and binding properties. Moreover, some sulfate or sulfonate anions imprinting works have been reported about 1-naphthalene sulfonic acid,[279] sulfated sugar,[280] and Ramazol Brilliant Red dye (RR).[281]

Other anionic template. Based on surface-enhanced Raman scattering (SERS) technique, Tian *et al.*[282] attained trace detection of 2,4,6-trinitrotoluene (TNT) by attaching p-aminothiophenol functionalized silver nanoparticles to silver molybdate nanowires (Ag-SMNs). Ruikui *et al.*[283] prepared ion imprinting material IIP-PEI/SiO_2 of chromate anion with high performance with respect to the PO_3^{4-}. Also for Cr, Chimuka and coworkers[284] obtained a linear copolymer for selective removal of Cr(VI) from sulphates and other metal anions. Moreover, other related reports have demonstrated arsenate[285] and phenolic acid[286] can also be recognized by means of IIT.

3.7. Secondary imprinting

The secondary imprinting means that metal ions as a part of the functional monomer contribute to the imprinting of molecules such as small molecules, amino acid, protein, and even DNA, by forming coordination bonds with metal ions. However, due to the requirement of finding metal ions which have a specific reaction with the target, the secondary imprinting is much more difficult. For example, in the process of protein imprinting, the metal ions are generally used for the proteins containing exposed histidine groups, and the binding forces between different proteins together with various metal ions are relatively large. Few studies in recent years are the result of the difficult secondary imprinting from mutual selection described above.

An imprinted polymer of bromide ion-lanthanum nitrate modified CTS[287] was prepared and H_2O_2 oxidation-extraction photometric method was used for the determination of bromide ion concentrations. A simple, low cost, selective and sensitive complex imprinted membrane (CIM) for solid-phase fluorescent detection was developed by Li *et al.*[288] with Tb(III) salicylate as complex template, applying into pharmaceuticals and human urine, and the imprinting process and mechanism are shown in Fig. 17A. The metal Tb(III) bridges the analyte salicylic acid (SA) and monomer MAA to form a complex via coordination bond. There is no doubt that the response of CIM to SA was much higher than the responses to the other four analogues, as seen from Fig. 17B. According to Ersöz's method[289], poly(methacryloyl histidine-Ni(II)-CN^-) was synthesized and able to specifically recognize the cyanide ion. The purpose of Ni(II) added is to form the coordination reaction with the template. The relative selectivity coefficients of CN^-/SCN^-, CN^-/S^{2-}, CN^-/Cl^-, CN^-/NO_3^- and CN^-/SO_4^{2-} are 43.37, 54.78, 109.1, 117.2 and 167.9, respectively. Ersöz *et al.*[290] also proposed a novel thiol ligand-capping method with methacryloylamido histidine-Pt(II) (MAH-Pt(II)) as metal-chelating monomer attached to gold-silver-nanoclusters reminiscent of a self-assembled monolayer for cholic acid recognition via Raman spectroscopy. And they even have made an attempt for DNA recognition:[291] MAH-Pt(II) as metal-chelating monomer and guanosine as template to form MIPs for single stranded DNA. Haupt[229] prepared nanofilament-based optical sensors for the analysis of enrofloxacin, an antibiotic widely used for human and veterinary applications, and its sensitive determination was realized with a Eu(III) developer. The synthesized polymer was anchored onto a glass support through UV polymerization. Chang *et al.*[292] reported a facile synthesis of a luminescence sensor based on Eu(III) for detecting chromophoric toxic chemicals. The Eu(III)-IIPs showed significant luminescence only after binding of chemicals bearing sensitizing chromophore moieties. A bi-functionalized molecularly imprinted silica (MIS)[293] mediated by Al was prepared for SPE of quercetin in Ginkgo biloba L. The presence of Al(III) improved the selectivity and efficiency for quercetin extraction. A kind of chiral recognition of proteins having L-histidine residues on the surface with Tb(III) complex were reported by Uzun *et al.*[294] The fluorescent NPs could be used for selective separation and fluorescent monitoring simultaneously. The recognition of C-terminal cholecystokinin pentapeptide (CCK-5) in the presence of nitrilotriacetic acid-nickel (Ni-NTA) complex was analyzed.[295] At the same time, Ni(II) was removed and substituted by other divalent ions such as Mg(II), Fe(II), Zn(II), Co(II) and Cu(II) to study which would be better. A new immobilized metal affinity chromatography (IMAC) matrix[296] was prepared by coordinating Cu(II) with CTS coated on non-porous silica gel. The grafting Cu(II) can provide a series of binding sites, for example, bovine serum albumin and trypsin can be bonded to Cu(II) steadily due to their amino acid sequences.

Figure 17

4. Conclusions and future outlook

In this review, we have summarized the current status of ion imprinting about the preparation and application of various IIPs. Elemental components and smart preparation techniques are outlined, and various types of IIPs are comprehensively reviewed including main group, transition, actinide, rare earth, metalloid, anion imprinting and secondary imprinting. As seen, IIPs are quite compatible with aqueous media which is remarkably advantageous over most MIPs, and can effectively identify, monitor and remove targeted ions in aqueous/biological environments, especially the major issued heavy metals, radioactive elements and anion pollutants. Obviously, the selective recognition, enrichment and removal of metal ions have important significances in environmental sustainability, human health protection, economy development and resource recycling. Although continuous advances and remarkable achievements have been attained in ion imprinting, there are still various substantial development challenges and opportunities, for example as follows.

(1) In terms of the top concerned selectivity and mechanism issues of ion imprinting, they are always the bottlenecks and effort directions. IIT develops relatively slow, mainly because it is often puzzled by the problem of low selectivity, since many ions have the same charges, similar ionic radiuses and properties. Besides employing dual/multiple functional monomers even creating novel monomers, dual/multiple template ions and composite reagents, more other effective and direct strategies should be explored as quickly, in order to improve the selectivity of IIPs. On the other hand, to explain the imprinting and recognition mechanism with the aid of advanced equipment is urgently required. Deep explorations of mechanisms will efficiently solve some bottleneck issues and broaden the application scopes of ion imprinting.

(2) In terms of the research content and scope, involving associated imprinting with common applications for the most part, innovation remains to be continuously digging. Based on thermal, electrical, optical, magnetic and other signals multi-responses,[70] combining IIT with certain testing tools realizes quantitative and continuous detection of ions, which is likely to be a breakthrough. As for secondary imprinting, using metal ions as part of the functional monomer facilitates molecules to form coordination bonds with metal ions. But in the process of protein imprinting, the metal ions are generally used in proteins that contain nudity histidine, which limits secondary imprinting. What’s more, speciation analysis, which includes organic or inorganic form, element valence and even isotope recognition, has received considerable attention owing to their higher importance and applicability than simple ions. With the rapid consumption of earth’s resources, strategic elements, such as uranium and rare earth elements, have obtained increasing national concerns for their extraction and enrichment. From the above, the stimuli-responsive imprinting, second imprinting, speciation analysis and strategic elements imprinting should be put much more emphasis to explore, which will bring a series of innovation for ion imprinting.

(3) In terms of the research target, more concentrations put on the transition metals compared with rare earth metals, actinide metals and metalloid ions. In future, related studies should be strengthened on the latter. Moreover, anion and the secondary imprinting even living cell imprinting should be increasingly investigated. IIT may have more sparks on the combination with biomacromolecules (nucleotides, polypeptide, protein, *etc.*) even living cells and organisms. Recently, with the aid of unique quenching, catalytic and solvent effects, some ions can drive some research hotspots such as quantum dots and click chemistry related studies.[63-65,92,102]

(4) In terms of the preparation technologies and methods, some boundedness and blindness on the selection of IIPs components are still existent. The general polymerization technologies will be continuously used, but related combining with other techniques and materials must be increased for appropriately improving the technologies in order to satisfy higher performance requirements. Various smart techniques and strategies are highly expected to apply for IIPs preparation. Researchers should put more concerns on the techniques and make more attempts in order to attain more variety and better IIPs. Furthermore, establishing complete and reliable guide systems, for example, theoretical calculations (computer simulation),[31,301] experimental design (Box-Behnken design)[149-151] and the correct metal ion-ligand stoichiometry[302] has become one important effort direction, which will greatly enrich the research connotations and effectively simplify preparation processes of IIPs. As well as, it is urgently imperative to exploit new preparation technologies and methods in order to attain higher imprinting efficiency and binding capacity of IIPs.

