Synthesis and Applications of Molecularly Imprinted Polymers Modified TiO₂ Nanomaterials: A Review

Lingna Sun 1, Jie Guan 1, Qin Xu 1,*©, Xiaoyu Yang 1, Juan Wang 1 and Xiaoya Hu 1,2,*

1 College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China; sunlna9610@163.com (L.S.); 18852726509@163.com (J.G.); yangxiaoy77@163.com (X.Y.);
15705276738@163.com (J.W.)
2 Guangling College, Yangzhou University, Yangzhou 225002, China
* Correspondence: xuqin@yzu.edu.cn or yz_xiner@163.com (Q.X.); xyhu@yzu.edu.cn (X.H.);
Tel.: +86-514-8797-5244 (Q.X.)

Received: 9 October 2018; Accepted: 8 November 2018; Published: 11 November 2018

Abstract: Titanium dioxide (TiO₂) nanomaterials have caused a widespread concern in the past several decades for their bulk characteristics and potential applications in many different areas. Lately, the combination between molecularly imprinted polymers (MIPs) and TiO₂ nanomaterials have been proven to improve the relative adsorption capacity, selectivity and accelerate the rate of mass transfer of analyte which is not possible using TiO₂ alone. Considering the unique performance of the MIPs modified TiO₂ nanomaterials, this review intends to give an overview of the recent progresses in the development of MIPs modified TiO₂ nanomaterials, the potential applications of their tailor-made characteristics. The limitations and challenges in this practically promising nanomaterials have also been raised and summarized. By means of the points raised in this article, we would like to provide some assistance for further development of preparation methodologies and the expansion of some potential applications in the field of MIPs modified TiO₂ nanomaterials.

Keywords: review; titanium dioxide; nanocomposites; molecular imprinting; synthesis; application

1. Introduction

Titanium dioxide (TiO₂) is a photosensitive substances which can produce conduction band electrons, valence holes, superoxide radicals, hydroxyl radicals and other active species under the excitation of light and then lead to a variety of organic compounds degradation [1], killing most of the microbes [2]. As a green photocatalyst, TiO₂ nanomaterials have attracted a lot of attention in the field of photochemistry. However, their applications are limited by their poor selectivity because of the strong non-selective oxidizability of holes and hydroxyl radicals generated by TiO₂ excited by ultraviolet light. When the target analytes were in a mixture or their concentrations are low, the application efficiency of TiO₂ nanocomposites would be severally hampered. Several procedures such as the surface’s electric charge control, double-region-structured photo-catalysts design procedure et al. have been developed to improve the selectivity of TiO₂ nanocomposites but these nanocomposites could only remove organics with charges but not the uncharged ones [3]. Therefore, using suitable organic or inorganic materials with special selectivity to modify TiO₂ nanocomposites is imperative to guarantee their functionality for specific recognition.

Polymers are a kind of modifiers that have been widely implemented for the modification of TiO₂. The polymer modification on TiO₂ could alter their hydrophobic/hydrophilic character, improve their dispersion in various media and introduce new functional groups for the reaction with organic molecules [4]. But polymers modified on TiO₂ prepared by direct mixing, sol-gel processing and in situ grafting polymerization process lack selectivity.
Molecular imprinting technology (MIT) offers the opportunity to endow TiO$_2$ based materials good selectivity because they can composite tailor-made receptors which can selectively recognize and bind target molecules with high affinity. This technology usually refers to a progress that the template molecules interact with the selected functional monomer to form main host-guest complexes and then a certain amount of cross-linking agent and initiator were added together into the complexes to obtain macromolecule polymers. Upon removing the template molecule, a recognition cavity which is complementary with the template molecule in shape, size and chemical functionality is formed in the highly cross-linked polymer matrix, so that the obtained MIPs have higher recognition ability and can selectively separate the specific template molecules [5]. This technique can be described as a ‘manual locking’ technique for identifying ‘molecular bonds’. MIPs have three distinct characteristics [6]: (1) Structure-activity predictability. Different MIPs can be prepared according to the working purposes to meet different needs. (2) Specific recognition. MIPs prepared according to the structure of the template molecule have specific recognition of the template molecule. (3) Wide practicability. The performance of MIPs can be compared with natural molecular recognition systems such as antigens and antibodies, enzymes and substrates, receptors and hormones [7]. MIPs are synthesized by chemical methods and have the advantages of high stability and long-term reusability. What’s more, MIPs can make up for the shortcomings of bimolecular which cannot be used in extreme environments [8] (such as strong acids, strong bases and organic solutions).

MIPs have been widely used in solid phase extraction, sensors construction, membranes, catalysts and drug delivery. Several reviews related to the development and application of MIPs have been reported [9–12]. Chen [13] published a review about imprinting methods, challenges and effective strategies for MITs and some significant applications of them. Wackerlig [14] reviewed MIPs’ application about analytical separation, artificial antibodies and in vivo applications. Gui [10] reported a review on molecularly imprinted sensors. Since MIPs have so many advantages and such widespread and multidisciplinary applications, novel techniques of MIP deposition, surface development of MIP films or introduction of unique properties are demanded in terms of selective and sensitive MIP layer fabrications. Special attentions have been paid to the synthesis of MIPs based nanomaterials by using nanoparticles as supports. The nanomaterials combine properties of both nanoparticles and MIPs. That is, the composites have the good selectivity of MIP layers and good optical, electrochemical or magnetic properties of the nanoparticles. This form of MIPs is very promising for the practical applications and fundamental research. Multiwalled carbon nanotubes [15], metal-organic framework [16], ZnO [17,18], magnetic nanoparticles [19], silica particles [20] et al. have been used as the support for molecular imprinting. Niu [9] had reported the recent trends in core-shell nanoparticles coated with MIPs (core-shell MIPs). Yáñez-Sedeño [11] published a review which focused on the recent progress of magnetic-molecular imprinted polymers (MMIPs). Dai [12] reviewed on the recent developments of molecular imprinting techniques and applications based on the surface of carbon nanotubes (CNTs). A multitude of materials [21] (i.e., not limited to TiO$_2$ composites) for molecular imprinting and/or the application of MIPs in different areas have been reported [14,22]. The study of MIPs modified TiO$_2$ nanocomposites is one research focus and many articles in this area are updated each year. Table 1 listed the advantages and disadvantages of MIPs modified TiO$_2$ nanomaterials. Theses nanomaterials have been widely used in the field of sensor construction, separation process, pollutant removal and drug development. Nevertheless, a timely and overall review of the current development of MIPs modified TiO$_2$ nanomaterials is lacking. This review intends to introduce the MIPs modified TiO$_2$ nanomaterials during the past 20 years from the aspects of synthesis, related applications and prospects, furthermore, the challenges presently encountered and some feasible resolutions. By means of the points raised in this article, we would like to provide the understanding of the importance of the MIPs modified TiO$_2$ nanomaterials, some assistance for further development of preparation techniques and the expansion of their potential applications.
The introduction of the surface imprinted technique allows MIP particles to present highly uniform size and shape and the presence of recognition sites on the surface the substrate. As a consequence, the migration and combination of the reactive substances are fast, which is favorable for accelerating the reaction and reducing the embedding phenomenon. It also makes it easier to separate elution blotting molecules while increasing application efficiency.

## 2. General Method for the Preparation of MIPs Modified TiO₂ Nanomaterials

Different approaches have been performed for the integration of TiO₂-based nanomaterials into the MIPs matrix in the last decades via varieties of methods. These methods are generally classified as surface imprinting, precipitation polymerization and in situ polymerization. The following discussions summary each of the three general common methods and stress researches interest from the literature.

### 2.1. Surface Molecular Imprinting Technique

Surface molecular imprinting technique (SMIT) establishes a molecular recognition system with fitting binding sites for specific target molecules on the surface of a solid support or matrix material. Figure 1 displays the synthetic methods of MIPs modified TiO₂ nanomaterials in the last decades. The introduction of the surface imprinted technique allows MIP particles to present highly uniform size and shape and the presence of recognition sites on the surface the substrate. As a consequence, the migration and combination of the reactive substances are fast, which is favorable for accelerating the reaction and reducing the embedding phenomenon. It also makes it easier to separate elution blotting molecules while increasing application efficiency.

![Figure 1](image_url)

**Figure 1.** The annual numbers of journal publications on SMIT and other MITs from 2001 to 2018 (originated from Web of Science™) via searching publications including “TiO₂ molecular imprint” and “TiO₂ surface molecular imprint” (SMIT) in the topic.

As SMIT can not only imprint general small molecules but also apply to biological macromolecules such as proteins [26–32], this technology is gaining more and more attention in the field of molecular imprinting. Surface molecularly imprinted polymerization techniques include graft copolymerization, sacrificial carrier method, sol-gel method, sol-hydrothermal polymerization and so on.

---

**Table 1.** Advantages and disadvantages of MIPs modified TiO₂ nanomaterials.

| Materials | Advantages                      | Disadvantages                                      | Ref   |
|-----------|---------------------------------|---------------------------------------------------|-------|
| TiO₂/MIPs | • high oxidation efficiency     | • low utilization of visible-light                 | [3,23–25] |
|           | • nontoxicity                    | • rapid recombination of photogenerated electron/hole pairs |       |
|           | • great adsorption and photocatalytic capacity towards specific pollutants | • the limited and heterogeneity of the binding sites |       |
|           | • high photostability            | • cross-selectivity                                |       |
|           | • chemical inertness             | • leakage of template                              |       |
|           | • environmentally friendly nature| • limited application in biology                   |       |
|           | • low cost                       |                                                   |       |
|           | • mechanical, thermal and chemical stability |                                     |       |
|           | • high binding affinity          |                                                   |       |
|           | • easy way of preparation at a large scale |                               |       |
|           | • structure-activity predictability |                                                   |       |
|           | • specific recognition           |                                                   |       |
|           | • wide practicability            |                                                   |       |
2.1.1. Graft Copolymerization

Surface grafting copolymerization process is realized through the covalent reaction between different functional groups on the surface of the TiO$_2$ based nanomaterials and the grafting polymer brushes. Thin MIPs layer could be obtained through the grafting approach. The obtained polymer recognition site is located on the surface of the carrier, which facilitates the target to quickly approach the recognition site and has a higher binding rate, thereby reducing the nonspecific adsorption. Imprinting molecules on the surface of TiO$_2$ nanomaterials can give the material a richer function and make it more conducive to applications in various fields.

Yao et al. [33] synthesized TiO$_2$ hybrid molecular imprinted polymer by using bensulfuron-methyl (BSM) as the template molecule, methacrylic acid (MAA) as the functional monomer, and silane coupling agent 3-(trimethoxysilyl) propylmethacrylate (KH570) as organic–inorganic connective bridge. The obtained MIPs have stable chemical property, high mechanical strength, large specific surface area and adsorption capacity, good selectivity and easy desorption. Roy et al. [34] fabricated a membrane which exhibited high adsorption capacity with outstanding specific selectivity towards As (III) and As (V). They used a cysteine (Cys) derivative modified TiO$_2$ doped ZnS nanoparticle (Cys@ZnS:TiO$_2$ NPs) as the monomer. The selective he membrane was prepared by the combination of 'grafting-from' and MIT (Figure 2). In this procedure, acrylamide (AA) was firstly mixed with membrane precursors (carboxymethyl cellulose, CMC and polyvinyl alcohol, PVA) to form a base membrane. Then, a pre-polymer mixture which contained template (As (III) or (V)), functional monomers Cys@ZnS:TiO$_2$ NPs), cross-linker (N,N'-methylene bisacrylamide) and an initiator (APS) was added to the base membrane to generate the imprinted membrane. The adsorption capacity of this membrane towards As (III) and As (V) is 151.0 and 130.0 mg/g, respectively. Yang et al. [35] prepared a chemiluminescent sensor based on nitrobenzoxadiazole(NBD)-grafted anatase nanoparticles for detecting phenoxyacetic acid compounds sensitively and selectively, such as the herbicide 2,4-dichlorophenoxyacetic acid. This chemiluminescence sensor was constituted of anatase nanoparticles grafted with the NBD fluorophore and bis(2,4,6-trichlorophenyl)oxalate (TCPO). Firstly, anatase TiO$_2$ nanoparticles were functionalized with a hybrid monolayer of the NBD fluorophore and amino groups, then it was covalently linked with 3-aminopropyltriethoxysilane (APTS) by a nucleophile reaction. The sensor had a very low detection limit of 0.33 nM and can promote the development of sensors based chemiluminescent nanomaterials.

