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REVIEWS

Use of Micro- and Nanodimensional Inorganic Materials in Surface Molecular Imprinting

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Abstract—A review of methods of surface molecular imprinting using micro- and nanodimensional inorganic materials, including nanostructured ones, as substrates and methods of their application to analysis for increasing the selectivity and sensitivity of the determination. Molecularly imprinted polymers play an increasingly important role in the development of methods for the separation and preconcentration of organic substances and inorganic ions. Their main advantage over traditional adsorbents used in analytical chemistry consists in a combination of adsorption properties with the selective recognition of template molecules or related compounds. Recently much attention has been paid to surface molecular imprinting as a technology ensuring not only an increase in the efficiency of the selective preconcentration of analytes, but also in the sensitivity of their subsequent determination in complex matrixes, and also the reduction of the cost of the adsorbent material using substrates for preparing thin films of molecularly imprinted polymers on their surface.

Keywords: molecularly imprinted polymers, separation and preconcentration, adsorbents, templates, inorganic substrates

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Molecular imprinting is a universal and actual technique for the creation of molecularly imprinted polymers (MIPs), so-called "synthetic receptors," imitating the recognition ability of natural molecules [1–4]. In recent years, MIPs have widely been used in the development of chemical sensors [5] and biosensors [6], catalysis [7, 8], separation of chiral isomers [9, 10], solid-phase extraction (SPE) [11–13], etc. Traditionally MIPs are prepared by the method of bulk synthesis using the copolymerization (or block polymerization) of a functional monomer and a cross-linking agent in the presence of a template molecule. However, the subsequent mechanical disintegration and crushing of MIPs in this case can causes the partial destruction of molecular imprints, leading to a change in their shape and even the low adsorption capacity and poor availability of the imprints to guest molecules [14, 15]. Among the drawbacks of the method of block polymerization, let us also mention the formation of cavities of uncontrolled size because of the foaming of the solvent in the polymer vat elevated temperatures.

In the beginning of the 2000s, surface imprinting was proposed; its essence is in the preparation of MIPs with the high affinity of molecular imprints on the surface of suitable matrixes (for example, silica microparticles or polymeric microspheres, and also polymeric or a sol–gel materials). This allowed the researchers not only to increase adsorption capacity, but also to avoid problems with the diffusion barrier and decelerated mass transfer of template molecules [16–20]. As was showed by researches in the last years [14, 21–26], surface-molecularly imprinted materials are more efficient for the recognition of templates. Surface imprinting is usually performed by two methods: (1) a functional polymer is chemically attached to a particle surface followed by cross-linking in the presence of template molecules (Fig. 1) [27–29]; (2) a chemically modified (or activated) surface of a particle is involved in the polymerization of a functional monomer in the presence of a template [2, 17], as in traditional MIP synthesis. The main difference between these two approaches consists in different types of interaction with template molecules, which are basic for recognition mechanisms: in the first case, grafted functional polymers and, in the second case, functional monomers participate in the interaction [14]. In the third method of surface imprinting, the principle of water-emulsion polymerization is used; polymerization is conducted in the presence of water-soluble templates [30, 31]. In this review, we will dwell on the first two methods using inorganic materials as substrates for surface imprinting.

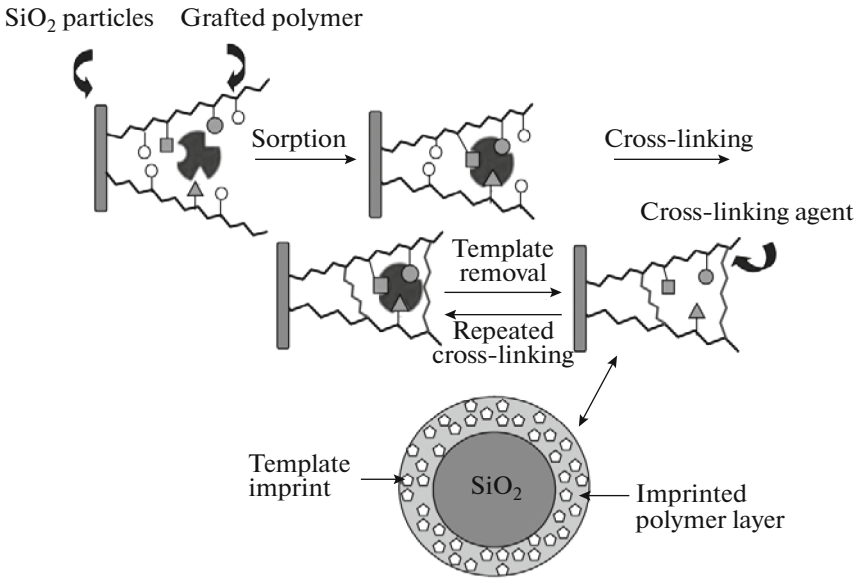

Fig. 1. Scheme of imprinting, in which a functional polymer is chemically attached to the surface of a particle followed by cross-linking in the presence of template molecules [29].

MICROPARTICLES BASED ON INORGANIC MATERIALS

In the last 10–15 years, molecular imprinting on the surface of chemically modified silica microparticles has received greatest attention. Silicas, which possess stable chemical properties, high hardness and mechanical strength, were chosen as carriers for the molecular imprinting of a number of organic and inorganic compounds [17, 32–36]. Thus, Gong and Cao [17] have first modified silica surface by vinyltriethoxysilane with the subsequent copolymerization of acrylamide and methacrylic acid using ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent and 2,2'-azobisizobutyronitrile (AIBN) as an initiator in the presence of artemisinin as a template. This gave a highly selective adsorbent with the maximum adsorption capacity of 37.13 mg/g for artemisinin, suitable for use in the technology of plant raw materials for the extraction and purification of artemisinin. The selectivity coefficients of molecular imprints of artemisinin to its derivatives arthemeter and arteether were 2.88 and 3.38, respectively. The authors explained the good selectivity of MIPs to template molecules by the formation of recognizing cavities (sites) on the surface of particles in the polymer film, corresponding to artemisinin molecules by size, shape, and the arrangement of functional groups. Imprints of antiviral agent dufulin [37], antibiotic cordycepin [38], herbicide propachlor [39], vanillic acid (with 4-vinylpyridine as a functional monomer) [40], etc. were obtained by a similar method. The obtained MIPs demonstrated high adsorption capacity (from 12 to 95 mg/g), rapid mass transfer, and high selectivity. They were used in solid-phase extraction (MIP–SPE) with the subsequent highly sensitive HPLC determination of templates (dufulin and propachlor) in various environmental samples; and also for their separation (cordycepin) and selective extraction (vanillic acid) from plant extracts.

An alternative approach to surface molecular imprinting, based on the complexation of proteins with metal ions on the surface of silica microparticles, was proposed in the 1990s [41]: a chelating monomer, *N*-(4-vinyl)-benzyl iminodiacetic acid was polymerized on the surface of SiO_2 particles modified (trimethoxysilyl)propyl methacrylate in the presence of the ribonuclease A enzyme and copper(II) ions. The obtained molecularly imprinted adsorbent was used in HPLC for the separation of a lysozyme and ribonuclease A.