(5) In terms of the application, most researches focus on separation/purification but lack in other aspects, and large-scale applications of IIPs have been hardly conducted. The applications of IIPs to chemo/biosensing, catalysis, degradation, physiological and clinical researches have a great development room. By virtue of various technologies and strategies and thereby integrating them, it is very possible that IIPs will be active in multi-aspects. Furthermore, the high throughput applications of IIPs in complex matrices are especially desirable.

As far as we know, high volume production and large-scale applications of IIPs have been rarely implemented. One major obstacle faced in transferring IIPs from lab to industry is the form factor of the IIPs synthesized, which make them unusable for large scale applications. For instance, immaturity of preparative techniques, relatively low preparation amounts and high costs, different operation conditions, green environmental protection requirements, etc., restrict the production scale. So, continuous investigation and improvement of various preparation technologies meeting with the needs of high amount, low cost, simple operation and eco-friendliness are urgently required. Several exploration ways are attempted to propose:

(i) Based on the existing preparation technologies, selectivity can be sacrificed to attain high scale production of IIPs. During the batch production, cost-saving is almost always the primary requirement, but selectivity is the secondary goal. The remarkable difference of operation conditions/scales between industry and lab certainly will decrease the selectivity of IIPs to some extent, which is still acceptable to provide high amounts but moderate selectivity IIPs. Hence, more work should be done to apply the suitable existing preparation technologies to produce large amounts of IIPs.

(ii) The development of various smart preparation technologies has promising prospective for up-scaling of IIPs production. Surface imprinting, stimuli-responsive imprinting, dual/multiple components imprinting strategies and so on will decrease preparation cost while remain/enhance selectivity of IIPs along with increased production efficiency and simplified processes. So, more efforts should be made to attempt the new smart technologies for producing large amounts of IIPs and thereby predictable large-scale practical applications.

(iii) The borrowing, reference, coupling and integration of various technologies for IIPs preparation will be an effective way. For example, solid-phase synthesis possesses the advantages of high scalability, reproducibility, controllability and easy automation, which has the great potential for up-scaling of MIPs production.[297–300] Consequently, it is highly anticipated to utilize the technology for IIPs preparation and thereby mass-produced and widely applied.

Therefore, more related endeavors and explorations should be continuously made to introduce various technologies and strategies into IIPs preparation in order to rapidly obtain high amounts of IIPs for industrialization applications.

Abbreviations

2,4-DCP	2,4-dichlorophenol
3-HBA	3-hydroxybenzoic acid
4-HBA	4-hydroxybenzoic acid
AA	acrylic acid
AAAPTS	3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane
AAPTS	3-(γ-aminoethylamino)-propyl-trimethoxysilane
AEDP	2-acryl aminoethyl dihydrogen phosphate
AFM	Atomic Force Microscopy
AFS	atomic fluorescence spectroscopy
AIBN	2,2-azobisisobutyronitrile
AIP	atomically imprinted polymers
AM	Acrylamide
AMP	adenosine monophoshate
APTES	3-aminopropyltriethoxysilane
ASP	Aspirin
BA	benzoic acid
BBD	Box-Behnken design
BPO	benzoylperoxide
cAMP	cyclic adenosine 3’:5’-monophosphate
CCK-5	C-terminal cholecystokinin pentapeptide
CME	capillary microextraction
CPMA	N-(o-carboxyphenyl)maleamic acid
CTAB	cetyltrimethylammonium bromide
CTS	Chitosan
CVAAS	cold vapor atomic absorption spectrometry
DBDA15C4	5,6;14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadecane-5,14-diene
DCQ	5,7-dichloroquinoline-8-ol
DEM	2-(diethylamino) ethyl methacrylate
DMSO	dimethylsulfoxide
DPC	diphenylcarbazide
DR	dual responsive
DVB	divinylbenzene
ECH	epichlorohydrin
EGDMA	ethylene glycol dimethacrylate
ETAAS	electrothermal atomic absorption spectrometry
FMR	fluorescence microplate reader
FTIR	Fourier transform infra-red spectroscopy
GF-AAS	graphite furnace atomic absorption spectrophotometer
GPTMS	γ-glycidoxypropyltrimethoxysiloxane
HAQ	1-hydroxy-2-(prop-20-enyl)-9,10-anthraquinone
HEMA	2-hydroxyethyl methacrylate
ICP-OES	inductively coupled plasma-optical emission spectrometry
IIPs	ion imprinting polymers
IMAC	immobilized metal affinity chromatography
IUPAC	International Union of Pure and Applied Chemistry
LOD	limit of detection
MAA	methacrylic acid
MAC	N-methacryloyl-(L)-cysteine methylester
MAGA	N-Methacryloyl-L-glutamic acid
MIPs	molecular imprinted polymers
MIT	molecular imprinting technology
MPA	methylphosphonic acid
MPABA	4-[(4-methacryloyloxy)phenylazo]benzoic acid
MPPM	microporous polypropylene membrane
MPTS	3-mercaptopropyltrimethoxysilane
MTMAAm	5-methyl-2-thiozylmethacrylamide
MWCNTs	multi-walled carbon nanotubes
NIPAM	N-isopropylacrylamide
NPs	nanoparticles
PAA	polyacrylic acid
PETRA	pentaerythritol triacrylate
Pir	Piroxicam
PMC	N-[pyridylmethyl]-chitosan
PMP	pinacolyl methylphosphonate
PVA	poly(vinyl alcohol)
PVDF	polyvinylidene fluoride
QDs	quantum dots
RAFT	reversible addition–fragmentation chain transfer
RLS	resonance light-scattering
RR	Ramazol Brilliant Red dye
RTP	room temperature phosphorescence
SA	Salicylic acid
SBSE	stir bar sorptive extraction
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
SERS	surface enhanced Raman scattering
SPE	solid-phase extraction
SPRS	surface plasmon resonance spectroscopy
TEOS	tetraethoxysilane
T-IPTS	thymine-3-isocyanatopropyltriethoxysilane
TMPTM	trimethylolpropane trimethacrylate
TMSPMA	3-(trimethoxysilyl)propylmethacrylate
TNT	2,4,6-trinitrotoluene
TPED	N-[3-(Trimethoxysilyl)propyl]ethylenediamine
TPED	N-[3-(trimethoxy-silyl) propyl]ethylenediamine
TS-FF-AAS	thermospray flame furnace atomic absorption

	spectrometry
VB	Styrene
VBIDA	N-(4-vinyl)-benzyl iminodiacetic acid
VP	vinyl pyridine
XRD	X-ray diffractometer
γ-MPS	γ-methacryloxypropyltrimethoxysilane

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[a] Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China
[b] College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China
*Corresponding author. Fax: +86 535 2109130, Tel: +86 535 2109130.
E-mail: lxchen@yic.ac.cn (L. Chen)

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Table (1-5)

Table 1 The preparation and performance of Pb-IIPs

Polymerization techniques	Monomers	Detection	LOD	Sample source	Traits	Ref
Sol-gel process	TMSPMA & 1-vinylimidazole	TS-FF-AAS	0.75 μg/L	Water, injection, urine	Low density, high flexibility and long shelf life	43
Solution polymerization	DPC	FAAS	<1.3 μg/L	Meat, water	Simply, rapidly and stably	68
Suspension polymerization	MAA&VP	AAS	0.19 μg/L	Water	Dual monomer synergy	84
Sol-gel process	CTS	ICP-AES	——	Water	High selectivity	110
Thermal polymerization	CTS	AAS	——	Waste water	Good thermostability	111
Grafting polymerization	CTS	AAS	——	——	High selectivity	112
Inverse emulsion polymerization	4-Vinylbenzo-18-crown-6	AAS	——	Lake water	Novel monomer and polymerization	113
s-IPN technique	PVA&PAA	ICP-OES	——	Contaminated water	An innovative technique	114
Precipitation polymerization	DEM	ICP-OES	1.88 μg/L	River, lake	Convenient and quick method	115
Sol-gel process	APS	ICP-OES	0.20 μg/L	Plants, water	Simple method	116