![Figure 2](image)

**Figure 2.** Graphical representation for the fabrication of imprinted membrane synthesized via 'grafting-from' (GFM) approaches. Reprinted with permission from ref [34]. Copyright 2016 American Chemical Society.

2.1.2. Sacrificial Carrier Method

The sacrificial carrier method fixes the imprinted molecule on the surface of the carrier in a solvent and removes the imprinted molecule and dissolves the carrier when the polymerization reaction is finished. During the procedure, the template molecules are firstly immobilized on the surface of the solid support by chemical bonding and then the support is placed in the monomer solution for polymerization. After the polymerization reaction is completed, the carrier is chemically dissolved...
and the template molecule is eluted to obtain a molecularly imprinted polymer having a binding site on the surface.

Xu et al. [36] prepared a novel MIPs based on surface imprinting technique with nano-TiO$_2$ as a sacrificial support matrix, dibenzo-thiophene (DBT) as the imprinted molecule, 4-vinylpridine (4-VP) as a functional monomer and ethylene glycol dimethacrylate (EGDMA) as a cross-linker. As illustrated in Figure 3, they composited the imprinted mixture on the surface of nano-TiO$_2$ during the polymerization and then, dissolved and removed nano-TiO$_2$ to obtain uniformly hollow particles which consist of the imprinted polymer (H-MIPs). Li et al. [37] prepared hollow chlorogenic acid imprinted polymer by using nano-TiO$_2$ as a sacrificial support matrix, 4-VP or MAA as a functional monomer and EGDMA as cross-linker.

![Figure 3. Schematic representation of the route for the synthesis of H-MIPs. Reprinted with permission from ref [36]. Copyright 2011 American Chemical Society.](image-url)

2.1.3. Sol-Gel Polymerization

Sol-gel process usually starts with dissolving metal or semimetal alkoxide in alcoholic or other organic solvents to form a solution and then adds a little amount of water to initiate the hydrolysis and condensation reaction. With the process of the reaction, the viscosity of the matrix increases which means the transformation of sol into the rigid, porous and network-like gel. After aging, the final product was formed.

Sol-gel technique was also used to prepare molecularly imprinted membranes by dip-coating and spin-coating on a substrate. This method has the advantages of low synthesis temperature [38] high purity, uniform film formation, simple process and easy doping. A large number of articles have summarized the sol-gel process and their applications as well as their physical and chemical properties [39]. Sol-gel preparation of molecularly imprinted materials always involves three steps. The first step is the selection of the template. The second step is the incorporation of the template into the polymer network and the last step was the removal of the template.

Takahara et al. [40] deposited β-cyclodextrin/bisphenol A (β-CD/BPA) complex and Ti(O-Bu-n)$_4$ alternately on a quartz crystal microbalance (QCM) to prepared the bisphenol A imprinted TiO$_2$ film by sol-gel method. The imprinted TiO$_2$/β-CD/BPA, 2:1 film showed about 7-fold higher selectivity than the non-imprinted TiO$_2$/β-CD film and a sensitivity lower than 50 ppb to BPA. Wei et al. [41] utilized the inorganic Fe$_3$O$_4$@SiO$_2$ composite as the imprinted matrix, 4-nitrophenol as a template molecule, and Ti(oBu)$_4$ as a cross-linking agent to prepare the final core-shell molecularly imprinted TiO$_2$/WO$_3$-coated magnetic nanocomposite. The degradation rate of this composite for 4-nitrophenol...
was 2.5 times that of the non-imprinted nanocomposite. Luo et al. [42] prepared inorganic-framework molecularly imprinted TiO$_2$/WO$_3$ nanocomposites with molecular recognitive photocatalytic activity using the sol-gel method by using 2-nitrophenol and 4-nitrophenol as template molecules and tetrabutylorthotitanate as a titanium source and the precursor to functional monomer (Figure 4). The molecularly imprinted TiO$_2$/WO$_3$ exhibits higher stability and selective than non-imprinted TiO$_2$/WO$_3$. Cai et al. [43] used metallothionein (MT) as template and TiO$_2$ sol as imprinting matrix to synthesize MT blotted TiO$_2$ films by surface sol-gel method. According to Li et al. [44], SMIT combined with sol-gel process was applied to synthesis a new Pb(II)-imprinted polymer with nano-TiO$_2$ as a solid substrate, glycidoxy propyltrimethoxysilane (GPTMS) as both a crosslink and a silane coupling agent. Song et al. [45] prepared the new molecularly imprinted inorganic-framework Fe–TiO$_2$ composites (MIPs/Fe–TiO$_2$) based on the sol-gel method with acid orange II (AOII) as the template molecule and TiO$_2$ as the matrix material. Liu [46] used n-naphthacene-9-carboxylic acid as the imprinting molecular to construct a novel molecularly imprinted TiO$_2$ thin film modified TiO$_2$ nanotube array photocatalyst by the sol-gel method. Compared with unmodified TiO$_2$ nanotube and non-imprinted TiO$_2$ film modified TiO$_2$ nanotube, the MIPs modified TiO$_2$ nanotube has higher adsorption capacity for target pollutants and enhanced photocatalytic activity in the photodegradation of pollutants.

**Figure 4.** Route for preparation of inorganic–framework molecularly imprinted TiO$_2$/WO$_3$ nanocomposite. Reprinted with permission from ref [42]. Copyright 2013 American Chemical Society.

### 2.1.4. Sol-Hydrothermal Polymerization

Sol-hydrothermal method is a combination of the sol-gel and hydrothermal synthesis process. This method can not only reduce the reaction temperature but also avoid high-temperature calcinations so that cannot influence the grain growth. What’s more, it promotes full contact between the reactants, so that the reaction can be fully carried out.

According to Deng et al. [47], they used 4-nitrophenol (4-NP) as template through sol-hydrothermal method and then prepared inorganic-framework molecularly imprinted TiO$_2$/SiO$_2$ nanocomposite (MIPs-TiO$_2$/SiO$_2$) successfully. Later, Deng et al. [48] prepared inorganic-framework molecularly imprinted TiO$_2$ nanoparticles by sol-hydrothermal method using tetrabutylorthotitanate as titanium source as well as precursor of functional monomer and 4-NP as template. The obtained MIPs-TiO$_2$ is highly reusable for its stable inorganic framework and the facilely released active sites during regeneration process.
2.2. Precipitation Polymerization

Precipitation polymerization, also known as heterogeneous solution polymerization, means that the functional monomers, cross-linking agents and initiators used in the polymerization are dissolved in a dispersant to form a homogeneous mixed solution. The resulting polymer is insoluble in the reaction medium and precipitates. Precipitation polymerization method can be divided into two stages. Firstly, oligomers formed in the two-phase interface reach a certain concentration by crosslinking nucleation and then gather together into polymer particles. Secondly, these particles do not overlap or coalesce but can capture oligomers and functions monomers in the diluted reaction system to grow up individually [49] and eventually form uniform and highly crosslinked polymer microspheres [50,51]. The final morphology of the obtained polymers is directly influenced by the template [52] and functional monomer [53] which are used in polymerization. This method does not need to add any surfactants and stabilizers in the polymerization process. Therefore, the surface of the prepared polymer microspheres is clean, which can effectively avoid the non-selective adsorption of the imprinted molecules by surfactants and stabilizers [54]. This review describes two precipitation polymerization producers: the liquid deposition and precipitation methods.

2.2.1. Liquid Deposition Method (LPD)

Liquid deposition is a process of spontaneous deposition of crystals from a supersaturated solution or forming a thin film on the substrate by adding reactants which can react with the raw materials. Currently, the liquid deposition method mainly uses metal fluoride as a reaction precursor. The metal fluoro-complex ion ([MFₙ]ₘ₋ₙ) undergoes a ligand displacement reaction with the fluoride ion-depleting agent in the solution to promote the hydrolysis equilibrium of the metal fluoride [55], thereby depositing the metal oxide to form a thin film. The method deposits a metal oxide film on the surface of the substrate by adding boric acid (H₃BO₃), water or aluminum metal to [MFₙ]ₘ₋ₙ solution. Boric acid not only be used as a fluoride ion-consuming agent but can react with hydrogen fluoride to generate water to further promote the reaction [56].

Figure 5 illustrated the MIPs modified TiO₂ nanomaterials via the LPD procedure. When liquid phase deposition method was used to prepare the molecularly imprinted TiO₂ thin films, the template molecules are usually added into (NH₄)₂TiF₆ and H₃BO₃ precursor solution to obtain TiO₂ thin films containing template molecules. The template molecules are then removed by solution washing or UV radiation. This method is a typically homogeneous mixing system based on a liquid phase. Therefore, multi-component oxide films with uniformly distributed imprinting sites can be synthesized easily. In addition, this method has the advantages of low processing temperature, simple equipment, high selectivity, uniform film, high film quality, low cost [57], and so on.

Wang et al. [58] prepared the imprinted TiO₂ films by using acetaminophen as a template molecule and p-tert-butyl calixarene as a functional monomer in the presence of (NH₄)₂TiF₆ and H₃BO₃. The imprinted acetaminophen can be removed completely by washing with ethanol. Wang, H. et al. [59] synthesized tetracycline hydrochloride (TC) molecularly imprinted titania modified TiO₂ nanotubes by added template molecule TC into (NH₄)₂TiF₆ and H₃BO₃ precursor solution. The obtained MIPs can improve the molecular recognition ability of the photocatalyst toward template molecules. Feng et al. [60] used L-glutamic acid (GA) as template molecule and synthesized the GA-imprinted TiO₂ films by liquid-phase deposition in the presence of (NH₄)₂TiF₆ and H₃BO₃. Tatemichi et al. [61] added the template molecule pepsin to the (NH₄)₂TiF₆ precursor solution to deposit the nano-TiO₂ along with the complex of pepsin and polylysine onto the gold substrate. The place where the complex was retained in the template membrane after deposition and the pepsin was subsequently removed to prepare a molecularly imprinted nanoparticle coating containing pepsin holes. Xu et al. [62] synthesized the molecularly imprinted TiO₂ hybridized magnetic Fe₃O₄ nanoparticles by using LPD method with estrone as a template molecule and then the target estrone can be removed with the irradiation of UV light.
2.2.2. Seed Precipitation Polymerization

Seed precipitation polymerization (Figure 6) is a typical multi-step swelling and polymerization method. In the initial stage of reaction, when some monomers reach the limit in the aqueous phase, basic particles are deposited. When these basic particles are very tiny, the seed particles will be adsorbed and form a shell layer on the seed surface, which will then become the polymerization reaction of MIPs place. Compared with the traditional molecular imprinting method, the polymer synthesized by ‘seed precipitation polymerization’ has high affinity and selectivity, more easily available sites and more uniform [63].