Gao with coauthors in [14, 27–29] synthesized a number of surface-imprinted polymers by the chemical attachment of a functional polymer to the surface of silica microparticles. Thus, to obtain an ion-imprinted polymer (IIP) [27], polyethyleneimine (PEI) was attached, which was then cross-linked by epichlorohydrin in the presence of Cu(II) or Cd(II) ions as templates. The obtained IIP–PEI–SiO_2 samples exhibited high affinity and selectivity to template ions. Adsorption capacity to copper(II) and cadmium(II) ions was twice as high as that of PEI–SiO_2, and selectivity coefficients for Zn(II), Ni(II), Cr(III), and Pb(II) were higher than 77. In addition, the obtained imprinted material was easily regenerated in hydrochloric acid solutions.

Surface molecularly imprinted polymers (SMIPs) on the basis of polymethacrylic acid (PMAA) attached to silica microparticles were first obtained by the

polymerization of methacrylic acid using 3-methacryloxypropyltrimethoxysilane [14, 28] (or 3-aminopropyltriethoxysilane, APTES [42]) followed by cross-linking with the ethyleneglycoldiglycidyl ether (or EGDGE). Molecular imprinting in this case was based on the formation of hydrogen bonds and electrostatic interaction between the attached polymer and pirimicarb [28], carbamate pesticide, creatinine [14], or adenine [42] molecules as templates. The obtained PMAA–SiO_2 MIPs showed good affinity to the binding of templates, and also high selectivity in comparison with other compounds with chemical structures similar to templates. In the mechanism of the recognition of template molecules in MIPs on the surface of silica particles, Gao et al. in [14] wrote about an important role of electrostatic interactions and hydrogen bonds between the molecules of the attached PMAA and creatinine. Guo with coauthors in [43] used this method to obtain MIPs on the surface of silica microparticles with chemically attached β-cyclodextrines and 8-hydroxyquinoline in the presence of prometrin, an s-triazine herbicide, as a template. This allowed them to use PMIP–SiO_2 in MIP–SPE followed by the HPLC determination of prometrin at the trace level in natural water, soils, and grain crops.

Sol–gel synthesis was proposed in [26] to obtain amorphous microporous silica, whose surface selectively adsorbed template molecules, i.e., well-known bicyclic terpenoids, (–)-borneol, (+)-fenchol, and (–)-camphor. The synthesis of these materials is based on the copolymerization of templates with tetraethoxysilane (TEOS) and methyltriethoxysilane and the subsequent removal of easily volatile templates on heating. The authors noted that the presence of imprints of template molecules on the silica surface as a result of imprinting was not obvious and must be refined. Later Chang et al. used the effect of thermally reversible chemical binding for the removal of the template by simple heating [44]. To obtain a monomer–template complex, they conducted a reaction between the izocyanate group of the 3-(triethoxysilyl) isocyanate monomer and the phenol hydroxyl of estrone (template) with the formation of a thermally unstable urethane bond. The MIP thus obtained showed good adsorption capacity to estrone and selectivity to its structural analogue testosterone propionate.

The further study of the sol–gel process in combination with surface imprinting on silica microparticles has gained intensive development in 2005–2010 [45–49]. In comparison with organic MIPs, molecularly imprinted silicas are more specific to template molecules, and the diffusion of analytes in them proceeds more rapidly [45, 46]. Thus, PMIP on the surface of SiO_2 microparticles was obtained by sol–gel synthesis using an enrofloxacin antibiotic as a template and also APTES and TEOS as functional monomers [50]. The obtained material was used as an adsorbent for the determination of template molecules in biological matrixes by HPLC with a limit of detection 8 ng/L. The recovery of enrofloxacin was higher than 70%. Similar PMIPs, combining surface imprinting with the sol–gel synthesis, were obtained for the extraction 3-methyl-quinoxalin-2-carbonic acid and quinoxalin-2-carbonic acid [51], polycyclic aromatic hydrocarbons (PAHs) [52], triazolam (a well-known antidepressant) [53], and tetrabromobisphenol A [54], and also some proteins, for example, hemoglobin [33]. The maximum imprinting factor for PAHs varied in the range 1.5–3.1 [52], and for triazolam [53] was 35. The authors proposed the use of the obtained surface-imprinted silicas as selective adsorbents for MIP–SPE followed by the determination of analytes by HPLC and GC–MS. In their opinion, MIP–SPE allowed the simplification and acceleration of the sample preparation stage [51, 52].

Organo-mineral PMIPs on the surface of silica particles were obtained by sol–gel synthesis from an organosilicon precursor, γ-glycidoxypropyltrimethoxysiloxane, a functional biopolymer (chitosan), and an imprinted polyethyleneglycol [55]. After washing off polyethyleneglycol and saturation with copper(II) cations, the obtained adsorbent was used in column chromatography for the extraction of bull serum albumine. In [56], the surface imprinting of human serum albumine was performed by the polycondensation of 3-aminophenylboric acid as a functional monomer on the surface of silica microparticles. The imprinting factor was 1.9. The mechanism of protein binding by MIPs involves the spatial recognition by the protein by the imprinted cavities and also a number of interactions of hydroxyl groups of the side chains of amino acids (serine, threonine, tyrosine) with $-B(OH)_2$ groups and hydrophobic interactions.

The sol–gel technology was also used to obtain surface ion-imprinted silicas with cadmium(II) as a template, and also of 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane and epichlorohydrin as a functional monomer and a cross-linking agent, respectively [57]. The sorption capacity of the obtained Cd-imprinted sorbent was higher than 30 mg/g from aqueous solutions.

Model templates, structural analogues of template molecules, are used in molecular imprinting for the prevention of washing of template analytes from MIPs obtained by the traditional method, and also for the extension of the list of extracted substances. Recently they have also been used in surface imprinting. Thus, 3-methyl-quinoxaline-2-carbonic acid was used as a model template for quinoxaline-2-carbonic acid [51], and *N,N'*-diethyl-phthaloylbis (11-decanoate), for the group of phthalic acid esters [55]. A PMIP film on the surface of SiO_2 microparticles (PMIP–SiO_2) was obtained by the sol–gel method from APTES and tetramethoxysilane (TMOS) [58]. The imprinting factor for PMIP–SiO_2 adsorbents varied from 1.8 to 3.0,

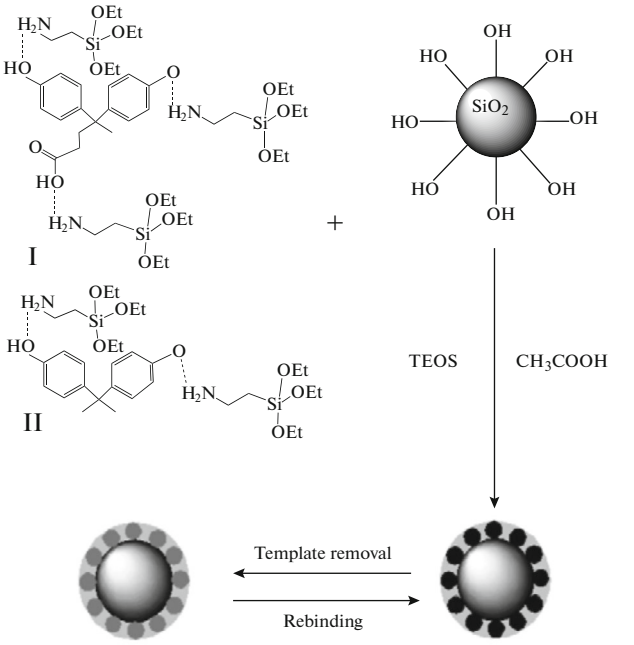

Fig. 2. Scheme of preparation of DPA- (I) and BPA-imprinted polymers (II) on a surface of silica particles [54].

depending on the phthalate nature, and high selectivity was observed to diamyl phthalate. The sorption equilibrium was attained rapidly (for about 5 min). The obtained adsorbents were tested in the analysis of orange juice by GC–MS: the recovery of phthalates at the trace level was higher than 72% (RSD < 10.2%).