Table 2 The preparation and performance of Hg-IIPs and MeHg-IIPs

Template	Polymerization techniques	Monomers	Detection	LOD	Sample source	Traits	Ref
Hg(II)	Sol-gel process	T-IPTS	AFS	0.03 μg/L	Tap, river water	Novel monomer	33
Hg(II)	Electrochemical polymerization	Ethylenediaminetetra-N-(3-pyrrole-1-yl)propylacetamide	Electrochemical	5×10^{-10} mol/L	——	Electrochemical sensor	34
Hg(II)	Graft polymerization	MAA	CVAAS	0.02 μg/L	Wine	Speciation analysis	45
Hg(II)	Thermal polymerization	4-VP	Electrochemical	5.2×10^{-10} mol/L	Tap, river, lake water	Electrochemical sensor	141
Hg(II)	Precipitation polymerization	Dithizone	ICP-AES	1×10^{-10} mol/L	Municipal, industry and petrochemical waste water	Electrochemical sensor	142
Hg(II)	Dispersion polymerization	MAA	CVAAS	0.006 μg/L	River, mineral water	Speciation analysis	143
Hg(II)	Dispersion polymerization	MAA	CVAAS	0.015 μg/L	Water sample	Speciation analysis	144
Hg(II)	Surface imprinting	MPTS	AAS	0.35 μg/L	Water sample	Higher binding selectivity	145
Hg(II)&CTAB	Surface imprinting	TPED	AAS	0.06 μg/L	Tap, river water	Compound templates	146
Hg(II)	Sol-gel process	APTES & dithizone	AFS	0.015 μg/L	Environmental, biological samples	Speciation analysis	147
MeHg(I)	Thermal polymerization	(4-ethenylphenyl)-4-formate-6-phenyl-2,2 –bipyridine	CVAAS	0.041 μg/L	Uman hair, soil	Novel monomer	35
MeHg(I)	Thermal polymerization	4-VP	FMR,ICP-MS	——	River	Fluorescence sensor	148

Table 3 The preparation and performance of Cu-IIPs

Template	Polymerization techniques	Monomers	Detection	LOD	Sample source	Traits	Ref
Cu(II)&PAR	Dispersion polymerization	4-VP or 4-VP&MAA	FAAS&ETAAS	0.01 μg/L	——	Combinations of various monomers	44
Cu(II)	Suspension polymerization	MAA&VP	AAS	——	——	Dual monomer	83
Cu(II) & Cd(II)	Sol-gel process	AEDP	Electrochemical	0.035&0.053 ng/mL	Tablet, human blood serum, cow’s milk, lake water	Dual template	85
Cu(II)	Sol-gel process	b-hydroxy-1,2,3-triazoles	——	——	——	Click synthesis; mesoporous organosilica nanocomposites	102
Cu-morin	Solution polymerization	4-VP	ICP-OES	0.12 μg/L	Water and biological samples	New experimental design technique	149
Cu-morin	Solution polymerization	4-VP	ICP-OES	0.14 μg/L	Food samples	New experimental design technique	150
Cu-morin	Solution polymerization	4-VP	ICP-OES	0.8 μg/L	Water	New experimental design technique	151
Cu(II)	Precipitation polymerization	MAA	AAS	——	——	Core-shell	152
Cu(II)	Bulk polymerization	MTMAAm	FAAS	0.9 μg/L	Sea, lake and tap water, hemodialysis concentrates and multivitamin/multielement supplements	Wide application	153
Cu(II)	Co-condensation	AAPTS	ICP-AES	——	Spiked river water, electroplating wastewater	Specific recognition and fast adsorption kinetics	154
Cu(II)&PAR	Dispersion polymerization	MAA	FAAS	0.001 μmol/L	Seawater	Low detection limit	155

Table 4 The preparation and performance of Cd-IIPs

Template	Polymerization techniques	Monomers	Detection	LOD	Sample source	Traits	Ref
Cd(II)	Bulk polymerization	(2Z)-N,N-bis(2-aminoethylic)but-2-enediamide	ICP-AES	0.14 μg/L	River, lake	Novel dual-ligand monomer	36
Cd(II)	Surface imprinting	APTES	Fluorescence spectrophotometer	1.9×10^{-6} mol/L	——	Fluorescent monomer; fluorescent sensors	37
Cd(II)	Sol-gel process	CTS	GC/MS	——	Water sample	Disposal of metals and organic pollutants simultaneously	46
Cd(II) & Pb(II)	Precipitation polymerization	DEM	ETAAS	0.21&0.67 ng/mL	Seafood samples	Dual template	86
Cd(II)	Sol-gel process	Tetradentate Schiffbases ligands	FAAS	——	Mine wastewater	Anchored chelating Schiff base	157
Cd(II)	Sol-gel process	GPTMS	AAS	——	Water sample	Organic–inorganic hybrid sorbent	160
Cd(II)	Surface imprinting	AAAPTS	FAAS	10 μg/L	——	Hydrothermal heating technique	161
Cd(II)	Sol-gel process	MPTS	ICP-MS	4.40 ng/L	Environmental water samples	Stir bar sorptive extraction	162
Cd(II)	Suspension polymerization	MAC	GFAAS	——	Human plasma	Applied to the human body	163
Cd(II)	Precipitation polymerization	4-VP	FAAS	0.2 μg/L	Food and water	Nanosized polymer	164

Table 5 The preparation and performance of UO_2^{2+}-IIPs

Polymerization techniques	Monomers	Detection	LOD	Recovery (%)	Sample source	Traits	Ref
Bulk polymerization	2,4-dioxopentan-3-yl methacrylate	ICP-AES	——	93.8±5.4	Sea water	New monomer	39
Bulk polymerization	Styrene	ICP-AES&AAS	——	80	Aqueous systems	Binary complex	50
Bulk polymerization	MAA&VP&SALO	ICP-AES&AAS	——	98	Waste water	Magnetic	67
Bulk polymerization	4-VP& HEMA	AAS	——	>99	Uranium mining industry	Detoxification; mining industry simulants	209
Bulk polymerization	SALO/MAA;VP/MAA; SALO/VP/MAA	GTA-AAS	5 μg/L	95.9±1.1	Ground, river and sea water	Salicylaldoxime; Ternary complex	210
Surface imprinting	MAA	ICP	1.6 ng/ml	103.8±1.8	Real water samples	On-line SPE	212
Precipitation polymerization	4-VP& HEMA	FAAS	——	>99	Sambhar salt lake, ground water	Simple way	213
Sol-gel process	APS&TEOS	FAAS	7.32 μg/L	93.02±3.5	Water sample	Magnetic	214
Sol-gel process	CTS&PVA	ICP-AES	——	——	Aqueous solutions	Interpenetration network ion-imprinting hydrogel	216
Precipitation polymerization	HAQ	ICP-AES	——	95	——	Anthraquinone based ion-imprinted copolymer	217
Sol-gel process	4-VP&Am	FAAS	——	——	Aqueous solutions	Magnetic	218

Figure (1-17)

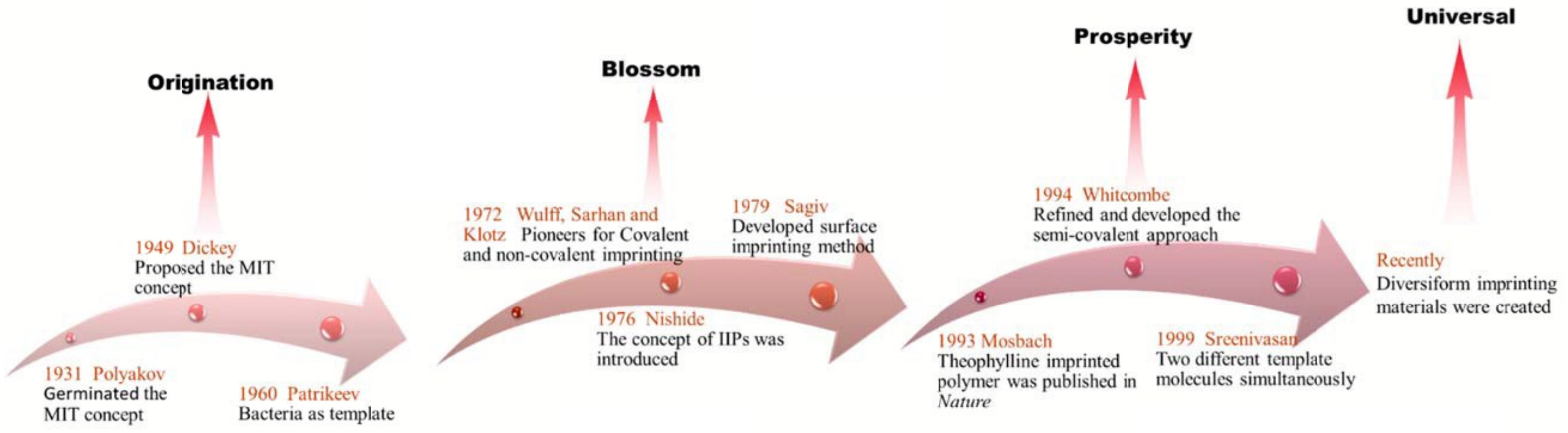

Fig. 1 A brief view of imprinting technology history.