Huang et al. [64] used nano-TiO$_2$ as the support matrix, 4-VP as the functional monomer, kaempferol as the template molecule, ethylene glycol dimethacrylate (EDMA) as the cross-linking agent to prepare kaempferol imprinted polymers and nano-TiO$_2$-based MIPs were obtained at last after removing the template. The polymer particles made in this work appear as uniform microspheres with high selectivity and template recognition.
2.3. In Situ Polymerization

In-situ polymerization is the method of synthesizing a MIPs solid phase in a specific container (such as chromatographic column) by mixing solvent, template molecule, functional monomer, cross-linking agent and initiator in a certain ratio [66,67]. Because this polymerization method is completed in one step in the column without the need of grinding, sieving, sedimentation and other processing steps, the preparation process is straightforward and can be directly used for analysis with strong practicability.

At present, the method of directly polymerizing MIPs on the surface of nanomaterials by ultraviolet light irradiation is widely used for its advantages of easy reaction process, easy operation, less dosage of initiator or cross-linking agent and high conversion rate [68,69]. UV irradiation is used to initiate the polymerization reaction, which has two advantages compared to thermal initiation. First, at low temperatures, strong complexes can be formed between template molecules and functional monomers, so UV light has been proved to be beneficial for MIPs synthesis which can be applied at extremely low temperatures. Second, UV light can also be used as an effective approach for preparing a detection window and controlling the overall length [70].

In comparison to other methods, the in situ synthesis of TiO$_2$-MIPs remains far less explored. Shen et al. [71] used excessive ortho-phenylenediamine (OPDA) as the monomer and the target compound (4-chlorophenol (4CP) or 2-chlorophenol (2CP)) as the template and then the MIPs layer was coated on the surface of TiO$_2$ particles through in-situ polymerization under UV irradiation. The finally MIPs-coated TiO$_2$ molecularly imprinted photocatalyst was obtained by removing the template molecules.

3. Application of TiO$_2$ and Their Composites Based Molecularly Imprinted Polymers

The combination of TiO$_2$ nanomaterials with molecular imprinting technology can enhance its stability and photocatalytic activity, improve its selectivity and broaden their application scope. Based on the TiO$_2$ nanomaterials and molecular imprinting properties, we mainly review the application of these materials in three aspects: selective photocatalysis, electrochemical and photoelectric sensing and other applications.

![Figure 6. Schematic depiction of the seeded precipitation polymerization mechanism: (1) homogeneous solution of monomers, TiO$_2$ seeds and initiator molecules; (2) Thermal decomposition of the initiator leads to initiator radicals; (3) oligomer radicals’ growth; (4) growth of polymer radicals and phase separation; (5) precipitation of oligomer/polymer radicals onto the surface of the TiO$_2$ nanoparticle seeds. Adapted from ref [65].](image-url)
3.1. Application in Photocatalytic Degradation

In 1972, Japanese scholars Fujishima and Honda reported the results of research using hydrogen peroxide to decompose water with TiO$_2$ under UV light irradiation [72], the application of semiconductor materials in photocatalytic degradation has been further studied [73]. TiO$_2$ has been widely used in the photocatalytic degradation of environmental pollutants due to its suitable electronic band structure [74], biological and chemical inertness [75], strong oxidizing capability, light stability and non-toxicity, which make it to be one of the most promising photocatalyst one [76–78]. However, TiO$_2$ shows poor photocatalytic selectivity because photocatalytic reactions based on TiO$_2$ are accompanied by the formation of highly reactive ·OH radicals which are typically nonselective [79]. Many of the researches have examined that the combination of MIPs with TiO$_2$ and its composite materials can improve the special recognition and selectivity of TiO$_2$ photocatalytic degradation [42,80–83], which is of great significance for the photocatalytic degradation of industrial wastewater [3]. Table 2 listed the details of some of the MIPs modified TiO$_2$ nanomaterials and their applications for photocatalytic degradation.

Environmental Estrogens (EEs) endanger the body’s endocrine system and affect the growth and reproductive functions of humans and animals [94]. Removing estrogenic chemicals from wastewater is a matter of great concern. Xu et al. [62] used estrone as the template molecule to prepare molecularly imprinted TiO$_2$ hybridized magnetic Fe$_3$O$_4$ nanoparticles by a LPD method. The estrone can be selectively degraded and removed under the irradiation of UV light (Figure 7). The obtained

| Template/Degraded Target | Monomer/Support/Synthesis Method | Characterization Techniques | Light Source | Absorption Amount of Degradation Target on MIPs | Reaction Rate Constant (k/min$^{-1}$) | Ref |
|--------------------------|---------------------------------|-----------------------------|--------------|-----------------------------------------------|--------------------------------------|-----|
| OPDA/2-NP, 4-NP          | MAA/P25/SMIT                    | UV-vis, HRTEM, FTIR         | 250 W Philips high-pressure mercury lamp | 0.84, 0.61 mg/g                           | 0.01073, 0.00706                     | [84]|
| 2-NP, 4-NP               | Ti(O-nBu)$_4$/TiO$_2$@WO$_3$/Sol-gel | XRD, SEM, UV-vis           | 300 W xenon lamp | 1.593, 0.139 mg/g                           | 0.00373                              | [42]|
| A0II                     | Ti(O-nBu)$_4$/Fe-TiO$_2$/Sol-gel | XRD, UV-vis, XRD, SEM       | 500 W mercury lamp | 9.35 mg/g                                    | 0.5861                               | [45]|
| 9-AnCOOH                 | Ti(O-nBu)$_4$/TiO$_2$/NTs/Sol-gel | XRD, FTIR, XRD, TEM         | 500W xenon arc lamp | 0.22 mg/g                                    | 0.1046                               | [46]|
| TC                       | TiO$_2$/LPD                     | TEM, FTIR, XRD              | 10 ng/L–1000 mg/L | 0.0732                                       |                                      | [85]|
| estrone                  | Fe$_3$O$_4$@SiO$_2$@TiO$_2$/LPD | TEM, FTIR, XRD              | 20 W UV light | 2.62 mg/g                                    | 0.069                                | [62]|
| 17β-estradiol            | MAA/TiO$_2$/NTs/precipitation polymerization | SPE, UV-vis, FTIR, XRD     | 500 W Xenon lamp | 3.40mg/g                                      | 0.0158                              | [86]|
| RhB                     | TiO$_2$/SMIT                    | XRD, TEM, UV-vis            | 400 W metal halide lamp | 0.48 mg/g                                  | 0.03606                             | [87]|
| RhB                     | OPDA/Co-TiO$_2$/SMIT            | XRD, FTIR, XPS, SEM, TEM, UV-vis DRS | 23 W UV-C light lamp | 0.812 μg/cm$^2$                            | 0.0036                              | [88]|
| PFOP                     | AA/TiO$_2$/NTs/SMIT             | XRD, FESEM, HPLC, UV-vis   | 300W UV lamp | 2.99 mg/g                                    | 0.0623                              | [89]|
| Norfloxacin              | TiO$_2$/SMIT                    | XRD, TEM, UV-vis DRS, XPS   | 400 W metal halide lamp | 1.33, 0.80 mg/g                           | 0.05233, 0.03028                     | [90]|
| DEP                     | TiO$_2$/hydrothermal method     | XRD, SEM, TEM               | 200 W UV lamp | 18.5 mg/g                                    | 0.12                                | [91]|
| DIC                     | Al$^3+$ doped TiO$_2$/SiO$_2$/Sol-gel | XRD, TEM, FTIR             | UV light irradiation | 8.6 mg/g                                     | -                                   | [92]|
| RB                      | Ti(OH)$_2$/CTNC/Sol-gel         | XRD, SEM, TEM               | UV light irradiation | 79.356 mg/g                                  | 0.0702                              | [93]|
| 2,4-DNP                  | OPDA/TiO$_2$/SMIT               | XRD, SEM, TEM               | 300 W xenon lamp | 7.16 mg/g                                    | 0.0026                              | [94]|

[Figure 7: Diagram of the estrone degradation process]
Fe$_3$O$_4$@SiO$_2$@imprinted TiO$_2$ demonstrated high adsorption and capacity selectivity, fast kinetics and excellent stability during long-time photocatalysis. The theoretical maximum adsorption amount of EEs on the Fe$_3$O$_4$@imprinted TiO$_2$ was 2.62 mg/g. This material can provide a potential application prospect for photocatalytic degradation and removal of trace target organic pollutants in the presence of high-level pollutant. Zhang et al. [85] took precipitation polymerization to synthesize the imprinted polymer-modified TiO$_2$ nanotubes (S-MIP-TiO$_2$ NTs) by using 17β-estradiol as the template, MAA as the functional monomer, triethylolpropanetriacrylate as the crosslinking agent, 4,4’-azobisisobutyronitrile (4-cyanovaleric acid) as the initiator. The experimental results showed that the adsorption range of residues in the environment. Li et al. [89] used surface molecular imprinting technique to modify TiO$_2$ nanoparticles (P25). The results of orthogonal experiment showed that the adsorption rate constant, maximum adsorption capacity and Langmuir constant of norfloxacin in MIPs were 0.49 g mg$^{-1}$ min$^{-1}$, 2.99 mg g$^{-1}$ and 2.4 L mg$^{-1}$, respectively. MIPs adsorbed norfloxacin more strongly than P25. In addition, the removal efficiencies of norfloxacin, ciprofloxacin, carbamazepine

Polymer...
and phenol by MIPs were 76.99, 78.81, 7.88 and 2.68%, respectively, indicating that MIPs have a higher level of selectively for norfloxacin and fluoroquinolone with similar structures. At the same time, MIPs showed good photocatalytic performance and had stable removal efficiency for norfloxacin after 5 adsorption-regeneration cycle tests. It can be widely used to remove norfloxacin in aquatic environment.

Figure 7. The Schematic illustrations for preparation estrone imprinted TiO$_2$ films on the surface of magnetic Fe$_3$O$_4$ nanoparticles (A) and the possible mechanism of selective photocatalyst degradation of target template by imprinted Fe$_3$O$_4$@SiO$_2$@TiO$_2$ (B). Reprinted with permission from ref [62]. Copyright 2014 American Chemical Society.

Figure 8. The schematic route for preparation of MIPs/Co–TiO$_2$ nanocomposites with RhB as the template molecule and its use in photocatalytic degradation. Reprinted with permission from ref [87]. Copyright 2016 American Chemical Society.
Diclofenac (DIC) is still one of the most frequently detected pharmaceuticals in the water environment and it has been detected in both the influents and effluents of wastewater treatment plants at concentrations up to mg/L level. Cicerò Coelho et al. [91] prepared a molecularly imprinted photocatalyst containing a low loading of TiO$_2$ and Cu$_2$O-doped TiO$_2$ by using a precipitation polymerization method, which showed target-specific molecular binding and degradation for DIC. In contrast to non-target reference molecules, the MIPs and the composite photocatalysts exhibited superior specific target recognition for selective degradation of DIC. The degradation of DIC with MIP25 reached 62.5% after 300 min UV light irradiation, which is much higher than that achieved with NIP25 and with NIP.