In the sol–gel synthesis of molecularly imprinted silica for the extraction and adsorption preconcentration of trace tetrabromobisphenol A (TBA) in water samples, model templates [54] were diphenolic acid (DPA) and bisphenol A (BPA). The obtained PMIPs with both model templates showed rather high selectivity to TBA; however, in the region of low concentrations, the sorption properties of DPA–PMIP were higher than those of BPA–PMIP. The authors explained this feature by the effect of strong interactions between the carboxyl group of DPA and the amino group of APTEOS on the formation of highly specific binding sites (Fig. 2 [54]). The maximum adsorption capacity of DPA– and BPA–PMIP were more than 1.5 and 2 times higher than those of the unimprinted polymer (UIP) and were 45 and 38 mg/g, respectively; the recovery of TBA from water samples and natural waters varied in the range from 85 to 97%. PMIPs obtained by the sol–gel by method on a surface of quartz fibers in the presence of diphenylol (bisphenol AF) were used in the MIP–SPE of bisphenol A [59].

A mixture of 16 PAHs was used as model templates in the synthesis of PMIP–SiO_2 for the group extraction of PAHs from natural waters [52]. The adsorption capacity of the obtained PMIP–SiO_2 to 16 PAHs varied in the range from 111 to 195 μg/g and imprinting factor, from 1.5 to 3.1. The recovery of PAHs from sea water by MIP–SPE was 93%.

The use of surface-imprinted silica microparticles can be limited, for example, in alkaline media and in the preparation of biocompatible materials [30]. In this connection, the attention of researchers has been also attracted by other inorganic materials, including those used for the synthesis of multipurpose materials. In one of the first works in this field [60], a molecularly imprinted silica layer was obtained on the surface of tin dioxide particles from TMOS after the preliminary adsorption of benzaldehyde.

Carbon microspheres (CMSs) with high surface areas, chemically, mechanically, and thermally stable are also highly promising for molecular imprinting. A MIP on their surface was obtained after modification with 3-methacryloxypropyltrimethoxysilane using methacrylic acid, EGDMA, AIBN, and dibenzothiophene (DBT) as a template [15]. The obtained MIP–CMSs well recognized DBT, and equilibrium adsorption capacity was 0.595 mmol/g. The adsorption isotherms of DBT on MIP–CMSs obeyed the Langmuir model, and the kinetics of the adsorption process followed the pseudo-second-order model. Yang et al. in [15] noted that similar molecularly imprinted materials can be used in the technology of fuel desulfurization.

A mesoporous composite based on potassium hexatitanate coated with silica layers ($K_2Ti_6O_{13}$–mSiO_2) was chosen as a substrate for preparing PMIPs using dibenzothiophene as a template and a 4-vinylpyridine as a functional monomer. The kinetics of the adsorption of dibenzothiophene obeys the pseudo-second-order model and the adsorption isotherm follows the Freundlich model, showing a layered PMIP structure. The selectivity of recognition and the affinity of the PMIPs to template molecules in comparison with other structural analogues are much higher than that of the unimprinted polymer. In addition, the adsorbent based on PMIPs can be regenerated up to eight times, which allowed the authors to demonstrate a possibility of its use for the desulfurization of fuels [2].

It is known that magnetic materials (for example, Fe_3O_4) have a number of evident advantages, including infinitely high supermagnetism, which simplifies the procedure of MIP separation under the effect of an external magnetic field. On the other hand, their surfaces can be easily modified (by the core–shell type), which gives magnetic MIPs, both stable and biocompatible. For example, magnetic Fe_3O_4 microspheres (~300 nm) were obtained by solvothermal [61] and sol–gel synthesis in the presence of TEOS coated with a thin (~50 nm) SiO_2 layer (Fe_3O_4–SiO_2, Fig. 3 [61]). Then the obtained Fe_3O_4–SiO_2 microspheres were modified by 4-vinylpyridine and PMIPs were obtained by a traditional method in the presence of benzene or 4-hydroxybenzoic acids as templates for

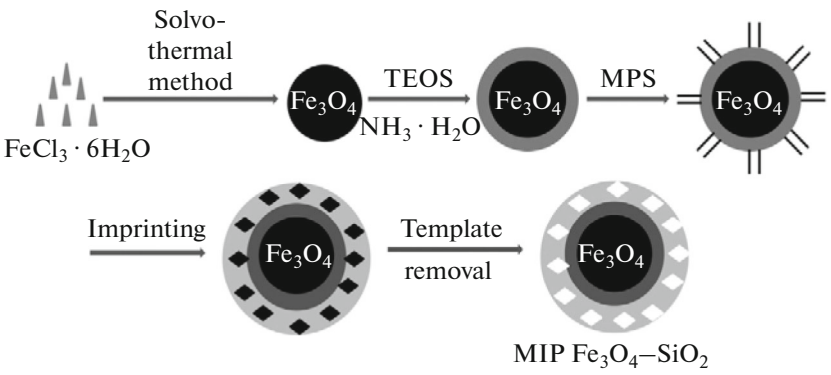

Fig. 3. Preparation of magnetic Fe_3O_4–SiO_2 PMIPs [61].

the extraction of hydroxybenzoic acids from water media [61] and protocatechuic acid from fruit juices [62], followed by their determination. The obtained PMIPs demonstrated high adsorption capacity, good selectivity, rapid binding (40 min) and magnetic separation (10 c), and good reproducibility (RSD < 4%) and stability (weight loss no more than 5–6% in 6 cycles). The completeness of extraction of the studied five hydroxybenzoic acids was above 80% and that of protocatechuic acid, more than 92%. Xie with coauthors in [63] used this method to synthesize mesoporous Fe_3O_4–mSiO_2–MIP microspheres in the presence of cetyltrimethylammonium bromide for the selective recognition of protocatechuic acid. This allowed a virtually twofold increase in the maximum adsorption capacity of mesoporous materials twice in comparison with nonporous ones. In addition, imprinting factor was increased from 1.42 to 1.87. The materials retained the advantages of magnetic PMIPs: the high rate and ease of extraction from solutions, stability and possibility of repeated use, availability of molecular imprints on the surface of SiO_2 coating, and high selectivity, which ensured their use for the extraction of template molecules from complex systems (for example, protocatechuic acid from clove tree leave extracts).