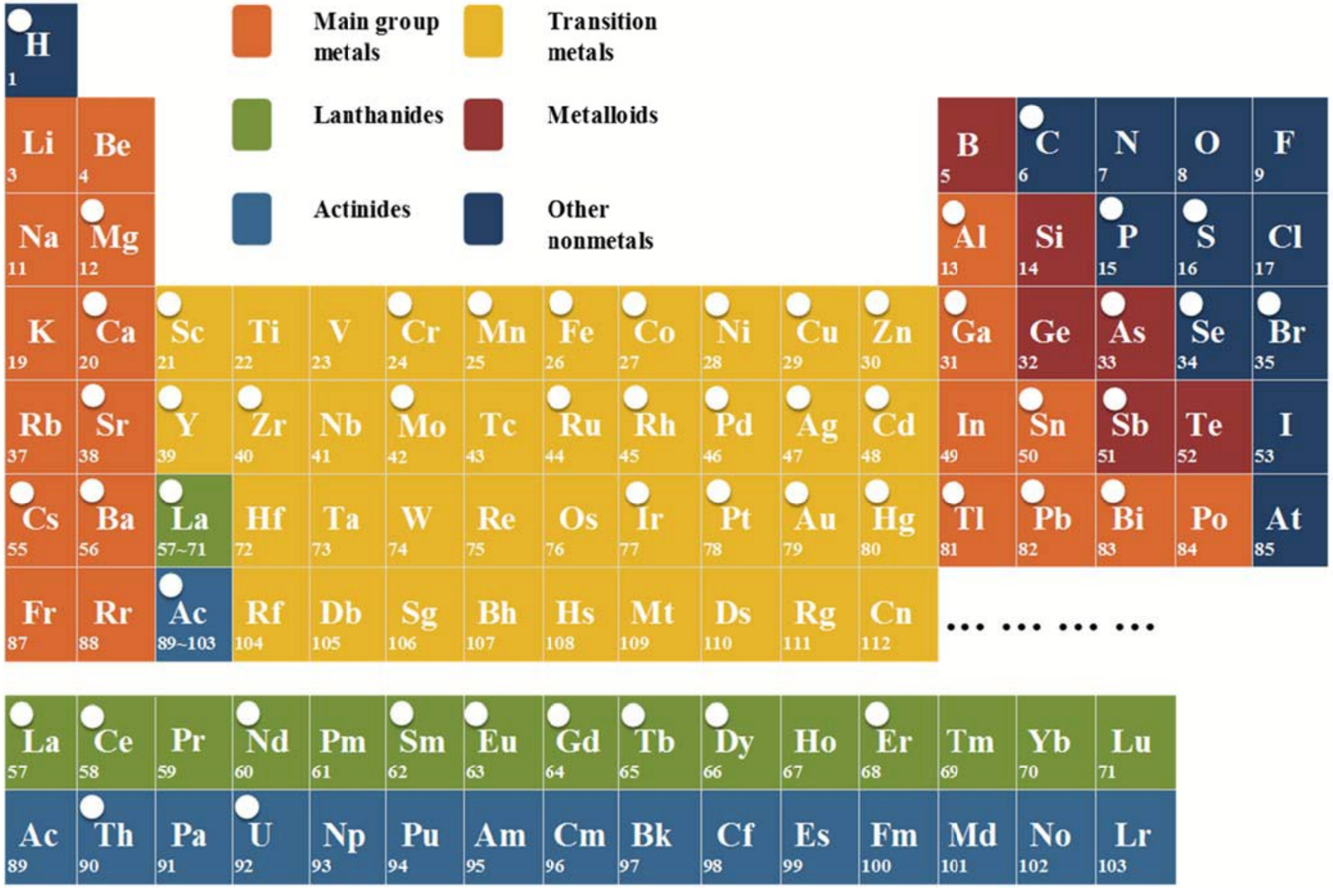

Fig. 2 Schematic illustration for all element marked with dot notation in periodic table of elements used for ion imprinting.

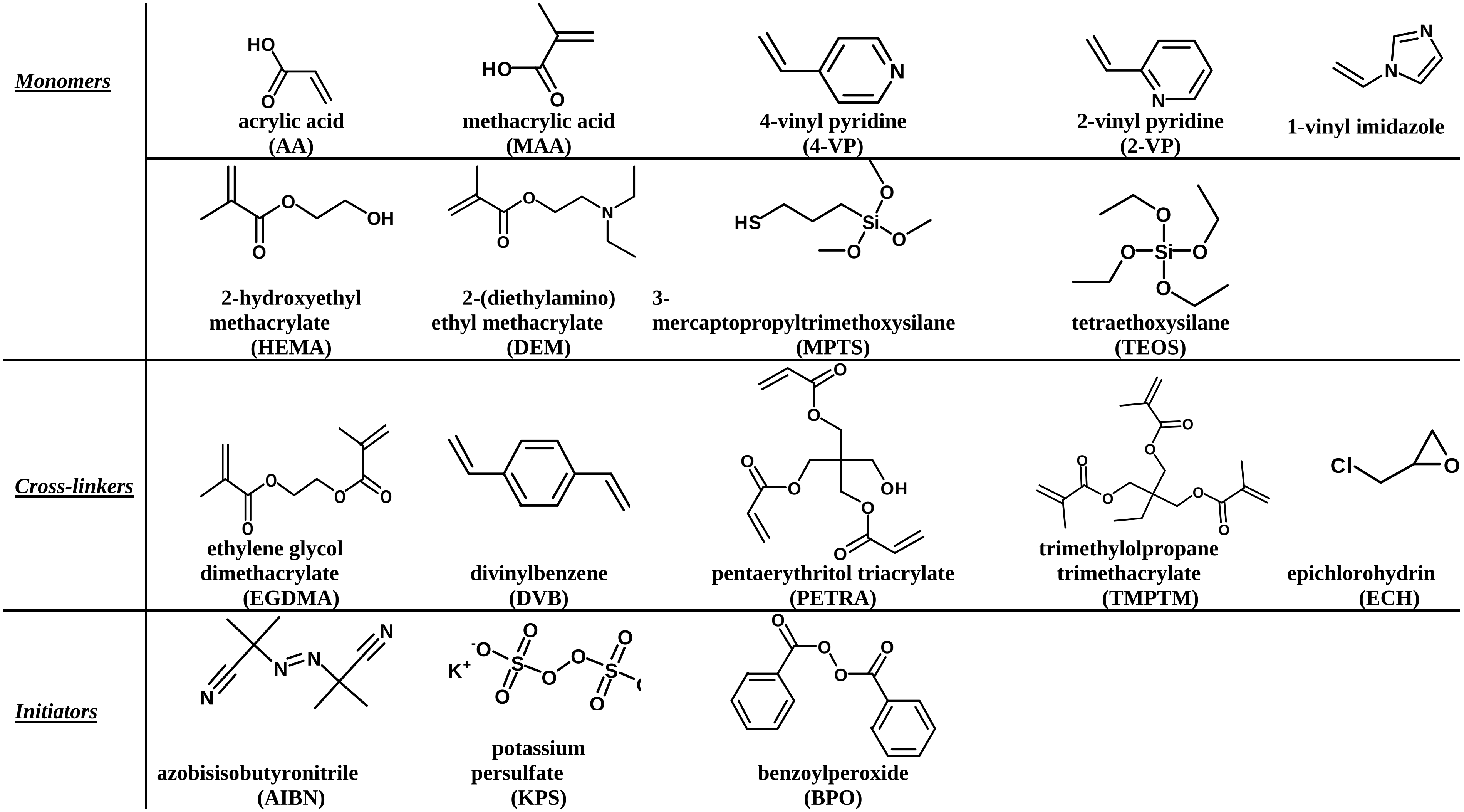

Fig. 3 Structures of commonly used functional monomers, cross-linkers and initiators.