In addition to estrogen chemicals, rhodamine B, perfluorides, norfloxacin and other common pollutants; some other waste organic matters have also been handled by MIPs modified TiO$_2$ nanomaterials. Wu et al. [83] successfully prepared N-F co-doped molecularly imprinted TiO$_2$ (MIP-NFTs) by ethanol-hydrothermal method using 2-nitrophenol (2-NP) and 4-NP as the template molecule and n-butyl titanate as the crosslinking agent. The k value for the photodegradation of 2-NP over 2-NP/MIP-NFTs was 0.05233 min$^{-1}$, being 267% of that over NIP-NFTs (0.01962 min$^{-1}$) and the k value for 4-NP over 4-NP/MIP-NFTs was 0.03734 min$^{-1}$, being 198% of that over NIP-NFTs (0.01882 min$^{-1}$). Compared with NIP-NFTs, MIP-NFTs showed higher photocatalytic activity and selectivity of target pollutants under simulated sunlight in addition, the reuse of MIP-NFTs showed a high degree of stability and reusability for its inorganic structure. Deng et al. [97] synthesized mesoporous molecularly imprinted nanosized TiO$_2$ with molecular recognition and photocatalytic ability by using CTAB and urea as the structure-directed agent. Taking 4-nitrophenol as the target pollutant, they found that the adsorption capacity of 4-nitrophenol was about 3 times higher than that of non-imprinted TiO$_2$ (control TiO$_2$) and the relative selectivity coefficient was 3.645. In addition, the mesoporous enzyme molecularly imprinted TiO$_2$ had good photocatalytic activity on 4-nitrophenol under simulated sunlight. The experimental results showed that the molecular imprinting technique and the fusion of mesoporous structures are the powerful bases for constructing highly efficient photocatalysts with high selectivity for certain organic pollutants. Shen et al. [90] used diethyl phthalate (DEP) as the template molecule to synthesize the inorganic molecularly imprinted polymers (IMIPs) photocatalyst to degrade DEP. The apparent rate constant k for the photodecomposition of DEP was 0.12 min$^{-1}$ over IMIPs-P25, being 14.0, 9.2, 4.6 and 2.5 times that over TiO$_2$/SiO$_2$ (0.013 min$^{-1}$), NIP-P25 (0.018 min$^{-1}$) and P25 (0.049 min$^{-1}$), which indicated that the IMIPs-P25 has stronger photocatalytic activity than other materials. It had been found experimentally that the IMIPs layer provided the molecular recognition capability for the photocatalyst and can achieve the selective adsorption and rapid mineralization of target pollutants with low concentration in other high concentration non-target pollutants. Compared to pure TiO$_2$ photocatalyst (Degussa P25), IMIPs-coated TiO$_2$ photocatalyst nearly eliminated the production of toxic aromatic by-products. In addition, the new photocatalyst consisted entirely of inorganic compounds, resistant to photochemical attack and had long life in the photocatalytic process. Shen et al. [84] prepared modified surface molecularly imprinted TiO$_2$ by using OPDA as a template molecule, MAA as a functional monomer. The k value of the target 4-NP over 4NP-P25 is 0.045 min$^{-1}$, being 346% and 188% of that over NIPs-P25 (0.013 min$^{-1}$) and P25 (0.024 min$^{-1}$) and the k value of 2-NP over 2NP-P25 is 0.040 min$^{-1}$, being 333% of that over NIP-P25 (0.012 min$^{-1}$) and 160% of that over P25 (0.025 min$^{-1}$). Photocatalytic degradation experiments confirmed that the molecular recognition provided by the MIPs layer for photocatalysts can result in the selective photocatalytic degradation of the target pollutants, that is, the selective removal of low concentration and high toxicity organic pollutants from the contaminated water. In addition, Sharabi et al. [98] took diisopropylmethylphosphonate (DIMP) and diethylhydroxymethylphosphonate (DEHMP) as the template molecule, TiOSO$_4$ as the titanium source and functional monomer to prepare molecularly imprinted polymer by a sol-gel method. It was found that the mineralization rate was improved by a factor of 3–4 in the presence of imprinted substrate and the substrate imprinted with DEHMP were very effective in the degradation of the homolog DIMP. This experiment proposed...
a method that a substrate with good affinity can be used to obtain a high surface concentration of active sites in the molecule and it is possible to avoid the aggregation problem that may occur when the target pollutant has low affinity with the substrate. To remove Rose Bengal (RB) dye from industrial wastewater selectively and quantitatively, Ahmed et al. [92] prepared a new MIP chitosan-TiO$_2$ nanocomposite (CTNC). The prepared MIP nanoparticles exhibited a high surface area (95.38 m$^2$/g) with relatively uniform mesoporous channels, which allowed an exceptional uptake of the dye (the maximum adsorption capacity: $Q_m = 79.365$ mg/g) and reflected the high selectivity of the prepared MIP compared to pure chitosan.

3.2. Applications of TiO$_2$ Nanomaterials Based MIPs in Sensors

During the past decades, MIPs have been regarded as an attractive tool for the analysis of complex matrices because of their special specificity towards the target and high stability. They have been combined with several transducers for the development of different sensors. An overview of various applications of TiO$_2$ nanomaterials based MIPs in sensors construction is listed in Table 3.

| Target (Analyze) | Monomer/Support/Synthesis Route | Techniques Used for Characterization | Detection Technique | Detection Range | LOD | Ref |
|------------------|---------------------------------|-------------------------------------|---------------------|----------------|-----|-----|
| Ephedrine        | MMA/Fe$_3$O$_4$@SiO$_2$@TiO$_2$/Sol-gel | FT-IR, XRD, SEM, TEM | EC                  | 0.090-2.8 mM   | 0.0036 mM | [99] |
| Phi-NO$_2$       | p-tert-butylcalix[4]arene ethanol/TiO$_2$/LPD | XRD | EC                  | 0.1-50 mM      | 0.04 µM  | [57] |
| APAP             | p-tert-butylcalix[4]arene ethanol/TiO$_2$/LPD | AFM, UV-vis | EC                  | 5-80 µM, 0.8-5 µM | 0.2 µM | [58] |
| BPA              | p(AN-co-AA)/Ti-TiO$_2$/SUNIT | SEM, UV-vis, EDX | EC                  | 4.4-0.13 mM    | 1.3 nM  | [100] |
| PFOS             | Acrylamide/TiO$_2$ NTs/UV polymerization pyrrole/TiO$_2$ | FTIR, FESEM | PEC                | 0.5-10 µM      | 86 ng/mL | [101] |
| 2,4-D            | Acrylamide/TiO$_2$ NTs/UV polymerization pyrrole/TiO$_2$ | UV-vis DRS | PEC                | 0.5-13 µM      | 10 nM  | [102] |
| BPA              | p(AN-co-AA)/Ti-TiO$_2$/SUNIT | SEM, UV-vis, EDX | PEC                | 4.5-0.108 mM   | 2.0 nM  | [103] |
| PFOS             | Acrylamide/TiO$_2$ NTs/UV polymerization pyrrole/TiO$_2$ | UV-vis, XRD, SEM | PEC                | 0.05-10 mM     | 0.96 nM  | [104] |
| CPF              | TiO$_2$ NRs/ethanol/[4]arene | SEM, TEM | PEC                | 0.029-2.85 mM   | 0.021 pM | [105] |
| CPF              | TiO$_2$ NRs/ethanol/[4]arene | SEM, TEM | PEC                | 0.029-2.85 mM   | 0.021 pM | [105] |
| MC-LR            | MWCNTs/Sol-gel | DRS, XRD, XPS, TEM, UV-vis | PEC                | 1.0 pm-3.0 nM  | 0.4 pM  | [107] |

3.2.1. Applications of TiO$_2$ Nanomaterials Based MIPs in Electrochemical Sensors

Electrochemical sensor (Figure 9) is the use of target substances react with specific inductive elements to generate the detection signal and then this detection signal through a specific transducer can be converted to a target electrical signal proportional to the concentration of identifiable, so as to achieve the purpose of qualitative or quantitative detection and analysis of target substance [108,109]. The combination of molecular imprinting technology and electrochemical sensors can improve the selectivity and sensitivity of electrochemical sensors [110,111], shorten the reaction time and reduce the cost of instrumentation [112].
Bagheri et al. [99] took sol-gel method to synthesis \( \text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{TiO}_2 \)-MIPs nanocomposites and used trimethylolpropane trimethacrylate as the crosslinking agent, 2,2’-azobis (2-methyl propionitrile) as the initiator. It was found that the introduction of \( \text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{TiO}_2 \) nanocomposites into MIPs enhanced the electrochemical signal and recognition ability of the sensor for the detection of ephedrine. This simple and selective sensor not only had good sensitivity to ephedrine but also had excellent reproducibility and stability. The detection range was 0.009–2.8 mM and the detection limit was 0.0036 mM. The sensor has been successfully used to detect ephedrine in biological fluids and drug samples, indicating that the sensor can be a useful tool in clinical and toxicology laboratories.

Wang et al. [57] used p-tert-butylcalix [6] arene and ethanol as functional monomers to prepare Phi-NO\(_2\) sensors based on molecularly imprinted TiO\(_2\) by liquid deposition. Due to the interaction between the molecularly imprinted binding site and the template, the deposited film showed better sensitivity, stability, selectivity and reproducibility to the analyte. The characterization of the imprinted TiO\(_2\) liquid-phase deposited films by X-ray diffraction (XRD) and electrochemical evidenced the feasibility of this method. The detection limit of Phi-NO\(_2\) was 0.04 \( \mu \text{M} \) and the detection range was 0.1–50 \( \mu \text{M} \). This simple and efficient method has great potential for application to the construction of sensors. Wang et al. [58] used p-tert-butylcalix [6] arene as the functional monomer and acetaminophen(APAP) as the template to prepare an electrochemical sensor based on a molecularly imprinted TiO\(_2\) thin film. The sensor showed good sensitivity, selectivity and reproducibility for acetaminophen. The detection limit of acetaminophen was 0.2 \( \mu \text{M} \) and the detection range was 5.0–80.0 \( \mu \text{M} \) and 8.0–5.0 \( \mu \text{M} \).

Qian [100] synthesized a recognition element of molecularly imprinted films (MIFs) on the surface of a Ti/TiO\(_2\) electrode for highly selective and sensitive electrochemical detection of bisphenol A (BPA). The blotting sites can selectively rebind BPA through hydrogen bonds, resulting in an increase in equilibrium currents in amperometric detection, which can electrochemically sense BPA. The detection limit of BPA was 1.3 nM and the detection range was 4.4–0.13 mM. Combined with the high selectivity of MIFs and the high sensitivity of electrochemistry, the MIFs based electrochemical sensor has showed high sensitivity and selectivity to BPA, with outstanding reusability, practicability and reliability.

### 3.2.2. Applications of TiO\(_2\) Nanomaterials Based MIPs in Photoredox-electrochemical Sensors

Photochemistry (PEC) sensor is a device that detects the process with the conversion of light energy to chemical energy and electricity [113,114]. The principle is that the photoactive can react with the analyte under the light irradiations. According to the relationship between the charge of...
photocurrent or photovoltaic voltage with the concentration of analyte, the quantitative analysis of the analyte could be achieved [115]. Photoelectrochemical analysis based on this phenomenon has the characteristics of high sensitivity, simple equipment and easy miniaturization [116,117]. In addition, PEC uses light as an excitation signal and an electrical signal as a detection signal, which is contrary to the traditional electrochemical analysis process and shows a higher sensitivity and selectivity [118,119]. TiO$_2$ is the most widely used metal oxide photoactive material. The combination between TiO$_2$ and MIPs can greatly improve the photoelectrical response of TiO$_2$ [120,121].

Thanhthuy et al. [101] fabricated a novel PEC sensor by imprinting a selective layer on highly ordered and vertically aligned nanotube arrays. The photocurrent was proportional to the concentration of PFOS in the range of 0.5–10 µM with a detection limit of 86 ng mL$^{-1}$. The prepared sensor (MIP/TiO$_2$ NATs) showed highly sensitive and selective characters to PFOS in water samples. Some other high concentration pollutants (such as twenty times 2,4-dichlorophenoxyacetic acid (2,4-D) and two times PFOA) did not interfere the determination of PFOS. The selective determination of PFOS in pollution water can make the application of the PEC sensor become a reality.