The use of magnetic materials (Fe_3O_4) simplifies the procedures of MIP separation and regeneration. However, Fe_3O_4 can be washed away during the sorption processes. To reduce losses of magnetic particles in molecular imprinting, one can use their combination with other materials, for example with the kaolinite clay mineral [64]. The obtained kaolinite–Fe_3O_4 composite after the modification of the surface of particles with amino groups and glutaric aldehyde acted not only as a substrate in the surface molecular imprinting of bisphenol A, but also as a functional monomer. The auxiliary monomer was methacrylic acid in the presence of polyvinylpyrrolidone and EGDMA. PMIPs in this case were characterized by high selectivity to template molecules. According to Guo et al., the main role in the mechanism of template binding into the molecular imprint was due to hydrogen bonds. In [65], magnetic PMIPs were obtained using magnetic particles on porous microspheres of power plant ashes (fly-ash-cenospheres–Fe_3O_4) as substrates for the selective adsorption extraction and separation of nonylphenol, which was a template in surface imprinting. The surface of magnetic particles was modified by 3-(methacryloxy)propyltrimethoxysilane (MPS), and the MIP film was obtained by the polymerization of methacrylic acid in the presence of AIBN, polyvinylpyrrolidone, and EGDMA. The authors believe that an important role in the mechanism of recognition was played by the formation of hydrogen bonds. The maximum adsorption capacity of the obtained PMIP to nonylphenol was as high as 434.8 mg/g.

Magnesium aluminosilicates (attapulgite and palygorskite) as chemically, mechanically, and thermally stable materials, and also available and inexpensive minerals, were used in surface imprinting for the extraction and preconcentration of 2,4-dichlorophenol from water media [66] and trace strontium(II) [67] from biological media. For preorganization with templates, researchers in the first case used cyclic β-cyclodextrin oligosaccharide with a hydrophobic internal cavity and, in the second case, natural chitosan polysaccharide. The sorption process into molecular [66] or ionic [67] imprints was considered as chemisorption through the formation of hydrogen and coordination bonds, respectively. The obtained adsorbents demonstrated high selectivity to templates and an ability to fourfold regeneration.

NANODIMENSIONAL INORGANIC MATERIALS

An alternative approach in surface molecular imprinting is the synthesis of molecularly imprinted nanomaterials. In this review, we will consider approaches based on the modification of the surface of nanoparticles by thin molecularly imprinted films. In addition to the advantages noted above, characteristic

for PMIPs, the use of this approach allows the easy modification of the surface of transducers (chemical sensors).

As was noted above, one of direct approaches in surface imprinting is the attachment of thin polymer films to a substrate, to make all binding sites on the polymer surface easily accessible to template molecules. However, such modification of the surface of chemical sensors usually leads to the considerable reduction of their sensitivity. To solve this problem, it was proposed to use nanomaterials with high specific surfaces for molecular imprinting [68–70]. Thus, in [71], carbon nanotubes and semiconductor quantum dots encapsulated in a polypyrrol film for increasing surface area in the device were used for microsolid-phase preconcentration through an increase in the roughness of the surface of nanoparticles. To obtain MIP films, molecules of 2,4,6-trinitrotoluene [72, 73], glutamic acid [74], β-estradiol, [75] and various proteins (albumine, hemoglobin, and cytochrome C) [70] were imprinted on the walls of uniform SiO_2-nanotubes and SiO_2-nanowires obtained in nanopores of an Al_2O_3 membrane. For this purpose, membrane pores were modified with APTES followed by the polymerization of the functional monomer (acrylamide, 4-vinylpyridine, etc.) or TEOS (sol–gel synthesis) in the presence of templates (Fig. 4 [72, 75]). Magnetic theophyllin-imprinted nanowires containing superparamagnetic $MnFe_2O_4$ were obtained by a similar method [76]. However, such an approach involves the synthesis of nanotubes or nanowires in membrane pores followed by chemical dissolution, which is rather laborious and takes a lot of time. Moreover, integrating units for direct detection on the basis of molecularly imprinted SiO_2 nanotubes, according to the opinion of Xie et al., should still be developed [73].

Mehdinia with coauthors in [77] used SBA-15 silica nanopores as a substrate for molecular imprinting. On its negatively charged surface, they polymerized positively charged aniline in the presence of 2,4-dinitrophenol as a template. The distribution coefficient of 2,4-dinitrophenol for MIPs was 3 times higher than that for NIPs. The obtained MIPs in the silica core was used as selective adsorbents for SPE followed by the HPLC determination of 2,4-dinitrophenol in the presence of other phenolic compounds in water media (tap and sea water) with recovery higher than 96% and RSD < 3.2%.

In [78], Choong et al. used vertical carbon nanotubes (CNTs) as a 3D platform with a high surface area and high porosity for preparing PMIPs. Thin polypyrrol films were attached to the surface of CNTs on a silicon substrate in the presence of template molecules. An advantage of the thus organized 3D structure was the thickness of the molecularly imprinted polypyrrol film, which might be selected in accordance with the molecule size of the template in the range from 10 nm for small to 100 nm for big molecules. On the other hand, the adsorption properties of such MIPs could be controlled by varying the height and density of the CNT on the substrate. This approach was implemented for the surface molecular imprinting of caffeine followed by its determination by pulsed voltammetry. The sensitivity of the presented amperometric CNT–PMIP sensor was 15 times higher compared to the sensitivity of sensors based on conventional films.

A sensitive and selective electrochemical sensor on the basis of MIPs on the surface of a glass electrode modified by graphene for the determination of trimethoprim, an active agent with antibacterial properties, was developed by the electropolymerization of pyrrol in an aqueous solution [79]. The recovery of the template (trimethoprim) by the MIP film was more than 94%, and the limit of detection by square-wave voltammetry was 1.3×10^{-7} M, which allowed the use of this sensor in the analysis of urine.

Surface ion-imprinted CNTs were used as composite adsorbents for the SPE and preconcentration of gallium(III) contained in ashes [80]. Ga(III)-imprinted copolymers were obtained by the polymerization of methacrylic acid in the presence of EGDMA and AIBN using a complex of gallium(III) with 8-hydroxyquinoline as a template on the surface of multiwall CNTs with attached vinyl groups. The obtained ion-imprinted adsorbents demonstrated high sorption rates and selectivity to aluminum and zinc. The imprinting factor to Ga(III) was 2.6. Similar selective organic MIPs on the surface of modified CNTs were obtained by the copolymerization of methacrylic acid trimethylolpropane trimethacrylate in the presence of dopamine as a template [81]. The obtained composites were used for the modification of the surface of a glassy carbon electrode and the determination of dopamine by chronoamperometry in a wide concentration range of 5.0×10^{-7}–2.0×10^{-4} M.