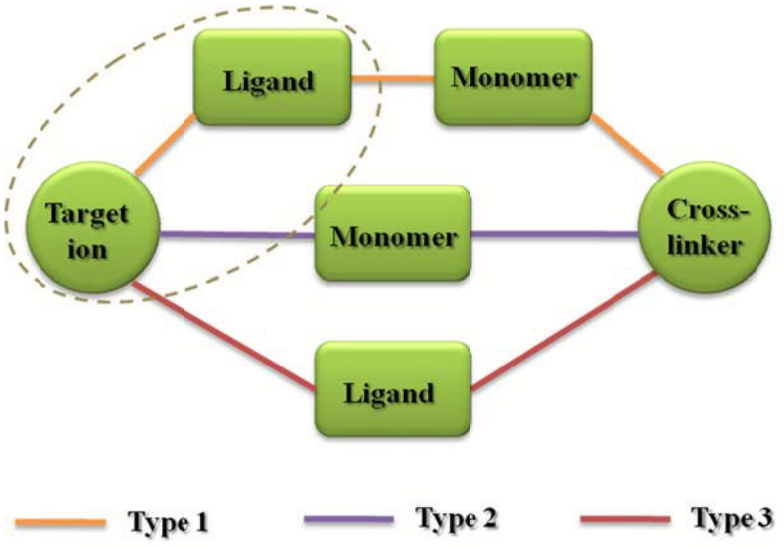

Fig. 4 Schematic illustration for three modes related to monomer and ligand.

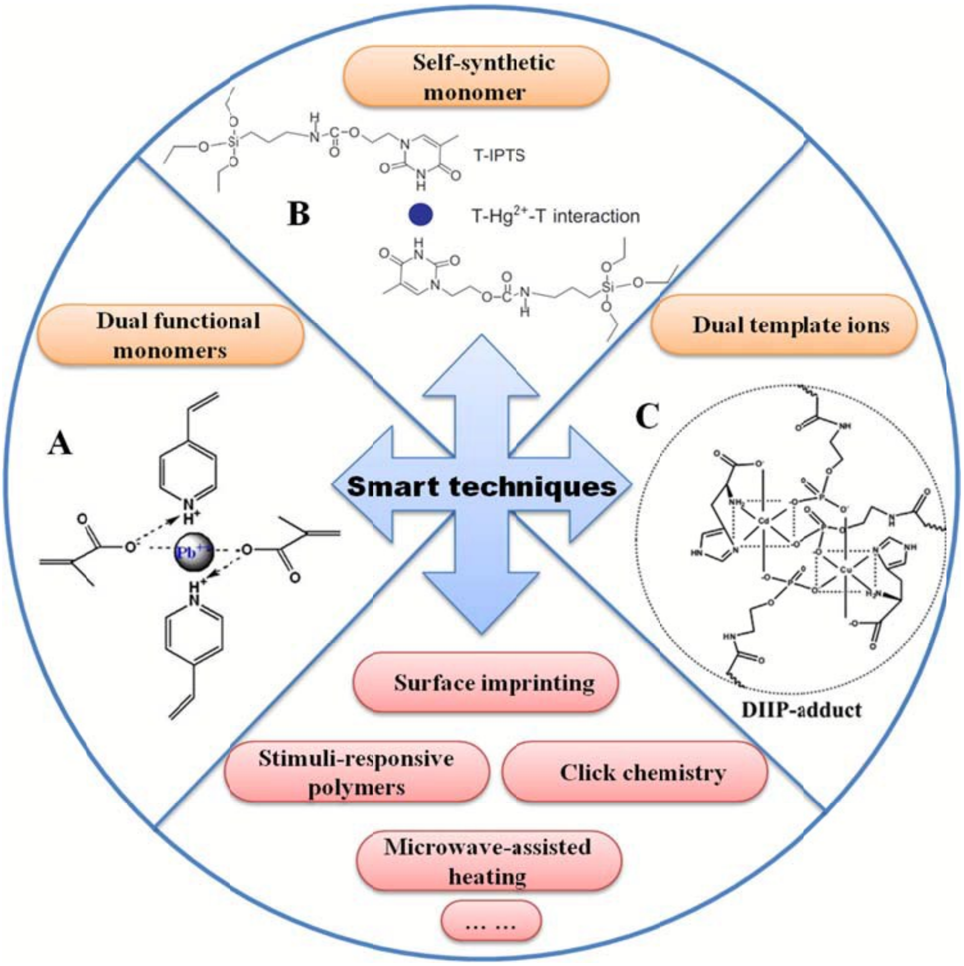

Fig. 5 Related smart techniques for IIPs preparation: (A) Pb(II)-IIPs employing dual functional monomers of MAA and 4-VP. [ref. 84] (B) Schematic illustration for the interaction of T-Hg^{2+}-T employing self-synthetic monomer T-IPTS. [ref. 33](C) DIIP-adduct using dual template ions: Cd(II) and Cu(II) bindings simultaneously in their respective imprinted cavities. [ref. 85]

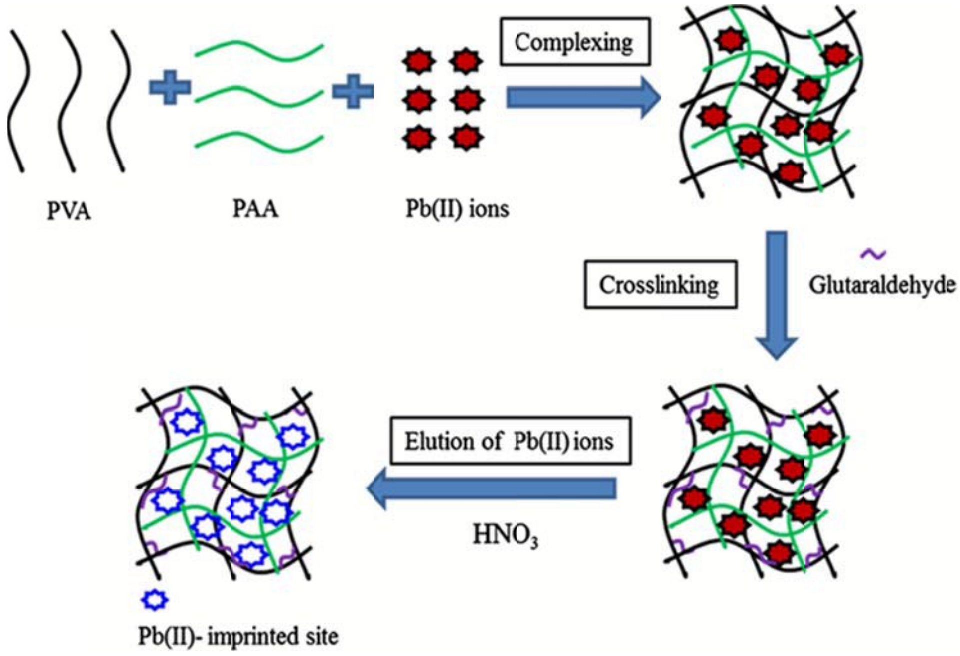

Fig. 6 Schematic diagram of preparation of Pb(II)-imprinted membrane by s-INP technique. Reprinted with permission from ref. 114. Copyright 2014 Elsevier Inc.

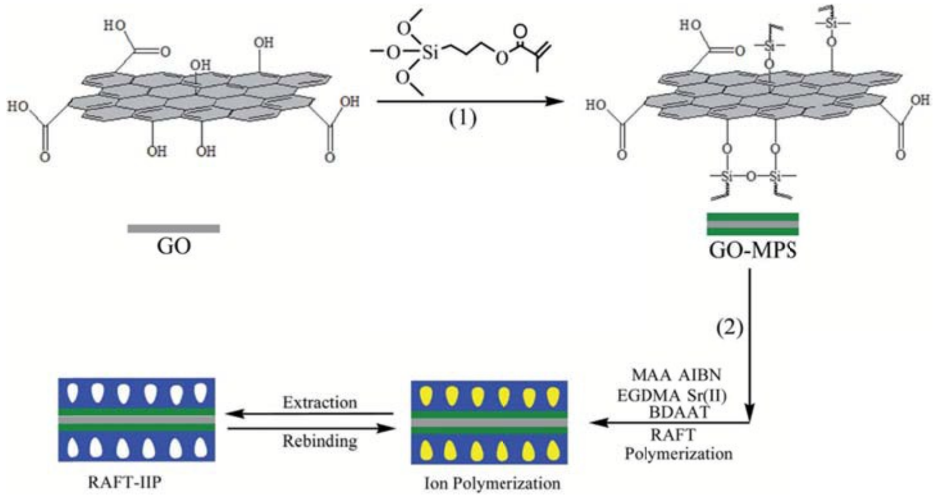

Fig. 7 Scheme depicting the ion-imprinting process on GO surface by RAFT polymerization. Reprinted with permission from ref. 121. Copyright The Royal Society of Chemistry 2015.