Shi et al. [102] prepared a PEC sensor with a low detection limit based on modified TiO$_2$ nanotubes (TiO$_2$ NTs) to detect 2,4-D (2,4-D, a putative endocrine disruptor which lacks electrochemical activity) selectively and sensitively (Figure 10). The detection range was 0.5–13 µM and the detection limit was 10 nM. Thereafter, Lu et al. [103] fabricated a novel PEC sensor based on vertically aligned TiO$_2$ nanobutes with surface molecularly imprinted PPy to detect another endocrine disruptor BPA. The photocurrent was proportional to the concentration of BPA in the range of 4.5–108 nM, with a detection limit of 2.0 nM. The results showed that the prepared sensor had highly selectivity and sensitivity and can determine BPA from other high concentration substances in water samples. What’s more, the PEC sensor showed good applicability and high stability in real water, which made a successful attempt in developing highly selective and sensitive PEC sensors for endocrine disruptors monitoring.

Wang et al. [104] imprinted o-phenylenediamine (o-PD) monomers and chlorpyrifos(CPF) template molecules on gold nanoparticle-modified TiO$_2$ nanotubes to prepare molecularly imprinted polymer films for the detection of CPF molecular by photoelectrochemical method. The experimental results showed that under visible light irradiation, the excited electrons were migrated from CPF to AuNPs and then to the conduction band of TiO$_2$NTs. Under the optimal experimental conditions, the photocurrent was proportional to the concentration of CPF in the range of 0.05–10 µM with a detection limit of 0.96 nM. The MIPs-based PEC sensor was extremely specific and promising in applications of organochlorine pesticides and can be used to detect CPF in green vegetables. Sun et al. [105] also constructed a PEC sensor based on MIP modified hierarchical branched TiO$_2$ nanorods (B-TiO$_2$ NRs) by the hydrothermal method, which can detect CPF sensitively and efficiently. The PEC sensing platform is developed for the detection of CPF in the linear range from 0.01 to 100 ng mL$^{-1}$ with a low detection limit of 7.4 pg mL$^{-1}$. Later, Wang et al. [106] used lindane instead of CPF as a template molecule and aminothiophenol as a functional monomer to construct a molecularly imprinted polymer film for the detection of lindane via the photoelectrochemical method. Similarly, the MIPs-based PEC sensor with a linear range from 0.1–10 µM and detection limit of 0.03 µM had excellent specificity and could be successfully applied to the identification and detection of lindane in real samples.

In order to rapidly and accurately detect microcystin (MC-LR, a strong liver tumor promoter), Liu et al. [107] took MC-LR as the template molecule to prepare molecularly imprinted TiO$_2$ coated multi-walled carbon nanotubes (MI-TiO$_2$ @ CNTs) by the sol-gel method. The MI-TiO$_2$ @ CNT PEC sensor with a linear range from 1.0 pM–3.0 nM and detection limit of 0.4 pM exhibited higher photooxidation capability to MC-LR compared to conventional TiO$_2$ and non-imprinted (NI-) TiO$_2$ @ CNTs. What’s more, the sensor had high photocurrent sensitivity and excellent selectivity. It can provide a promising PEC analysis platform for future generations.
In addition to their use as synthetic receptors in sensor platforms, there is also a recent trend to employ MIPs in various applications that go beyond analytical detection. Takahara et al. [40] deposited a complex of β-CD/BPA and Ti (O-Bu-n)₄ alternately on the QCM and prepared the BPA imprinted TiO₂ film by the sol-gel method on the gas phase surface. They confirmed the film formation and sensitivity of TiO₂/(β-CD/BPA) films by QCM frequency measurements. In addition, the sensitivity of the imprinted TiO₂/(β-CD/BPA) film was as low as 50 ppb to BPA. This method has the potential of detecting various organic compounds in liquids and gases.

Geng et al. [122] prepared a new surface molecularly imprinted polymer based on nano-TiO₂ by using propazine (Pro) as the template molecule, EGDMA and 2,2'-dimethacrylate acid as the crosslinking agent, methacrylic acid as the functional monomer, and isobutyronitrile as the initiator. The tests on all kinds of properties of this MIPs showed that it had good adsorption capacity and high recognition selectivity for promethazine. In the meantime, it also presented good cross-selectivity with 2-chloro-4,6-bis(ethylamino)-1,3,5-triazine(simazine, Sim) and 2-chloro-4-diethylamino- isopropylamino-1,3,5-triazine (Atrazine, Atr). In addition, new SMIPs based on nano-TiO₂ were used as solid phase extraction (SPE) materials and three pesticide residues in water, soil, corn plants and grain samples were extracted, purified and determined by MIPs-SPE and high performance liquid chromatography (HPLC). The result substantiated that the MIPs enabled the high selectivity and enrichment of Pro, Atr and Sim from complex environmental media. This technology provided an analytical platform for quantitative analysis of traces of Pro, Sim and Atr residues in multi-environment media and food sources.

Khoddami et al. [123] used 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) as the functional monomer, tetraethyl orthosilicate as the crosslinking agent and Co (II) as the template and then synthesized Co (II) ions magnetic molecularly imprinted polymer (Fe₃O₄ @ TiO₂ @ SiO₂-IIP) using a sol-gel method. The magnetic ion imprinted polymer which had been consumed can be refreshed by simply washing with HNO₃ aqueous solution and the adsorption capacity did not have a significant drop after up to seven cycles of testing, indicating that the Fe₃O₄ @ TiO₂ @ SiO₂-IIP is stable
and reusable. In addition, the preparation of the compound was relatively easy and the experimental
data fit the pseudo-second-order kinetic model, which was in good agreement with the Langmuir
adsorption isotherm. Based on the properties demonstrated in this study, Fe₃O₄ @ TiO₂ @ SiO₂-IIP
was a candidate for the selective determination of Co (II) in biological and environmental samples.

4. Conclusions and Outlook

This up-to-date review has clearly shown that MIPs modified TiO₂ nanomaterial has attained
much attention because they combined the good photo catalytic characters of TiO₂ and the excellent
selectivity of MIPs. MIPs modified TiO₂ nanomaterials have been prepared in a controlled way by
applying different technologies and surface chemistry. Because of the better recognition ability, higher
selectivity and stronger adsorption capacity than non-imprinted ones towards analytes especially
when the analytes were of low concentration or in a mixture, MIPs modified TiO₂ nanomaterials have
exhibited remarkable advantages for the application in pollutant removal, sensors, separation and so
forth. Many successful examples for the development of MIPs modified TiO₂ nanomaterials and their
applications have been reported.

In spite of the tremendous progress that has been made in the MIPs modified TiO₂ nanomaterials,
many challenges summarizing in Table 1 (e.g., limited usage of visible light, applications in biology)
remain to be addressed. These existing problems restricted the working efficiency and advanced
applications of MIPs modified TiO₂ nanomaterials. The main challenges includes: (1) Extending
light utilization to visible light range and reducing the recombination of electron-holes of TiO₂.
TiO₂ doping or choosing suitable monomers for imprinting could improve the photo related characters
of the nanocomposite; (2) Enhancing the binding sites and binding capacities between template and
monomers. New synthetic techniques, such as controlled radical polymerizations (CRPs), could
be introduced in the MIPs modified TiO₂ nanomaterials preparation process which would lead to
improved affinity. (3) Preventing the collapse or deformation of the imprinted cavities on MIPs during
the application procedure. Balancing the good affinity and the stability of the imprinted cavities is
one of the significant factors to be considered. Presumably, the higher porosity polymers contains
more cavities are easier to collapse leading to the changes in binding properties. Efficient imprinting
technology or elution method should be studied; (4) Exploring imprinting methods to broaden target
molecules from small molecules to biological macromolecules, such as proteins and even to living
cells. TiO₂ has been regarded as a biocompatible material but their real applications in biological
areas or clinical trials are very rare. The development of MIPs modified TiO₂ nanomaterials with
biocompatible properties is a challenge that can be expected to yield a new generation of sensors
materials for biomedical applications. (5) Decreasing or eliminating cross-selectivity, that is the binding
to molecular similar to the native template. Initial template interactions with functional monomers
largely determine the recognition properties the matrix. Therefore, it is necessary to seek suitable
monomers capable of forming better, more stable and strong interactions with the template. Computer
aided design would help to seek for the suitable monomers.

In short, with the continuous development of computer aided design method, synthesis methods
and detection technologies, the theoretical system of MIPs modified TiO₂ nanomaterials will be
becoming more perfect and widely used. Great prospects of these synthetic materials in the sensor,
catalyst, electrode array and so forth, can be seen in the future.

Acknowledgments: We gratefully thank NSFC (21675140, 21575124 and 21705141), the High-end Talent Project
of Yangzhou University, the 14th six talent peaks project in Jiangsu Province (SWYY-089), Higher Education
Outstanding Scientific and Technological Innovation Team of Jiangsu Province (2017-6), Young academic leaders
of Jiangsu Province (2018), the Natural Science Foundation of Jiangsu Province (BK20181219), the project
funded by the PAPD and TAPP. We also thank the Test Center of Yangzhou University for the XPS, SEM and
TEM characterizations.

Conflicts of Interest: The authors declare no conflict of interest.
List of Abbreviations

TiO$_2$  
titanium dioxide
MIPs  
molecularly imprinted polymers
NIPs  
non-imprinted polymers
MMIPs  
magnetic-molecular imprinted polymers
CNTs  
carbon nanotubes
SMIT  
surface molecular imprinting technique
MAA  
methacrylic acid
BSM  
sulfur-benzuron-methyl
KH570  
3-(trimethoxysilyl) propylmethacrylate
Cys  
cysteine
Cys@ZnS:TiO$_2$ NPs  
cysteine derivative modified TiO$_2$ doped ZnS nanoparticle
AA  
acrylamide
CMC  
carboxymethyl cellulose
PVA  
polyvinyl alcohol
APS  
ammonium persulfate
2,4-D  
2,4-dichlorophenoxyacetic acid
NBD  
nitrobenzoxadiazole
TCPO  
bis(2,4,6-trichlorophenyl)oxalate
APTS  
3-aminopropyltriethoxysilane
GFM  
grafting-from
DBT  
dibenzothiophene
4-VP  
4-vinylpyridine
EGDMA  
ethylene glycol dimethacrylate
β-CD  
β-cyclodextrin
BPA  
bisphenol A
QCM  
quartz crystal microbalance
GPTMS  
glycidoxy propyltrimethoxysilane
MIPs/Fe–TiO$_2$  
molecularly imprinted inorganic-framework Fe–TiO$_2$ composites
AOII  
acid orange II
4-NP  
4-nitrophenol
2-NP  
2-nitrophenol
LPD  
liquid deposition method
TC  
tetracycline hydrochloride
GA  
L-glutamic acid
EDMA  
ethylene glycol dimethacrylate
OPDA  
ortho-phenylenediamine
4-CP  
4-chlorophenol
2-CP  
2-chlorophenol
EEs  
Environmental Estrogens
RhB  
Rhodamine B
PDA  
phenylenediamine
PFCs  
perfluorinated chemicals
PFOA  
perfluorooctanoic acid
PFOS  
perfluorooctane sulfonate
CTNC  
chitosan-TiO$_2$ nanocomposite
RB  
Rose Bengal
AIBN  
azobisisobutyronitrile
P25  
a kind of TiO$_2$ particles
CTAB  
cetrimonium bromide
DEP  
diethyl phthalate
IMIPs  
inorganic molecularly imprinted polymers
DIMP  
diisopropyl methylphosphonate
DEHMP  
diethylhydroxymethylphosphonate
XRD X-ray diffraction
Phi-NO$_2$ O,O-dimethyl-(2,4-dichlorophenoxyacetoxyl)(30-nitrobenzyl)methinephosphonate
APAP acetaminophen
MIFs molecularly imprinted films
BPA bisphenol A
PEC photochemistry
o-PD o-phenylenediamine
MC-LR microcystin
Pro propazine
Sim simazine
Atr Atrazine
HPLC high performance liquid chromatography
SPE solid phase extraction
AAPTS 3-(2-aminoethylamino) propyltrimethoxysilane