To prepare surface molecularly imprinted nanomaterials, also based on CNTs, the researchers usually use low-molecular compounds as templates. Rather less works were devoted to the imprinting of macromolecules, such as proteins. Thus, Zhang et al. in [82] synthesized molecularly imprinted membranes (MIMs) on the surface of multiwall CNTs using bovine serum albumine (BSA) as a template, and also acrylamide (functional monomer), *N,N'*-methylenebisacrylamide (cross-linking agent), and ammonium persulfate (initiator). The maximum adsorption capacity of MIM–CNT was 5.53 mg/g of BSA, which is higher than that for similar proteins, such as human serum albumine, hemoglobin, pepsin, and others. The imprinting factor of MIM–CNT to BSA was 2.6.

MIPs with theophyllin imprints on the surface of a modified single-wall CNT were obtained using methacrylic acid [81, 82], EGDMA, 2,2-dimethoxy-2-phenylacetophenone [83], and theophyllin (template). The modification and preparation of CNTs

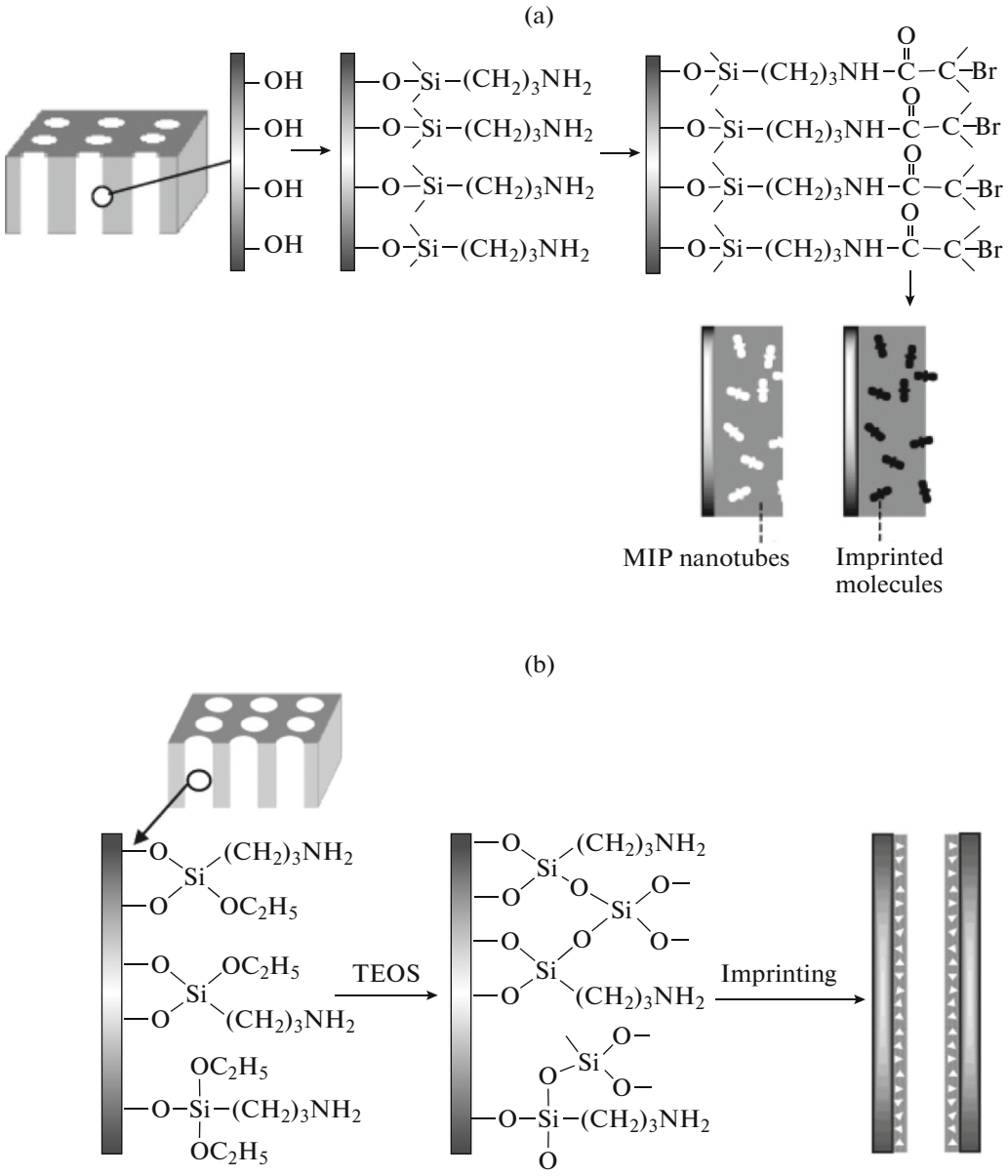

Fig. 4. Preparation of trinitrotoluene-imprinted SiO_2 nanotubes in nanopores of an Al_2O_3 membrane using (a) organic monomers [75] and (b) sol–gel synthesis [72].

using photopolymerization were performed by the immobilization of a nonionic surfactant (Twin 20) followed by the attachment of acrylic acid [83] or *N,N'*-diethyldithiocarbamate [84] residues. The theophyllin-imprinted polymer on the CNT possessed higher adsorption capacity in comparison with nonimprinted one; the selectivity of binding theophyllin was higher than those for caffeine and theobromine [84]. The polymer was used for the development of a multiple-use biosensor based on a field-effect transistor.

A promising approach to surface imprinting for the extraction and preconcentration of fluoroquinolone from eggs using surface imprinted magnetic CNTs (MCNTs) was proposed in [85]. MCNTs were obtained by the method of solvothermal synthesis, which allows the easy regulation of the size, distribution, and density of Fe_3O_4 grains on the CNT surface. As the carriers for imprinting, they are characterized by easy separation from solutions in a magnetic field, high active surface, and good mechanical properties. MIP films on the surface of MCNTs were prepared using ofloxacin as a model template, methacrylic acid, and EGDMA. The obtained MCNT–MIPs demonstrated high adsorption rate and selectivity to fluoroquinolone. An SPE method using MCNT–MIPs in combination with HPLC was developed for the simultaneous determination of four fluoroquinolones in eggs; the limits of detection were 0.25–0.40 ng/g.

Surface imprinted CNTs were also obtained using the sol–gel technology [86, 87]. CNTs were modified by a thin silica layer (CNT–SiO_2) using the sol–gel method and TEOS and APTES in the presence of cetyltrimethylammonium bromide and also triclosan [86] and phenol [87] as templates. The thickness of the triclosan-imprinted polymer layer was 15–20 nm. The MIP-nanocomposite combined the advantages of surface imprinting and CNTs. Thus, they were characterized by the high rate of binding, high adsorption capacity, and selectivity to the template, and also by the good reproducibility and ability to regeneration. The maximum imprinting factor for phenol was 3.5 [87] and that for triclosan, 4.1 [86]. It was shown that the proposed MIP-nanocomposite can be used for the sorption preconcentration and determination of triclosan and phenol in natural waters, and also as selective coatings of electrochemical and piesoelectric quartz sensors for monitoring environmental pollution.