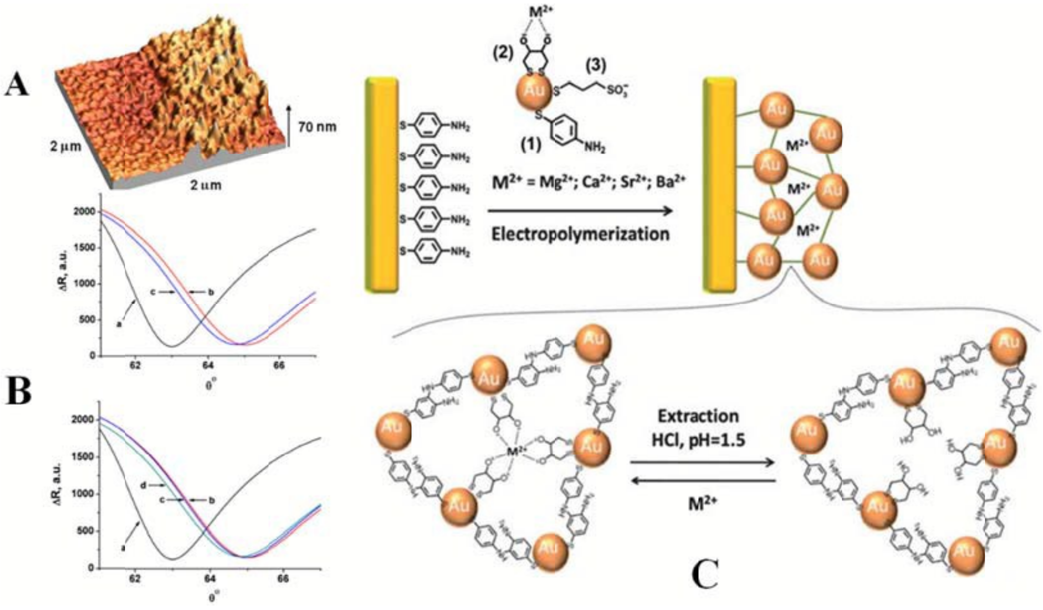

Fig. 8 A case of alkaline-earth metal imprinting: (A) AFM image of the boundary region corresponding to the electropolymerized Au NPs composite on the bare Au electrode surface. (B) Upper: SPR curves corresponding to: (a) The thioaniline-modified Au surface before electropolymerization. (b) The bis-aniline-crosslinked Au NPs composite electropolymerized on the Au surface in the presence of Ba^{2+}, 10 mM. (c) The Ba^{2+}-imprinted bis-anilinecrosslinked Au NPs matrix, following the treatment of the matrix with HCl, 0.03 M, for 5 minutes. Below: SPR curves corresponding to: (a) The thioaniline-modified Au surface before electropolymerization. (b) The bis-aniline-crosslinked Au NPs composite electropolymerized on the Au surface in the presence of Ba^{2+}, 10 mM. (c) The Ba^{2+}-imprinted bis-anilinecrosslinked Au NPs matrix, following the treatment of the matrix with water, for 10 minutes. (c) The Ba^{2+}-imprinted bis-aniline-crosslinked Au NPs matrix, following the treatment of the matrix with water, for 5 hours. (C) Schematic presentation for the electropolymerization of a bis-aniline-crosslinked Au NPs composite on a Au-coated electrode for the sensing of Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} using dithiothreitol as a ligand for the imprinted metal ions. Reprinted with permission from ref. 122. Copyright the Royal Society of Chemistry 2012.

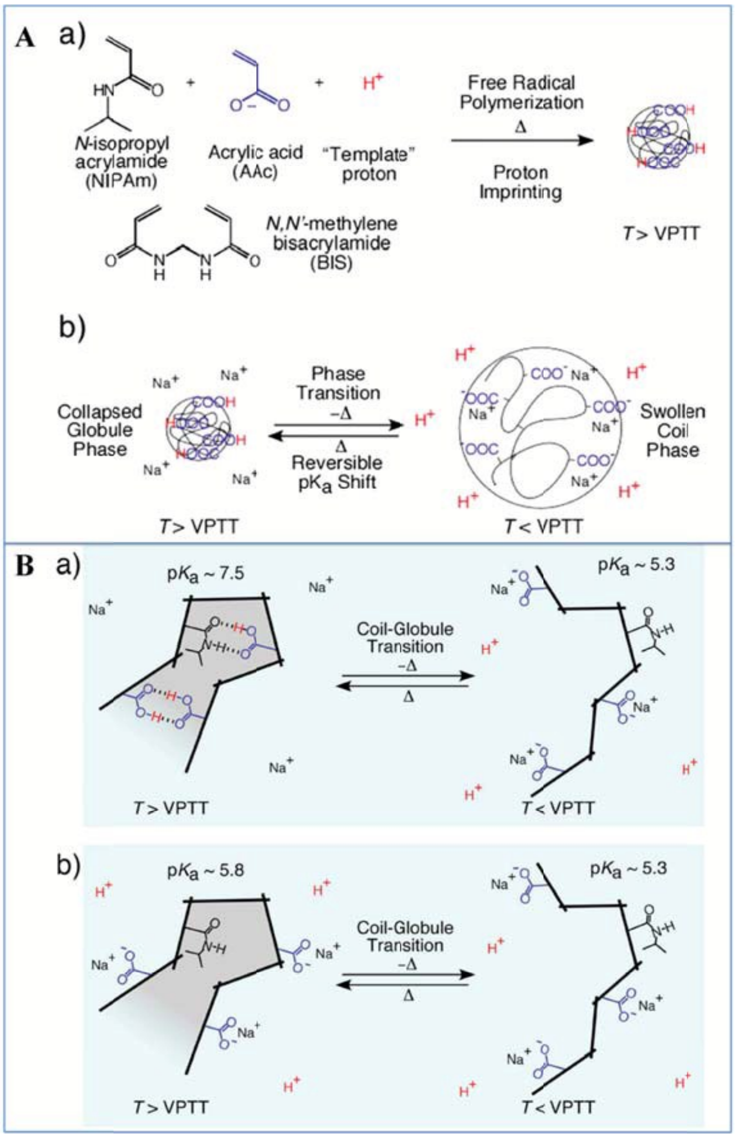

Fig. 9 (A) a) Preparation of proton-imprinted NPs. (b) Reversible pK_a shift of carboxylic acids in NPs triggered by the phase transition of NPs. (B) Proposed mechanism of temperature-responsive pK_a shift of (a) proton-imprinted and (b) nonimprinted NPs triggered by the phase transition. NIPAm, AAc, and protons are printed in black, blue, and red, respectively. Hydrophobic and hydrophilic microenvironments are printed in gray and sky blue, respectively. Reprinted with permission from ref. 27. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

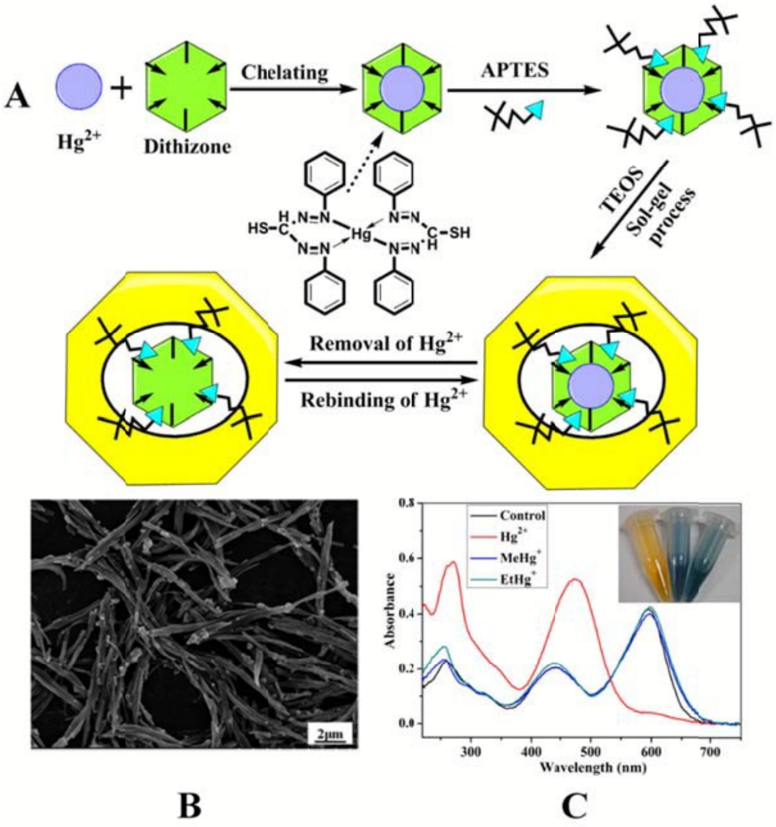

Fig. 10 (A) Schematic illustration of the preparation and imprinting process of Hg^{2+}-IIPs. (B) SEM image of Hg^{2+}-IIPs. (C) UV-vis spectra of dithizone alone (Control), and the dithizone with Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$, respectively. The inset image shows dithizone with Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ from left to right. Reproduced with permission from ref. 147. Copyright the Royal Society of Chemistry 2014.