References
1. Teh, C.M.; Mohamed, A.R. Roles of titanium dioxide and ion-doped titanium dioxide on photocatalytic degradation of organic pollutants (phenolic compounds and dyes) in aqueous solutions: A review. *J. Alloys Compd.* 2011, 509, 1648–1660. [CrossRef]
2. Foster, H.A.; Ditta, I.B.; Varghese, S.; Steele, A. Photocatalytic disinfection using titanium dioxide: Spectrum and mechanism of antimicrobial activity. *Appl. Microbiol. Biotechnol.* 2011, 90, 1847–1868. [CrossRef] [PubMed]
3. Lai, C.; Zhou, X.; Huang, D.; Zeng, G.; Cheng, M.; Qin, L.; Yi, H.; Zhang, C.; Xu, P.; Zhou, C.; et al. A review of titanium dioxide and its highlighted application in molecular imprinting technology in environment. *J. Taiwan Inst. Chem. Eng.* 2018, 91, 517–531. [CrossRef]
4. Kubacka, A.; Fernández-García, M.; Cerrada, M.L.; Fernández-García, M. Titanium Dioxide–Polymer Nanocomposites with Advanced Properties; Springer: Berlin/Heidelberg, Germany, 2012; pp. 119–149.
5. Jo, C.W.; Hee, Y.S.; Faiz, A. Molecular imprinted polymers for separation science: A review of reviews. *J. Sep. Sci.* 2013, 36, 609–628.
6. Yang, S.; Wang, Y.; Jiang, Y.; Li, S.; Liu, W. Molecularly imprinted polymers for the identification and separation of chiral drugs and biomolecules. *Polymers* 2016, 8, 216. [CrossRef]
7. Mosbach, K.; Ramstrom, O. The emerging technique of molecular imprinting and its future impact on biotechnology. *Bio-Technology (New York)* 1996, 14, 163–170. [CrossRef]
8. Beyazit, S.; Bui, B.T.S.; Haupt, K.; Gonzato, C. Molecularly imprinted polymer nanomaterials and nanocomposites by controlled/living radical polymerization. *Prog. Polym. Sci.* 2016, 62, 1–21. [CrossRef]
9. Niu, M.; Pham-Huy, C.; He, H. Core-shell nanoparticles coated with molecularly imprinted polymers: A review. *Microchim. Acta* 2016, 183, 2677–2695. [CrossRef]
10. Gui, R.; Jin, H.; Guo, H.; Wang, Z. Recent advances and future prospects in molecularly imprinted polymers-based electrochemical biosensors. *Biosens. Bioelectron.* 2018, 100, 56–70. [CrossRef] [PubMed]
11. Yáñez-Sedeño, P.; Campuzano, S.; Pingarrón, J.M. Electrochemical sensors based on magnetic molecularly imprinted polymers: A review. *Anal. Chim. Acta* 2017, 960, 1–17. [CrossRef] [PubMed]
12. Dai, H.; Xiao, D.L.; He, H.; Li, H.; Yuan, D.H.; Zhang, C. Synthesis and analytical applications of molecularly imprinted polymers on the surface of carbon nanotubes: A review. *Microchim. Acta* 2015, 182, 893–908. [CrossRef]
13. Chen, L.; Xu, S.; Li, J. Recent advances in molecular imprinting technology: Current status, challenges and highlighted applications. *Chem. Soc. Rev.* 2011, 40, 2922–2942. [CrossRef] [PubMed]
14. Wackerlig, J.; Schirhagl, R. Applications of molecularly imprinted polymer nanoparticles and their advances toward industrial use: A review. *Anal. Chem.* 2016, 88, 250–261. [CrossRef] [PubMed]
15. Liu, S.; Zhang, X.; Ma, Y.; Bai, X.; Chen, X.; Liu, J.; Pan, J. Immobilization of boronic acid and vinyl-functionalized multiwalled carbon nanotubes in hybrid hydrogel via light-triggered chemical polymerization for aqueous phase molecular recognition. *Chem. Eng. J.* 2019, 355, 740–751. [CrossRef]
16. Zhang, W.; Duan, D.; Liu, S.; Zhang, Y.; Leng, L.; Li, X.; Chen, N.; Zhang, Y. Metal-organic framework-based molecularly imprinted polymer as a high sensitive and selective hybrid for the determination of dopamine in injections and human serum samples. *Biosens. Bioelectron.* 2018, 118, 129–136. [CrossRef] [PubMed]

17. Hassanzadeh, J.; Khataee, A.; Oskoei, Y.M.; Fattahi, H.; Bagheri, N. Selective chemiluminescence method for the determination of trinitrotoluene based on molecularly imprinted polymer-capped zno quantum dots. *New J. Chem.* 2017, 41, 10659–10667. [CrossRef]

18. Usha, S.P.; Gupta, B.D. Urinary p-cresol diagnosis using nanocomposite of zno/mos2 and molecular imprinted polymer on optical fiber based lossy mode resonance sensor. *Biosens. Bioelectron.* 2018, 101, 135–145. [CrossRef] [PubMed]

19. Zhong, M.; Wang, Y.-H.; Wang, L.; Long, R.-Q.; Chen, C.-L. Synthesis and characterization of magnetic molecularly imprinted polymers for enrichment of sanguinarine from the extraction wastewater of m. Cordata. *J. Ind. Eng. Chem.* 2018, 66, 107–115. [CrossRef]

20. Wang, H.; Xu, Q.; Wang, J.; Du, W.; Liu, F.; Hu, X. Dendrimer-like amino-functionalized hierarchical porous silica nanoparticle: A host material for 2,4-dichlorophenoxyacetic acid imprinting and sensing. *Biosens. Bioelectron.* 2018, 100, 105–114. [CrossRef] [PubMed]

21. Lei, Y.; Zhou, T.; Shen, X. Molecular imprinting in particle-stabilized emulsions: Enlarging template size from small molecules to proteins and cells. *Mol. Impr.* 2016, 2, 8–16.

22. Feinle, A.; Elsaesser, M.S.; Huesing, N. Sol-gel synthesis of monolithic materials with hierarchical porosity. *Chem. Soc. Rev.* 2016, 45, 3377–3399. [CrossRef] [PubMed]

23. Daghrir, R.; Drogui, P.; Robert, D. Modified tio2 for environmental photocatalytic applications: A review. *Ind. Eng. Chem. Res.* 2013, 52, 3581–3599. [CrossRef]

24. Van Nostrum, C.F. Molecular imprinting: A new tool for drug innovation. *Drug Discov. Today Technol.* 2005, 2, 119–124. [CrossRef] [PubMed]

25. Gupta, S.M.; Tripathi, M. A review of tio2 nanoparticles. *Chin. Sci. Bull.* 2011, 56, 1639–1657. [CrossRef]

26. Zhang, X.F.; Du, X.Z. Protein surface imprinting technology. *Prog. Chem.* 2016, 28, 149–162.

27. Shiomi, T.; Matsui, M.; Mizukami, F.; Sakaguchi, K. A method for the molecular imprinting of hemoglobin on silica surfaces using silanes. *Biomaterials* 2005, 26, 5564–5571. [CrossRef] [PubMed]

28. Wang, Y.; Zhou, Y.; Sokolov, J.; Rigas, B.; Levon, K.; Rafailovich, M. A potentiometric protein sensor built with surface molecular imprinting method. *Biosens. Bioelectron.* 2008, 24, 162–166. [CrossRef] [PubMed]

29. Liu, D.; Ulbricht, M. A highly selective protein adsorber via two-step surface-initiated molecular imprinting utilizing a multi-functional polymeric scaffold on a macroporous cellulose membrane. *RSC Adv.* 2017, 7, 11012–11019. [CrossRef]

30. Bossi, A.; Piletsky, S.A.; Piletska, E.V.; Righetto, P.G.; Turner, A.P.F. Surface-grafted molecularly imprinted polymers for protein recognition. *Anal. Chem.* 2001, 73, 5281–5286. [CrossRef] [PubMed]

31. Li, Y.; Yang, H.H.; You, Q.H.; Zhuang, Z.X.; Wang, X.R. Protein recognition via surface molecularly imprinted polymer nanowires. *Anal. Chem.* 2006, 78, 317–320. [CrossRef] [PubMed]

32. Zhang, W.; Qin, L.; He, X.-W.; Li, W.-Y.; Zhang, Y.-K. Novel surface modified molecularly imprinted polymer using acryloyl-beta-cyclodextrin and acrylamide as monomers for selective recognition of lysozyme in aqueous solution. *J. Chromatogr. A* 2009, 1216, 4560–4567. [CrossRef] [PubMed]

33. Yao, Q.Z.; Zhou, Y.M.; Sun, Y.Q.; Ye, X.Y. Synthesis of tio(2) hybrid molecular imprinted polymer for ethofumesate linked by silane coupling agent. *J. Inorg. Organomet. Polym. Mater.* 2008, 18, 477–484. [CrossRef]

34. Roy, E.; Patra, S.; Madhuri, R.; Sharma, P.K. A single solution for arsenite and arsenate removal from drinking water using cysteine@zn5Tio2 nanoparticle modified molecularly imprinted biofouling-resistant filtration membrane. *Chem. Eng. J.* 2016, 304, 259–270. [CrossRef]

35. Yang, L.; Guan, G.; Wang, S.; Zhang, Z. Nano-anatase-enhanced peroxyoxalate chemiluminescence and its sensing application. *J. Phys. Chem. C* 2012, 116, 3356–3362. [CrossRef]

36. Xu, W.Z.; Zhou, W.; Xu, P.P.; Pan, J.M.; Wu, X.Y.; Yan, Y.S. A molecularly imprinted polymer based on tio2 as a sacrificial support for selective recognition of dibenzothiophene. *Chem. Eng. J.* 2011, 172, 191–198. [CrossRef]

37. Li, H.; Li, G.; Li, Z.; Lu, C.; Li, Y.; Tan, X. Surface imprinting on nano-tio2 as sacrificial material for the preparation of hollow chlorogenic acid imprinted polymer and its recognition behavior. *Appl. Surf. Sci.* 2013, 264, 644–652. [CrossRef]
38. Wang, Z.C.; Helmersson, U.; Kall, P.O. Optical properties of anatase tio2 thin films prepared by aqueous sol-gel process at low temperature. Thin Solid Films 2002, 405, 50–54. [CrossRef]

39. Marx, S.; Zaitsman, A.; Turyan, I.; Mandler, D. Parathion sensor based on molecularly imprinted sol-gel films. Anal. Chem. 2004, 76, 120–126. [CrossRef]

40. Takahara, N.; Wang, T.; Lee, S.-W. Selective adsorption of molecules by imprinted titania nanohybrid thin films with anchored cyclodextrin host molecules. Kobunshi Ronbunshu 2013, 70, 214–220. [CrossRef]

41. Wei, S.; Liu, H.; He, C.; Liang, Y. Molecurarily imprinted tio2/wo3-coated magnetic nanocomposite for photocatalytic degradation of 4-nitrophenol under visible light. Aust. J. Chem. 2016, 69, 638–644. [CrossRef]