Other carbon nanomaterials are also used in addition to CNTs. For example, MIPs were synthesized on the graphene surface by the free radical polymerization of 4-vinylpyridine in the presence of 4,4'-methylenediphenylamine template for the determination 4,4'-methylenediphenylamine and aniline by pulse voltammetry [88].

SiO_2 nanoparticles obtained directly by the sol–gel technology are convenient carriers for surface imprinting. Thus, Ma et al. synthesized MIPs for the extraction of 17β-estradiol on the surface of SiO_2 nanoparticles (SiO_2–MIP) [89]. Uniform SiO_2 nanoparticles obtained by the sol–gel process from TEOS were chemically modified by methacryloxypropyltrimethoxysilane for surface imprinting in the presence of methacrylic acid, EGDMA, AIBN, and 17β-estradiol as a template. The obtained SiO_2-MIPs showed high selectivity, high sorption capacity, which fivefold exceeded that for NIPs, and also high rate of binding (sorption equilibrium was attained in 25 min). They were successfully used as adsorbents for SPE for the selective extraction and subsequent HPLC determination of estrogens (17β-estradiol and an estriol) in poultry feed.

Magnetic nanoparticles have recently received wide acceptance in separation methods and biosensors; they are also used in catalysis and environmental remediation [90] and in biomedicine and biotechnology research [91]. They have obvious advantages, such as small size, active and easily modified surface, high magnetic susceptibility, biocompatibility and stability, low toxicity and ease of preparation and, therefore, have found application in surface molecular imprinting. In addition, the simplicity and efficiency of their separation in a magnetic field exclude laborious steps of analysis, such as packing of sorbent into SPE devices, centrifuging, filtering.

Magnetic Fe_3O_4 nanoparticles, surface silanized by TEOS and modified by allyltriethoxysilane (v-mSiO_2–Fe_3O_4) [92] or MPS [93], were used to obtain ion-imprinted polymers on their surface. The functional monomer was vinyldiphenylcarbazide [92], whose complex with lead(II) was imprinted on the surface of v-mSiO_2–Fe_3O_4 in the presence of EGDMA and AIBN. To obtain a thermally stable Sr(II)-imprinted polymer, Liu et al. copolymerized *N*-isopropylacrylamide, methacrylic acid and *N,N'*-methylenebisacrylamide in the presence of Sr(II) and AIBN. The obtained nanocomposites were used as adsorbents for the separation, preconcentration, and highly sensitive determination of Pb(II) with a limit of detection of 1.3 μg/L and RSD ~2.9% in food products.

Surface imprinting on magnetic nanoparticles was used for the adsorption preconcentration and determination of 4-nitrophenols in water media [87], sulfamethazine in poultry feed [94], and indole in fuels [95]. The surface of Fe_3O_4 nanoparticles was modified by TEOS and MPS and then methacrylic acid was polymerized in the presence of EGDMA and AIBN, using 4-nitrophenol [90], sulfamethazine [94], and indole [95] as templates. The obtained MIPs possessed high adsorption capacity to the templates (maximum 57.8 mg/g [90], 344.8 μg/g [94], and 50.25 mg/g [95]), high imprinting factor (9.5 [94]), good selectivity (including that to other representatives of sulfanilamides) and rapid binding [94, 95]. HPLC in combination with sorption preconcentration using PMIPs showed a wide analytical range of 25–1000 μg/L for 4-nitrophenol [90] and 0.050–20 μg/mL for sulfamethazine [94], and also a good reproducibility. It was applied to the analysis of sea water [90] and poultry feed [94].

Magnetic nanoparticles with molecularly imprinted model templates, benzoic acid [96] and erythromycin [97], were used not only for the selective extraction and HPLC determination of trace amounts of salicylic acid in fruits of kiwi *Actinidia chinensis* [96], but also for the group extraction of macrolide antibiotics followed by their HPLC determination in samples of food products [97]. Magnetic PMIPs prepared by the core–shell principle [90, 94] in the presence of 4-vinylpyridine [93] and methacrylic acid [97] as monomers possessed high sorption volume of 94.1 mg/g [97] and imprinting factor of 11.9 [97] in relation to the templates, good selectivity, rapid binding, ability to be separated in a magnetic field, good reproducibility of the results (RSD < 4 [96] and 12.4% [97], respectively), and stability (4% losses within 6 cycles [96]).

Wang et al. in [91] synthesized magnetic Fe_3O_4, nanoparticles surface-imprinted with estrone, following the principle of semi-covalent imprinting. A monomeric complex for the sol–gel process on the surface of nanoparticles modified by TEOS was

obtained by the reaction between 3-(triethoxysilyl)propyl isocyanate and estrone. The urethane bond in this complex after the synthesis broke on heating, which gave specific estrone imprints on the surface of the SiO_2 coating [91]. It was shown that the adsorption isotherms obeyed the Scatchard equation, and the maximum adsorption capacity for estrone was 183.4 μmol/g. Thus obtained hybrid nanoparticles were used for the biochemical separation of estrons.

In recent years, to prevent the loss of magnetic nanoparticles and, consequently, increase the stability of magnetic composites, analysts pay special attention to their combinations with other materials. Thus, the use of natural magnesium aluminosilicate minerals considerably reduced the cost of the technology of preparation of such nanocomposites. Pan with coauthors [98, 99] synthesized magnetic molecularly imprinted nanocomposites by attaching Fe_3O_4 nanoparticles to the surface of halloysite nanotubes [98] and attapulgite fibers [99] followed by the polymerization of methacrylic acid in the presence of EGDMA and AIBN, and also 2,4,6-trichlorophenol and 2,4-dichlorophenol as templates, respectively. The thickness of the thermally stable and regenerated MIP film was 5–15 [98] and 16 nm, respectively [99]. Nanocomposites showed high adsorption capacity of 246.73 and 145.79 mg/g for 2,4,6-trichlorophenol and 2,4-dichlorophenol, respectively, and also high affinity and selectivity to templates in the presence of other phenolic compounds. The authors believed that the main contribution to the mechanism of recognition was due to the formation of hydrogen bonds between methacrylic acid and the templates. The obtained nanocomposites were successfully applied to the analysis of environmental samples.

Nanocomposites based on CNTs (CNT–Fe_3O_4) or graphene oxide and magnetic nanoparticles were used for surface imprinting with model templates (4-tertoctylphenols [100], propionamide [101], and evodiamine [102]). MIPs obtained from 4-vinylpyridine and TEOS [100] and from acrylic acid and EGDMA [101] demonstrated high selectivity to 4-nonylphenol and acrylamide, respectively. The maximum sorption capacity was 52.4 [100] and 3.68 mg/g [101], respectively, and adsorption equilibrium was attained in 20–30 min. Magnetic molecularly imprinted nanocomposites used in SPE for the separation and preconcentration of 4-nonylphenol and acrylamide followed by their determination by HPLC in natural waters and food samples, respectively, and also for the group extraction of evodiamine and rutaecaprine alkaloids [102] from *E. fructus* extracts.