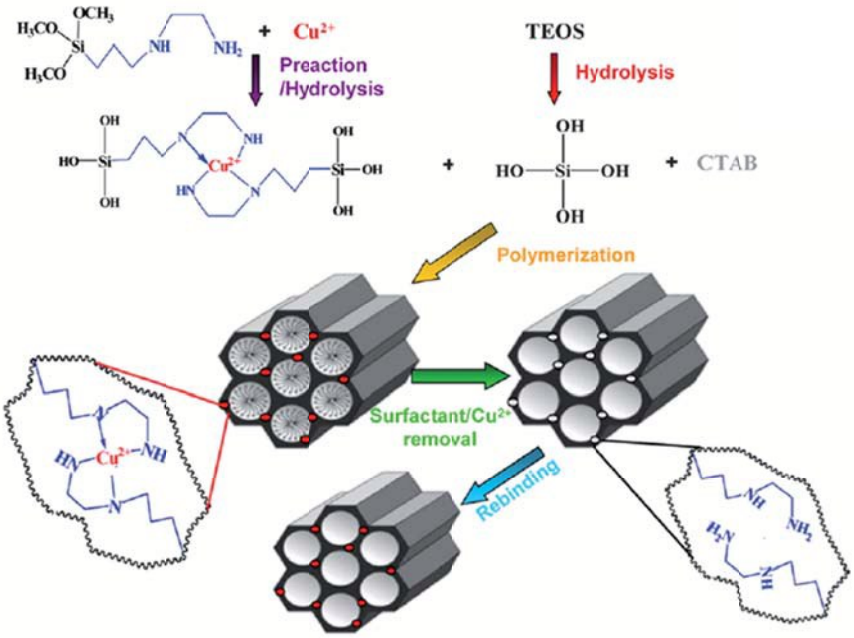

Fig. 11 Schematic procedure for synthesizing Cu ion imprinted mesoporous silica. Reprinted with permission from ref.154. Copyright the Royal Society of Chemistry 2013.

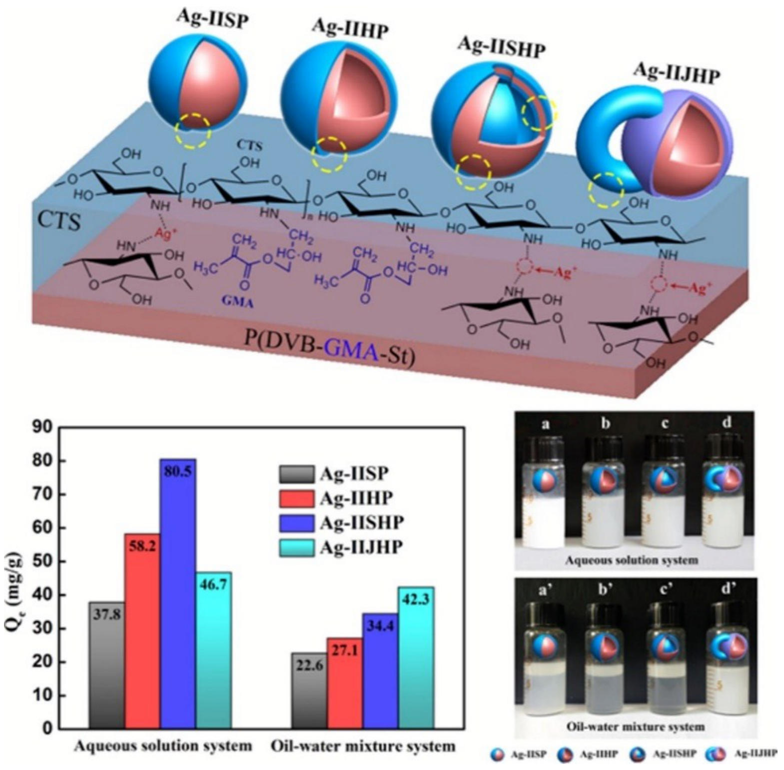

Fig. 12 (Upper) Schematic for Ag^+ adsorption onto the Ag-IIPs. (Below) Effects of the morphologies on Ag^+ absorption onto the Ag-IIPs. Reprinted with permission from ref. 174. Copyright 2015 American Chemical Society.

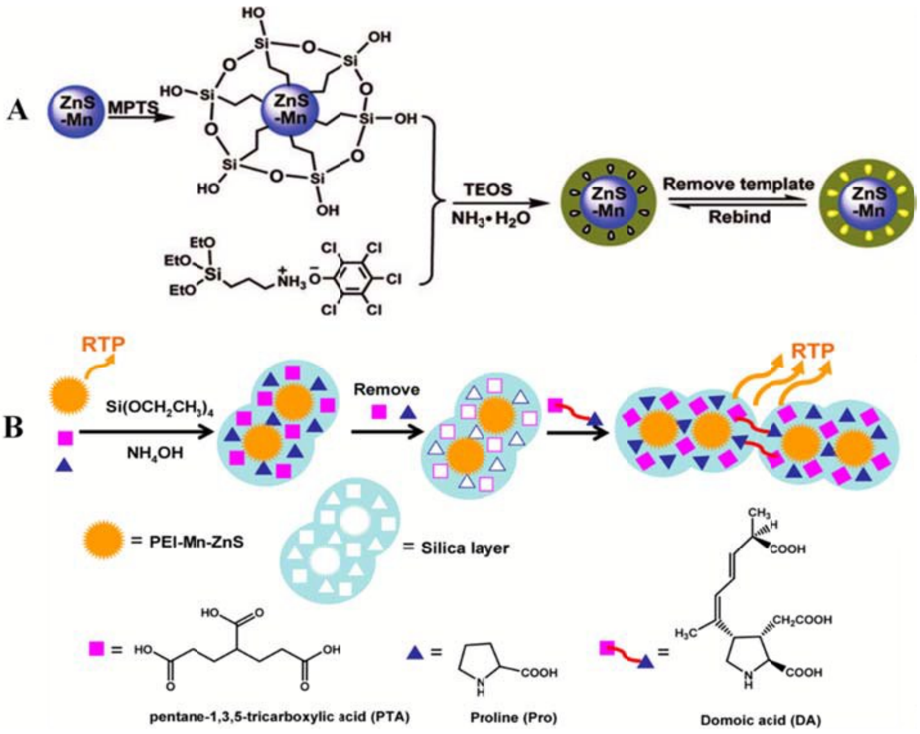

Fig. 13 (A) Schematic illustration for fabricating MIP-capped Mn-doped ZnS QDs. Reprinted with permission from ref. 64. Copyright 2009 American Chemical Society. (B) Schematic illustration for constructing Mn-ZnS QD imbedded two-fragment imprinting silica for enhanced RTP assay of DA. Reprinted with permission from ref. 65. Copyright 2013 American Chemical Society.

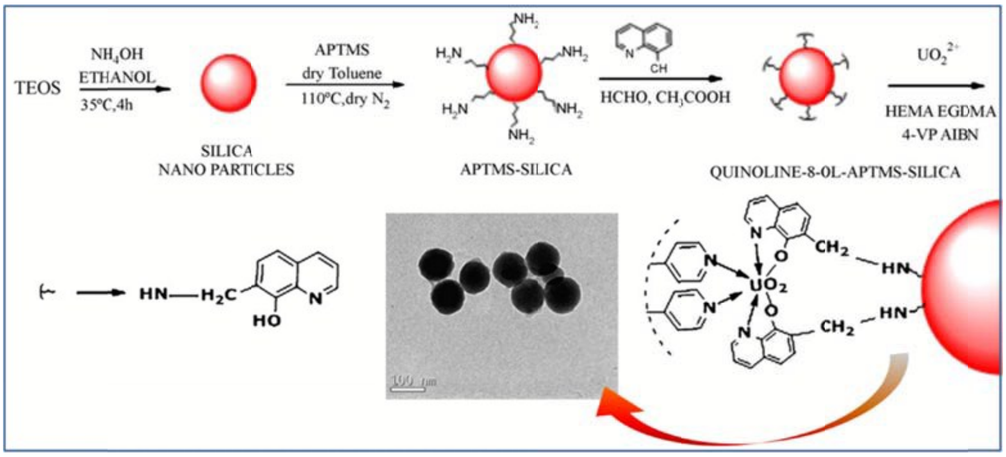

Fig. 14 Schematic representation of uranyl ion nanosurface imprinting and TEM of optimized imprinted polymer nanospheres in ethanol. Reproduced with permission from ref. 212. Copyright 2011 Elsevier B.V.