42. Luo, X.; Deng, F.; Min, L.; Luo, S.; Guo, B.; Zeng, G.; Au, C. Facile one-step synthesis of inorganic-framework molecularly imprinted tio2/wo3 nanocomposite and its molecular recognitive photocatalytic degradation of target contaminant. Environ. Sci. Technol. 2013, 47, 7404–7412. [CrossRef] [PubMed]

43. Cai, Z.-F.; Dai, H.-J.; Si, S.-H.; Ren, F.-L. Molecular imprinting and adsorption of metallothionein on nanocrystalline titania membranes. Appl. Surf. Sci. 2008, 254, 4457–4461. [CrossRef]

44. Li, C.; Gao, J.; Pan, J.; Zhang, Z.; Yan, Y. Synthesis, characterization, and adsorption performance of pb(ii)-imprinted polymer in nano-tio2 matrix. J. Environ. Sci. 2009, 21, 1722–1729. [CrossRef]

45. Song, Y.; Rong, C.; Shang, J.; Wang, Y.; Zhang, Y.; Yu, K. Synthesis of an inorganic-framework molecularly imprinted fe-doped tio2 composite and its selective photo-fenton-like degradation of acid orange ii. J. Chem. Technol. Biotechnol. 2017, 92, 2038–2049. [CrossRef]

46. Liu, Y.; Liu, R.; Liu, C.; Luo, S.; Yang, L.; Sui, F.; Teng, Y.; Yang, R.; Cai, Q. Enhanced photocatalysis on tio2 nanotube arrays modified with molecularly imprinted tio2 thin film. J. Hazard. Mater. 2010, 182, 912–918. [CrossRef] [PubMed]

47. Deng, F.; Liu, Y.; Luo, X.; Wu, S.; Luo, S.; Au, C.; Qi, R. Sol-hydrothermal synthesis of inorganic-framework molecularly imprinted tio2/sio2 nanocomposite and its preferential photocatalytic degradation towards target contaminant. J. Hazard. Mater. 2014, 278, 108–115. [CrossRef] [PubMed]

48. Deng, F.; Zhao, X.; Pei, X.; Luo, X.; Li, W.; Au, C. Sol-hydrothermal synthesis of inorganic-framework molecularly imprinted tio2 nanoparticle and its enhanced photocatalytic activity for degradation of target pollutant. Sci. Adv. Mater. 2016, 8, 1079–1085. [CrossRef]

49. Jing, T.; Gao, X.D.; Wang, P.; Wang, Y.; Lin, Y.F.; Hu, X.Z.; Hao, Q.L.; Zhou, Y.K.; Mei, S.R. Determination of trace tetracycline antibiotics in foodstuffs by liquid chromatography–tandem mass spectrometry coupled with selective molecular-imprinted solid-phase extraction. Anal. Bioanal. Chem. 2009, 393, 2009–2018. [CrossRef] [PubMed]

50. Yoshimatsu, K.; Reimhult, K.; Krozer, A.; Mosbach, K.; Sode, K.; Ye, L. Uniform molecularly imprinted microspheres and nanoparticles prepared by precipitation polymerization: The control of particle size suitable for different analytical applications (vol 584, pg 112, 2007). Anal. Chim. Acta 2010, 657, 215. [CrossRef] [PubMed]

51. Wang, J.F.; Cormack, P.A.G.; Sherrington, D.C.; Khoshdel, E. Monodisperse, molecularly imprinted polymer microspheres prepared by precipitation polymerization for affinity separation applications. Angew. Chem. Int. Edit. 2003, 42, 5336–5338. [CrossRef] [PubMed]

52. Cacho, C.; Turiel, E.; Martin-Esteban, A.; Perez-Conde, C.; Camara, C. Clean-up of triazines in vegetable extracts by molecularly-imprinted solid-phase extraction using a propazine-imprinted polymer. Anal. Bioanal. Chem. 2003, 376, 491–496. [CrossRef] [PubMed]

53. Sambe, H.; Hoshina, K.; Moaddel, R.; Wainer, I.W.; Haginaka, J. Uniformly-sized, molecularly imprinted polymers for nicotine by precipitation polymerization. J. Chromatogr. A 2006, 1134, 88–94. [CrossRef] [PubMed]

54. Li, G.L.; Moehwald, H.; Shchukin, D.G. Precipitation polymerization for fabrication of complex core-shell hybrid particles and hollow structures. Chem. Soc. Rev. 2013, 42, 3628–3646. [CrossRef] [PubMed]

55. Maki, H.; Okumura, Y.; Ikuta, H.; Mizuhata, M. Ionic equilibria for synthesis of tio2 thin films by the liquid-phase deposition. J. Phys. Chem. C 2014, 118, 11964–11974. [CrossRef]

56. Shen, X.; Zhu, L.; Liu, G.; Tang, H.; Liu, S.; Li, W. Photocatalytic removal of pentachlorophenol by means of an enzyme-like molecular imprinted photocatalyst and inhibition of the generation of highly toxic intermediates. New J. Chem. 2009, 33, 2278–2285. [CrossRef]

57. Wang, C.; Li, C.; Wang, F.; Wang, C. Phosphonate electrochemical recognition by molecularly imprinted deposited film. Appl. Surf. Sci. 2006, 253, 2282–2288. [CrossRef]
58. Wang, C.; Li, C.; Wei, L.; Wang, C. Electrochemical sensor for acetaminophen based on an imprinted tio2 thin film prepared by liquid phase deposition. Microchim. Acta 2007, 158, 307–313. [CrossRef]

59. Wang, H.; Wu, X.; Zhao, H.; Quan, X. Enhanced photocatalytic degradation of tetracycline hydrochloride by molecular imprinted film modified tio2 nanotubes. Chin. Sci. Bull. 2012, 57, 601–605. [CrossRef]

60. Feng, L.A.; Liu, Y.J.; Hu, J.M. Moleurally imprinted tio2 thin film by liquid phase deposition for the determination of l-glutamic acid. Langmuir 2004, 20, 1786–1790. [CrossRef] [PubMed]

61. Tatemichi, M.; Sakamoto, M.A.; Mizuhata, M.; Deki, S.; Takeuchi, T. Protein-templated organic/inorganic hybrid materials prepared by liquid-phase deposition. J. Am. Chem. Soc. 2007, 129, 10906. [CrossRef] [PubMed]

62. Xu, S.; Lu, H.; Chen, L.; Wang, X. Molecularly imprinted tio2 hybridized magnetic fe3o4 nanoparticles for selective photocatalytic degradation and removal of estrone. RSC Adv. 2014, 4, 45266–45274. [CrossRef]

63. Yong, L.; Yin, X.F.; Chen, F.R.; Yang, H.H.; Zhuang, Z.X.; Wang, X.R. Synthesis of magnetic molecularly imprinted polymer nanowires using a nanoporoporous alumina template. Macromolecules 2006, 39, 4497–4499.

64. Huang, Z.J.; Zhang, Z.M.; Xia, Q.; Li, C.L.; Yun, Y.B. Surface molecularly imprinted polymer microspheres based on nano-tio2 for selective recognition of kaempferol. J. Appl. Polym. Sci. 2017, 134. [CrossRef]

65. Rauh, A.; Honold, T.; Karg, M. Seeded precipitation polymerization for the synthesis of gold-hydrogel core-shell-particles: The role of surface functionalization and seed concentration. Colloid Polym. Sci. 2016, 294, 37–47. [CrossRef]

66. Du, T.; Cheng, J.; Wu, M.; Wang, X.; Zhou, H.; Cheng, M. An in situ immobilized pipette tip solid phase microextraction method based on molecularly imprinted polymer monolith for the selective determination of difenoconazole in tap water and grape juice. J. Chromatogr. B 2014, 951–952, 104. [CrossRef] [PubMed]

67. Moen, M.M.; Javanbakht, M.; Akbari-Adergani, B. Molecularly imprinted polymer cartridges coupled on-line with high performance liquid chromatography for simple and rapid analysis of dextromethorphan in human plasma samples. J. Chromatogr. B 2011, 879, 777–782. [CrossRef] [PubMed]

68. Corcione, C.E.; Striani, R.; Frigione, M. Organic–inorganic uv-cured methacrylic-based hybrids as protective coatings for different substrates. Prog. Org. Coat. 2014, 77, 1117–1125. [CrossRef]

69. Lee, S.W.; Park, J.W.; Park, C.H.; Lim, D.H.; Kim, H.J.; Song, J.Y.; Lee, J.H. Uv-curing and thermal stability of dual curable urethane epoxy adhesives for temporary bonding in 3d multi-chip package process. Int. J. Adhes. Adhes. 2013, 44, 138–143. [CrossRef]

70. Nilsson, J.; Spegel, P.; Nilsson, S. Molecularly imprinted polymer formats for capillary electrochromatography. J. Chromatogr. B 2004, 804, 3–12. [CrossRef] [PubMed]

71. Shen, X.; Zhu, L.; Li, J.; Tang, H. Synthesis of molecular imprinted polymer coated photocatalysts with high selectivity. Chem. Commun. 2007, 1163–1165. [CrossRef] [PubMed]

72. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972, 238, 37. [CrossRef] [PubMed]

73. Wang, J.; Cai, Q.; Li, H.; Cui, Y.; Wang, H. A review on nanotube film photocatalysts prepared by liquid-phase deposition. Int. J. Photoenergy 2012, 2012, 4651–4657. [CrossRef]

74. Zhang, J.; Xiao, X.; Nan, J. Hydrothermal-hydrolysis synthesis and photocatalytic properties of nano-tio2 with an adjustable crystalline structure. J. Hazard. Mater. 2010, 176, 617–622. [CrossRef] [PubMed]

75. Lee, C.K.; Fen, S.K.; Chao, H.P.; Liu, S.S.; Huang, F.C. Effects of pore structure and surface chemical characteristics on the adsorption of organic vapors on titanate nanotubes. Adsorption 2012, 18, 349–357. [CrossRef]

76. Pelaez, M.; Nolan, N.T.; Pillai, S.C.; Seery, M.K.; Falaras, P.; Kontos, A.G.; Dunlop, P.S.M.; Hamilton, J.W.J.; Byrne, J.A.; O’Shea, K. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl. Catal. B 2012, 125, 331–349. [CrossRef]

77. Hoffmann, M.R.; Martin, S.T.; Choi, W.; Bahnemann, D.W. Environmental applications of semiconductor photocatalyst. Chem. Rev. 1995, 95, 69–96. [CrossRef]

78. Bouarioua, A.; Zerdaoui, M. Photocatalytic activities of tio2 layers immobilized on glass substrates by dip-coating technique toward the decolorization of methyl orange as a model organic pollutant. J. Environ. Chem. Eng. 2017, 5, 1565–1574. [CrossRef]