Titanium dioxide is well-known because of its high photocatalytic activity, chemical stability, and rather low cost. Many organic pollutants, being stable toxic substances (dyes, pesticides, herbicides, etc.) decompose in the presence of TiO_2 catalysts under the action of UV radiation [103]. Therefore, the use of TiO_2 nanoparticles in molecular imprinting will improve the properties of the obtained nanocomposites and make them multipurpose. Recently Shen with coauthors [104, 105] have developed new a approach to increasing the photocatalytic activity of TiO_2 nanoparticles by the imprinting of target molecules on their surface. Thus, it was shown that, in addition to an increase in the efficiency of photocatalysis by TiO_2 nanotubes [104, 106] or composites based on TiO_2 nanoparticles and graphene [107], their selectivity could also be significantly increased by modifying their surface with organic MIPs obtained by the polymerization of *o*-phenylenediamine [104, 107] and methacrylic acid [106] in the presence of 2- or 4-chlorophenol, bisphenol, and tetracycline hydrochloride as templates, respectively. In other works [108, 109], MIPs, synthesized on the surface of TiO_2 nanoparticles (MIP–TiO_2) by the polymerization of methacrylic acid in the presence of EGDMA, AIBN, and propazine [108] and kaempferol [109] as templates were used for the extraction of total triazine herbicides by MIP–SPE followed by their determination by HPLC–spectrophotometry. Good sorption capacity (~7 [108] and 5 mg/g [109]) and high selectivity of MIP–TiO_2 ensured their use for the determination of trace propazine, simazine, and atrazine in environmental and food samples.

To improve sorption properties in surface imprinting, analysts use the technology of removal by the chemical dissolution of the core from the MIP shell, which is an inorganic substrate. Because of the high specific surface and porosity in comparison with traditional adsorbents in chromatography, these MIPs are characterized by rapid and specific binding and also by high sorption capacity [110, 111]. Thus, porous dibenzothiophene-imprinted adsorbents (H–MIP–TiO_2) obtained [112] from porous TiO_2 nanoparticles 50–75 nm in size. For this purpose, 4-vinylpyridine was polymerized on their surface in the presence of dibenzothiophene and EGDMA, which gave a nonporous adsorbent (T–MIP–TiO_2), whose nanoparticles were then dissolved in hydrofluoric acid. The sorption capacity and selectivity to the template for H–MIP–TiO_2 were higher than those for T–MIP–TiO_2, NIP–TiO_2, and initial TiO_2 nanoparticles. The obtained adsorbent can be used for the sorption extraction of other organosulfur compounds, benzothiophene derivatives. In addition, the adsorbent is easily regenerated. H–MIP–TiO_2 was used for the desulfurization of petrols and the determination of trace dibenzothiophene in them.

Later, with the development of the technology of molecular imprinting, researchers have preferred to use more chemically stable inorganic materials. Molecularly imprinted TiO_2 films obtained by liquid-phase sedimentation or by the sol–gel technique demonstrated good sensitivity and selectivity of the determination or electrocatalysis of template mole-

cules [111–119]. The procedures of preparing such films differ by simplicity and availability, were implemented on the surface of TiO_2 nanoparticles for the development of bifunctional materials, characterized by high specific sorption and photocatalytic activity.

TiO_2 nanotubes obtained by anode oxidation were used as substrates for the surface molecular imprinting by liquid-phase sedimentation in the presence of tetracycline antibiotic as a template [103]. The principle on which the preparation of thin TiO_2 films was based on consisted in the slow decomposition and hydrolysis of the titanium(IV) fluoride complex in the presence of boric acid. The obtained PMIP–TiO_2 possessed not only high sorption capacity to tetracycline molecules, but also increased photocatalytic activity in comparison with NIP–TiO_2.

An sorbent based on titanium dioxide for the group extraction of phytoecdysteroids was obtained by molecular imprinting [120]. The selective imprinted layer was applied onto the surface of TiO_2 nanoparticles by the hydrolysis titanium *N*-butoxide. The template in molecular imprinting was ecdysterone, the most widespread phytoecdysteroid, and also its complex with 3-aminophenylboric acid. The obtained adsorbents were used as cartridges for SPE for the group adsorption of six phytoecdysteroids from a *Serratula coronate* extract; thus, the target compounds could be separated from the main matrix components of the plant extract. In comparison with C18-silica, the recovery of phytoecdysteroids by the proposed adsorbent was higher and that of matrix components was lower. The adsorbent obtained by the imprinting of a complex of ecdysterone with 3-aminophenylboric acid was most efficient. The recoveries of phytosteroids by the imprinted sorbents were 2–3 times higher than that by the nonimprinted adsorbent.

Abou-Gamra et al. in [121] used chitosan as a biotemplate in the sol–gel synthesis of spherical porous TiO_2 nanoparticles, which after synthesis were washed with water and calcined at 500°C. The authors believed that the natural biopolymer reduced the agglomeration of nanoparticles and increased their sorption capacity; in addition, it was an excellent adsorbent for the extraction of organic dyes.

Organic MIPs obtained by the copolymerization of 2-hydroxyethylmethacrylate with EGDMA on the surface of selenium nanoparticles were proposed in [122] for the extraction of cholesterol from biological media. The maximum imprinting factor did not exceed 1.51 and recovery, 40.2%.

Semiconductor quantum dots, used as fluorescent biological tags, have a number of advantages (photostability, high quantum yield, and narrow photoluminescence radiation profile with the wavelength determined by the dot size). This allowed their use in surface molecular imprinting. In this sense, CdS quantum dots, synthesized in water media, are more convenient and more economic in comparison with CdSe quantum dots. Now sensors based on molecularly imprinted quantum dots and combining the selectivity of MIPs with the high sensitivity of quantum dots are developed for the determination of organic compounds, such as pentachlorophenol, 4-nitrophenol, pyrethroids, proteins, and domoic acid [123].

The introduction of quantum dots into molecularly imprinted polymers was used for the development of selective sensors, which are luminescet in response to the repeated binding of templates [124]. Thus, composites based on quantum dots and a copolymer of ethylene with vinyl alcohol were obtained using creatinine, albumin, and lysozyme as templates [125]. The authors believe that the prepared MIP is promising for the selective recognition and determination of target molecules in biological fluids using short-wave laser light-emitting diodes. The sol–gel method using TEOS and APTES was also applied to the synthesis of MIPs on the surface of CdTe quantum dots in the presence of 4-aminophenol [126]. In the rebinding of the template, the researchers observed the quenching of the fluorescence of quantum dots, and the sensor on their basis was used in the analysis of tap water and natural waters.

In [127], cysteine methacrylamide attached to the surface of CdS quantum dots (core) was used for the reconstruction of the surface of the MIP shell for the selective recognition of DNA. In this approach, the chelate complex of platinum(II) with histidine methacrylamide was the monomer and guanosine, the template. Guanosine in its turn also forms chelate complexes with Pt(II) ions, which determines the ligand-exchange mechanism of the binding of guanosine and its analogs by the molecularly imprinted polymer on the surface of CdS quantum dots. It was also shown that the affinity of the obtained nanosensor to single-strandeed DNA was higher than that to the double-stranded DNA; and the increase in fluorescence intensity was proportional to the concentration of guanosine and its analogs. Thus, guanosine-imprinted CdS quantum dots can be used not only for the determination of guanosine and its analogs, but also for the study of mutations and the detection of defects in DNA.