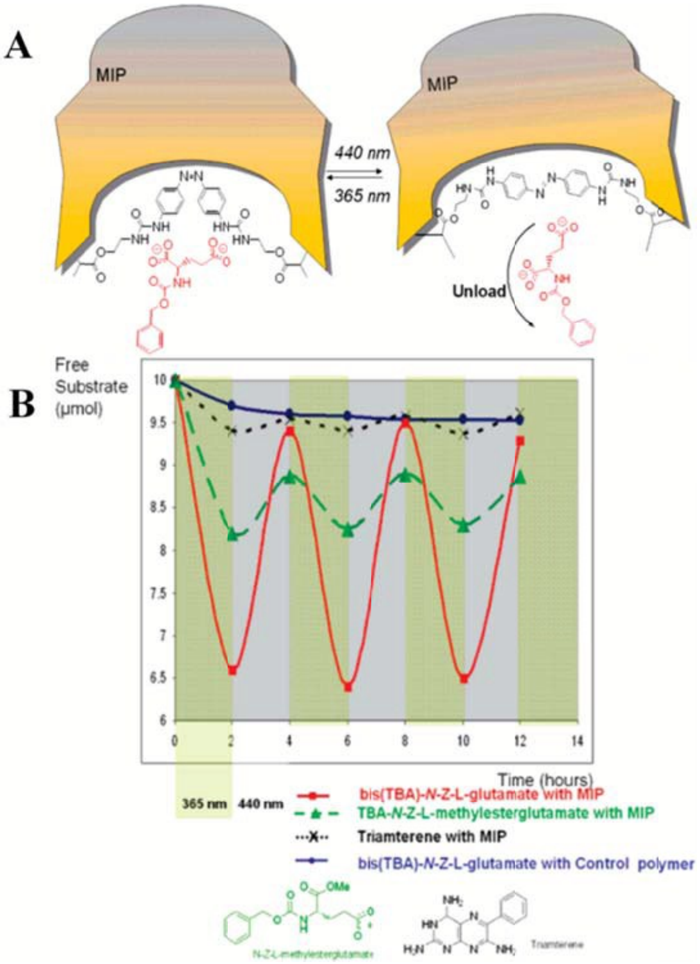

Fig. 15 (A) Schematic representation of photoresponsive MIP. (B) Photoregulated release and uptake of bis(TBA)-N-Z-Lglutamate by the MIP and the control polymer. The initial amount of ligands was 10 µmol for 10 mg MIP in 2 mL of DMSO. Reprinted with permission from ref. 269. Copyright 2007 American Chemical Society.

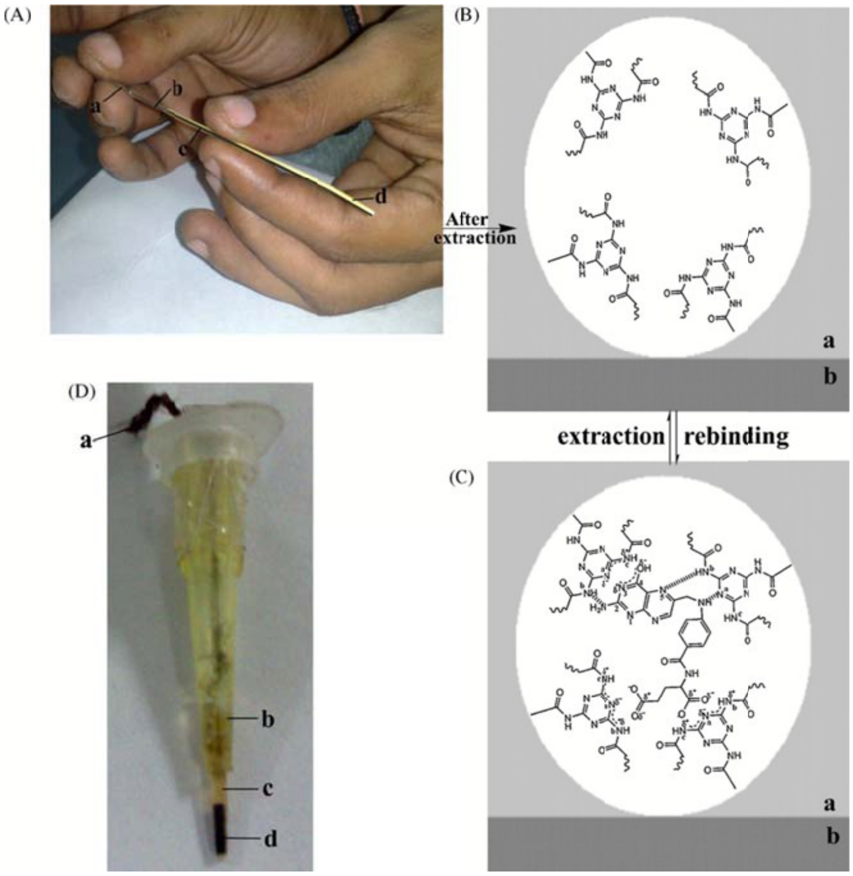

Fig. 16 (A) Picture of MIP–FA adduct–carbon composite fiber: (a) an insertible wire to push fiber out from glass capillary, (b) glass capillary, (c) fiber portion inside the capillary, and (d) pushed out fiber embossed with a visible black carbon strip. (B) and (C) show template (FA) extraction and rebinding processes in aqueous medium, respectively [(a) polymer zone and (b) carbon zone]. (D) Picture of fabricated MIP-fiber sensor: (a) copper wire, (b) micropipette tip, (c) agarose solution, and (d) MIP–carbon composite fiber. Reprinted with permission from ref. 270. Copyright 2010 Elsevier B.V.

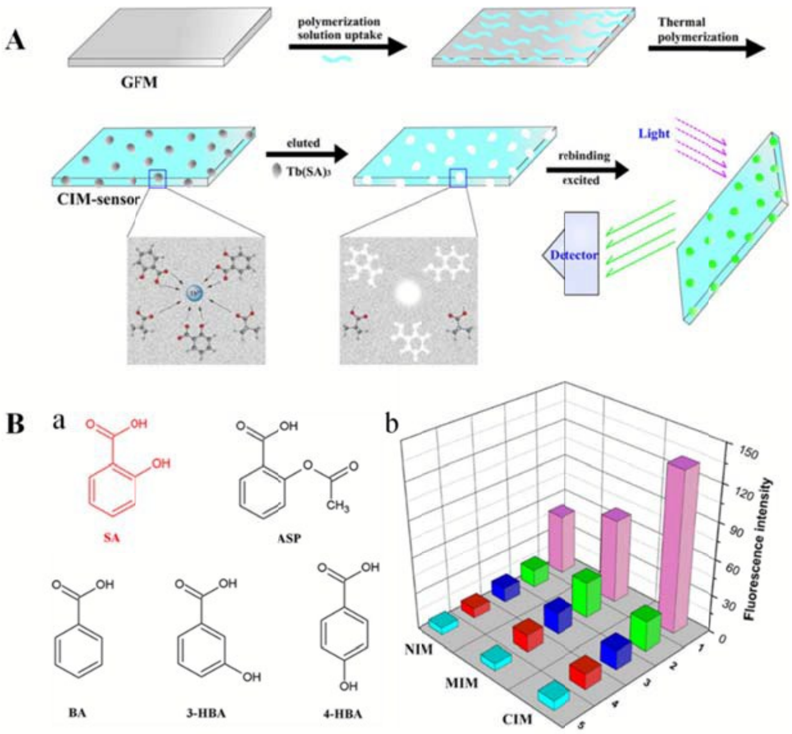

Fig. 17 (A) Schematic fabrication of the preparation and employment of Tb(SA)$_3$ complex imprinted membrane based on solid phase surface fluorescent detection. (B) (a) Molecular structures of SA and its analogues. (b) Fluorescent response of CIM, MIM and NIM to SA and its analogues. (1) SA, (2) ASP, (3) BA, (4) 3-HBA, (5) 4-HBA. Concentration: 2.0 mg/L [TbCl$_3$-ligand], adsorption time: 10 min. Reprinted with permission from ref. 288. Copyright 2013 Elsevier B.V.