79. Xiang, Q.; Yu, J.; Jaroniec, M. Tunable photocatalytic selectivity of tio2 films consisted of flower-like microspheres with exposed [001] facets. Chem. Commun. 2011, 47, 4532. [CrossRef] [PubMed]
80. Deng, F.; Li, Y.; Luo, X.; Yang, L.; Tu, X. Preparation of conductive polypyrrole/titania 2 nanocomposite via surface molecular imprinting technique and its photocatalytic activity under simulated solar light irradiation. Colloid Surf. A 2012, 395, 183–189. [CrossRef]
81. Ng, H.K.M.; Lee, C.P.; Abdullah, A.Z. Selective removal of dyes by molecular imprinted titania nanoparticles in polysulphone ultrafiltration membrane. J. Environ. Chem. Eng. 2017, 5, 3991–3998.
82. Zhang, C.; Chen, H.; Ma, M.; Yang, Z. Facile synthesis of magnetically recoverable Fe3O4/Al2O3/molecularly imprinted titania nanocomposites and its molecular recognitive photocatalytic degradation of target contaminant. J. Mol. Catal. A Chem. 2015, 402, 10–16. [CrossRef]
83. Wu, Y.; Dong, Y.; Xia, X.; Liu, X.; Li, H. Facile synthesis of N-f codoped and molecularly imprinted titania 2 for enhancing photocatalytic degradation of target contaminants. Appl. Surf. Sci. 2016, 364, 829–836. [CrossRef]
84. Shen, X.; Zhu, L.; Liu, G.; Yu, H.; Tang, H. Enhanced photocatalytic degradation and selective removal of nitrophenols by using surface molecular imprinted titania. Environ. Sci. Technol. 2008, 42, 1687–1692. [CrossRef] [PubMed]
85. Zhang, W.; Li, Y.; Wang, Q.; Wang, C.; Wang, P.; Mao, K. Performance evaluation and application of surface-molecular-imprinted polymer-modified titania nanotubes for the removal of estrogenic chemicals from secondary effluents. Environ. Sci. Pollut. Res. 2013, 20, 1431–1440. [CrossRef] [PubMed]
86. He, M.Q.; Bao, L.L.; Sun, K.Y.; Zhao, D.X.; Li, W.B.; Xia, J.X.; Li, H.M. Synthesis of molecularly imprinted polypyrrole/titania dioxide nanocomposites and its selective photocatalytic degradation of rhodamine B under visible light irradiation. Express Polym. Lett. 2014, 8, 850–861. [CrossRef]
87. Liu, Y.; Zhu, J.; Liu, X.; Li, H. A convenient approach of MIP/CO-titania 2 nanocomposites with highly enhanced photocatalytic activity and selectivity under visible light irradiation. RSC Adv. 2016, 6, 69326–69333. [CrossRef]
88. Wu, Y.; Li, Y.; Tian, A.; Mao, K.; Liu, J. Selective removal of perfluorooctanoic acid using molecularly imprinted polymer-modified titania nanotube arrays. Int. J. Photoenergy 2016. [CrossRef]
89. Li, S.; Fang, L.; Ye, M.M.; Zhang, Y. Enhanced adsorption of norfloxacin on modified titania particles prepared via surface molecular imprinting technique. Desalin. Water Treat. 2016, 57, 408–418.
90. Shen, X.T.; Zhu, L.H.; Huang, C.X.; Tang, H.Q.; Yu, Z.W.; Deng, F. Inorganic molecular imprinted titania dioxide photocatalyst: Synthesis, characterization and its application for efficient and selective degradation of phthalate esters. J. Mater. Chem. 2009, 19, 4843–4851. [CrossRef]
91. De Escobar, C.C.; Moreno Ruiz, Y.P.; Zimnoch dos Santos, J.H.; Ye, L. Molecularly imprinted photocatalysts for degradation of diclofenac in water. Colloid Surf. A 2018, 538, 729–738.
92. Ahmed, M.A.; Abdelbar, N.M.; Mohamed, A.A. Molecularly imprinted chitosan-TiO2 nanocomposite for the selective removal of rose bengal from wastewater. Int. J. Biol. Macromol. 2018, 107, 1046–1053. [CrossRef] [PubMed]
93. Zhou, X.; Lai, C.; Huang, D.; Zeng, G.; Chen, L.; Qin, L.; Xu, P.; Cheng, M.; Huang, C.; Zhang, C.; et al. Preparation of water-compatible molecularly imprinted thiol-functionalized activated titania dioxide: Selective adsorption and efficient photodegradation of 2, 4-dinitrophenol in aqueous solution. J. Hazard. Mater. 2018, 346, 113–123. [CrossRef] [PubMed]
94. Lin, Z.; He, Q.; Wang, L.; Wang, X.; Dong, Q.; Huang, C. Preparation of magnetic multi-functional molecularly imprinted polymer beads for determining environmental estrogens in water samples. J. Hazard. Mater. 2013, 252–253, 57–63. [CrossRef]
95. Liu, C.; Chang, V.W.; Gin, K.Y. Environmental toxicity of PFCS: An enhanced integrated biomarker assessment and structure-activity analysis. Environ. Toxicol. Chem. 2013, 32, 2226–2233. [CrossRef] [PubMed]
96. Jian, J.M.; Guo, Y.; Zeng, L.; Liu, L.-Y.; Lu, X.; Wang, F.; Zeng, E.Y. Global distribution of perfluorochemicals (PFCS) in potential human exposure source—A review. Environ. Int. 2017, 108, 51–62. [CrossRef] [PubMed]
97. Deng, F.; Lu, X.Y.; Pei, X.L.; Luo, X.B.A.; Luo, S.L.; Dionysiou, D.D.; Au, C. Urea- and cetyltrimethyl ammonium bromide-assisted hydrothermal synthesis of mesoporous enzyme-like molecularly imprinted titania nanoparticles with molecular recognitive photocatalytic activity. Sci. Adv. Mater. 2016, 8, 1737–1744. [CrossRef]
98. Sharabi, D.; Paz, Y. Preferential photodegradation of contaminants by molecular imprinting on titania dioxide. Appl. Catal. B 2010, 95, 169–178. [CrossRef]
Bagheri, H.; Pajooheshpour, N.; Afkhami, A.; Khoshsafar, H. Fabrication of a novel electrochemical sensing platform based on a core-shell nano-structured/molecularly imprinted polymer for sensitive and selective determination of ephedrine. *RSC Adv.* 2016, 6, 51135–51145. [CrossRef] [PubMed]

Yang, Q.; Wu, X.; Peng, H.; Fu, L.; Song, X.; Li, J.; Xiong, H.; Chen, L. Simultaneous phase-inversion and imprinting based sensor for highly sensitive and selective determination of bisphenol a. *Talanta* 2018, 176, 595–603. [CrossRef]

Shi, H.; Zhao, G.; Liu, M.; Zhu, Z. A novel photoelectrochemical sensor based on molecularly imprinted polymer modified tio2 nanotube arrays and its highly selective detection of 2,4-dichlorophenoxyacetic acid. *Electrochem. Commun.* 2011, 13, 1404–1407. [CrossRef]

Lu, B.; Liu, M.; Shi, H.; Huang, X.; Zhao, G. A novel photoelectrochemical sensor for bisphenol a with high sensitivity and selectivity based on surface molecularly imprinted polyppyrole modified tio2 nanotubes. *Electroanalysis* 2013, 25, 771–779. [CrossRef]

Wang, P.; Dai, W.; Ge, L.; Yan, M.; Ge, S.; Yu, J. Visible light photoelectrochemical sensor based on au nanoparticles and molecularly imprinted poly(o-phenylenediamine)-modified tio2 nanotubes for specific and sensitive detection chlorpyrifos. *Analyst* 2013, 138, 939–945. [CrossRef] [PubMed]

Sun, X.L.; Gao, C.M.; Zhang, L.N.; Yan, M.; Yu, J.H.; Ge, S.G. Photoelectrochemical sensor based on molecularly imprinted film modified hierarchical branched titanium dioxide nanorods for chlorpyrifos detection. *Sens. Actuators B Chem.* 2017, 251, 1–8. [CrossRef]

Wang, P.; Ge, L.; Li, M.; Li, W.; Li, L.; Wang, Y.; Yu, J. Photoelectrochemical sensor based on molecularly imprinted polymer-coated tio2 nanotubes for lindane specific recognition and detection. *J. Inorg. Organomet. Polym. Mater.* 2013, 23, 703–711. [CrossRef]

Liu, M.C.; Ding, X.; Yang, Q.W.; Wang, Y.; Zhao, G.H.; Yang, N.J. A pm leveled photoelectrochemical sensor for microcystin-lr based on surface molecularly imprinted tio2@cnts nanostructure. *J. Hazard. Mater.* 2017, 331, 309–320. [CrossRef] [PubMed]

Kimmel, D.W.; LeBlanc, G.; Meschievitz, M.E.; Cliffel, D.E. Electrochemical sensors and biosensors. *Anal. Chem.* 2012, 84, 685–707. [CrossRef] [PubMed]

Zhu, C.; Yang, G.; Li, H.; Du, D.; Lin, Y. Electrochemical sensors and biosensors on nanomaterials and nanostructures. *Anal. Chem.* 2015, 87, 230. [CrossRef] [PubMed]

Teng, Y.; Fan, L.; Dai, Y.; Zhong, M.; Lu, X.; Kan, X. Electrochemical sensor for paracetamol recognition and detection based on catalytic and imprinted composite film. *Biosens. Bioelectron.* 2015, 71, 137–142. [CrossRef] [PubMed]

Gomi, M.; Osaki, Y.; Mori, M.; Sakagami, Y. Synergistic bactericidal effects of a sublethal concentration of didecyldimethylammonium chloride (ddac) and low concentrations of nonionic surfactants against staphylococcus aureus. *Biocontrol Sci.* 2012, 17, 175–181. [CrossRef] [PubMed]

Yue, Z.; Lisdat, F.; Parak, W.J.; Hickey, S.G.; Tu, L.; Sabir, N.; Dorfs, D.; Bigall, N.C. Quantum-dot-based photoelectrochemical sensors for chemical and biological detection. *ACS Appl. Mater. Interfaces* 2013, 5, 2800–2814.

Zhang, Z.-X.; Zhao, C.-Z. Progress of photoelectrochemical analysis and sensors. *Chin. J. Anal. Chem.* 2013, 41, 436–444. [CrossRef]

Wang, G.; Xu, J.; Chen, H. Progress in the studies of photodetector sensors. *Sci. China Ser. B Chem.* 2009, 52, 1789–1800. [CrossRef]

Wang, G.L.; Jiao, H.J.; Liu, K.L.; Wu, X.M.; Dong, Y.M.; Li, Z.J.; Zhang, C. A novel strategy for the construction of photoelectrochemical sensors based on quantum dots and electron acceptor: The case of dopamine detection. *Electrochem. Commun.* 2014, 41, 47–50. [CrossRef]
119. Ma, W.; Han, D.; Gan, S.; Zhang, N.; Liu, S.; Wu, T.; Zhang, Q.; Dong, X.; Niu, L. Rapid and specific sensing of gallic acid with a photoelectrochemical platform based on polyaniline-reduced graphene oxide-tio2. *Chem. Commun.* 2013, 49, 7842. [CrossRef] [PubMed]

120. Zhang, Y.-N.; Dai, W.; Wen, Y.; Zhao, G. Efficient enantioselective degradation of the inactive (s)-herbicide dichlorprop on chiral molecular-imprinted tio2. *Appl. Catal. B* 2017, 212, 185–192. [CrossRef]

121. Rezaei, B.; Irannejad, N.; Ensafi, A.A. 3d tio2 self-acting system based on dye-sensitized solar cell and g-c3n4/tio2-mip to enhanced photodegradation performance. *Renew. Energy* 2018, 123, 281–293. [CrossRef]

122. Geng, H.R.; Miao, S.S.; Jin, S.F.; Yang, H. A newly developed molecularly imprinted polymer on the surface of tio2 for selective extraction of triazine herbicides residues in maize, water, and soil. *Anal. Bioanal. Chem.* 2015, 407, 8803–8812. [CrossRef] [PubMed]

123. Khoddami, N.; Shemirani, F. A new magnetic ion-imprinted polymer as a highly selective sorbent for determination of cobalt in biological and environmental samples. *Talanta* 2016, 146, 244–252. [CrossRef] [PubMed]

© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).