Recently phosphorescence properties of quantum dots have drawn attention of researchers for the development of optical sensors whose selectivity can be increased by the surface modification of quantum dots with MIPs. Thus, MIPs on the surface of Mn-doped of ZnS quantum dots [128] allowed an increase in the selectivity of the determination of trace pentachlorophenol using a phosphorescence optical sensor (limit of detection 86 nM, RSD ~2.8%). The surface of quantum dots was modified by 3-mercaptopropyltriethoxysilane followed by a sol–gel process in an ammonium–etanol medium of APTES and TEOS in

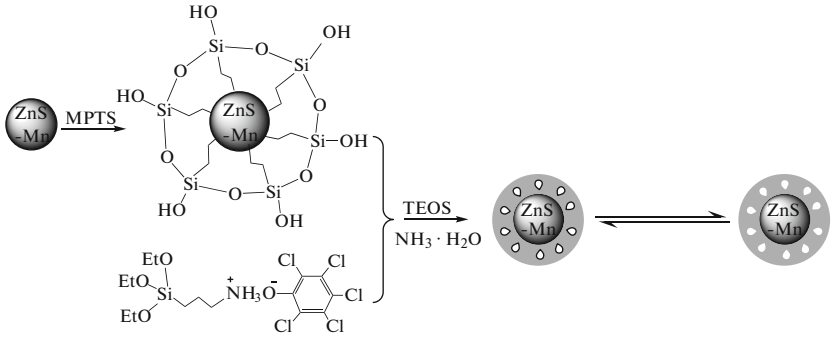

Fig. 5. Scheme of MIP preparation on the surface of manganese-doped ZnS quantum dots [128] (MPTS—3-mercaptopropyltriethoxysilane).

the presence of pentachlorophenol (Fig. 5 [128]). The maximum imprinting factor was 2.5 at pH 4.5–5.0.

Nanocomposites MIP-quantum dots were obtained by the noncovalent surface imprinting of proteins [129, 130] and sulfadimidine [131] using the sol–gel process in the presence of APTEOS and TEOS. 3-Mercaptopropionic acid was used for the stabilization of CdTe quantum dots [130]. Carboxyl groups on the surface participated in formation of a conjugate between cytochrome C (template) and quantum dots. It was shown that the attachment of various proteins to the surface of quantum dots led to a change in their photoluminescence properties. Cytochrome C was chosen as a template, because its immobilization was accompanied by the maximum quenching of luminescence. Instead of 3-mercaptopropionic acid, quantum dots were also stabilized by denatured BSA, which increased the intensity of photoluminescence and the efficiency of the recognition of imprints (imprinting factor at pH 6.2 was 2.33) [129]. The limit of detection for lysozyme in this case was 6.8 nm [129], which is much lower than that for cytochrome C (410 nm) [130].

A molecularly imprinted polymer with trinitrophenol imprints on the surface of CdTe quantum dots as a model template was prepared the sol–gel technology [129] and used for the determination 2,4,6-trinitrotoluene (TNT) by the quenching of the fluorescence of quantum dots [123] in the concentration range 0.8–30 μM with a limit of detection 0.28 μM. Imprinting factor under optimum conditions was ~1.8. A Meisenheimer complex containing TNT and primary amino groups formed on the surface of quantum dots in the presence of TNT in solution. The obtained sensor possessed high selectivity and affinity to TNT in comparison with other nitro derivatives (2,4-dinitrophenol, 4-nitrophenol, phenol, dinitrotoluene), which is explained by the enhancement of the electron-acceptor properties of the molecule and an increase in its size with an increase in the number of nitro groups. The sensor was successfully tested in the analysis of soils: the recovery of TNT was higher than 90%, RSD ~5.12%.

Thermosensitive MIPs on the surface of CdTe quantum dots were developed for preparing fluorescence thermosensitive materials with a high specificity of the recognition of target proteins [132]. By varying temperature, it was possible to control processes of the recognition and extraction of target molecules, which, in turn, represented a new approach to the surface molecular imprinting of proteins. To implement it, a surface of CdS quantum dots was modified by the sol–gel method with a SiO_2 coating, which not only retained the luminescence of quantum dots, but also ensured the formation of functional and biocompatible nanocomposites (SiO_2–CdS) with good dispersity in water. The subsequent copolymerization of *N*-isopropylacrylamide and *N,N'*-methylenebisacrylamide on the SiO_2–CdS surface was initiated by ammonium persulfate in the presence of bull hemoglobin as a template. The obtained MIP–SiO_2–CdS combines the advantages of the technology of the molecular imprinting of a thermosensitive polymer with the fluorescence properties of quantum dots. After the removal of template molecules on heating, the thermosensitive MIP layer on the surface of SiO_2–CdS can be used for the specific recognition of bull hemoglobin with an imprinting factor of 2.82.

Thus, composites based on surface molecularly imprinted quantum dots combine the selectivity of molecular imprinting with the fluorescence properties of quantum dots, which is promising for the recognition and detection of biomacromolecules. However, these approaches have still been insufficiently studied.

* * *

In summary, let us note that the prospects of research in surface imprinting are connected, first of all, with the reduction of the cost of the adsorbent material and the expansion of the range of target compounds, both templates and analytes, for sorption separation and preconcentration followed by their deter-

mination. The majority of works in this field were devoted to the use of silicas as carriers, on the surface of which organic and inorganic polymer films with imprints of not only molecules, but also ions were obtained and which were used as adsorbents for SPE with their subsequent HPLC and GC–MS determination in various samples, including biological ones. Recently much attention has been paid to the creation of organomineral, also monolithic, MIPs and multipurpose composite materials on their basis. The prospects for such an approach, for example, in the case of magnetic composite materials, are determined by their stability, biocompatibility, ease of modification, high selectivity, and also availability and the low cost of natural minerals and nanosamples used for their preparation. As nanomaterials are widely used in sensor devices, the use of molecularly imprinted films on various nanoparticles, including 3D platforms, for increasing the selectivity of sensors seems promising. In some cases, the high specific surface of nanoparticles results in an increase in sensitivity. Porous molecularly imprinted adsorbents obtained using TiO_2 nanoparticles are required in chromatographic methods. In addition, the number of biomacromolecules used as templates grows. Thus, molecularly imprinted semiconductor quantum dots are used for the highly sensitive determination and recognition of proteins and DNA by optical sensors, which is promising for genetic research. Methods of the further development of surface imprinting using inorganic materials, as is shown by the analysis of the available publications, are connected with the improvement of procedures for obtaining molecularly imprinted films on the surface of micro and nanodimensional particles for increasing their sorption capacity, selectivity, stability, and ability to regeneration; the creation of thermosensitive MIPs; expansion of the range of analyzed samples; and also urgent problems of present-day chemical analysis: selective extraction of natural compounds from plant extracts; group extraction of biologically active compounds, antibiotics, PAHs, phthalates, pesticides, and other pollutants; desulfurization of fuels; the delivery of drugs, etc.

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