



Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Review

A review of titanium dioxide and its highlighted application in molecular imprinting technology in environment

Cui Lai^{a,b,*}, Xiangxiang Zhou^{a,b}, Danlian Huang^{a,b}, Guangming Zeng^{a,b}, Min Cheng^{a,b}, Lei Qin^{a,b}, Huan Yi^{a,b}, Chen Zhang^{a,b}, Piao Xu^{a,b}, Chengyun Zhou^{a,b}, RongZhong Wang^{a,b}, Chao Huang^{a,b}

^a College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China

^b Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha, Hunan 410082, China

ARTICLE INFO

Article history:

Received 18 March 2018

Revised 23 May 2018

Accepted 23 May 2018

Available online xxx

Keywords:

TiO₂

Selectivity

MIT

Development

Toxicity

ABSTRACT

Over the past 40 years, Titanium dioxide (TiO₂) has focused continuously growing worldwide concern due to its novel characteristics such as large specific surface area, powerful oxidation strength, and chemical stability. Nevertheless, its poor selectivity restricted its promising application in specific detection and selective removal of target pollutants in mixing solution, especially the low concentration of highly toxic pollutants. Importantly, concerning on the formation of selective sites with the memory of a template, molecular imprinting technologies (MIT) can selectively remove the template and their structural analogues. With the appealing characteristics of combination of TiO₂ and MIT, the TiO₂-based molecular imprinting polymers (MIPs) can selectively detect and photo-degrades targets, and are widely utilized in chemical sensors, solid-phase extraction and artificial antibodies. Thus, we review the significant progress of MIT and highlighted applications of TiO₂-based MIPs during the past 10 years, especially emphasis on their origins, structure, functions, affecting factors, up-to-date development and main challenges faced in improving their working efficiency. Additionally, the review also covered the ecotoxicological effects of TiO₂-based MIPs nanomaterials (NMs) in environment and human beings.

© 2018 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Semiconductor photo-catalysis technology, as one of promising advanced oxidation technologies, has been widely used in solar fuels, photo-voltaics, and environmental remediation in the last four decades. TiO₂, SnO₂, V₂O₃, WO₃, ZnO, g-C₃N₄ and CdS are known as frequently used photo-catalysts, due to their appeal-

ing properties such as strong oxidization ability, reliability, chemical/biological inertness non-toxicity and low cost [1–7]. However, some semiconductors, including ZnO and CdS, can dissolve and generate toxic byproducts in the photo-catalysis process [8], resulting in a restricted application scope in environmental purification. Compared with other photo-catalysts, in the photo-degradation of organics, TiO₂ is much more promising due to its stability, non-corrosion, and having no toxic by-products [8–11]. Nevertheless, TiO₂ still faces some difficulties, such as nonspecific selectivity, wide band gap, low utilization of visible-light (less than 5% of the solar spectrum), fast recombination of photo-generated electron-hole pairs, etc.

Specially, TiO₂ is limited by its poor selectivity, which is attributed to the formation of highly reactive radical species (i.e., •OH) which are usually nonselective [12–14]. When was proposed for the first time in 1931 [15], molecular imprinting technology (MIT) was recognized as a promising method for generating tailor-made binding sites with a memory of the size, shape, and functional groups of the template molecules, thus can specific recognition and selective removal of template and their structural analogues.

List of abbreviations and acronyms: AA, acrylamide; ABVN, 2, 2'-Azobis-2, 4-dimethylvaleronitrile; AIBN, 2, 2-Azobisisobutyronitrile; APTES, 3-Aminopropyltriethoxysilane; BPA, bisphenol A; DMF, N, N-dimethylformamide; EDC, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride; GO, graphene oxide; GR, grapheme; MAA, methacrylic acid; MAIBN, 4, 40-azobis (4-cyanovaleic acid); MIPs, molecular imprinting polymers; MISPE, solid-phase extraction; MISPME, solid-phase micro-extraction; MIT, molecular imprinting technologies; MO, methyl orange; NB, nitrobenzene; NP, nitrophenol; NMs, nanomaterials; OPDA, o-phenylenediamine; RhB, rhodamine B; SA, salicylic acid; TBAM, tetrabutylammonium methacrylate; TRIM, trimethylolpropane trimethacrylate; TEOS, tetraethyl orthosilicate; TiO₂, Titanium dioxide; Ti (OBU)₄, tetrabutyl orthotitanate; UV-Vis, UV-Vis spectrometer; 2, 4-D, 2, 4-dichlorophenoxyacetic acid; 2, 4-DCP, 2, 4-dichlorophenol; 2- and 4-NP, 2- and 4- nitrophenol.

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China.

E-mail address: laicui@hnu.edu.cn (C. Lai).

<https://doi.org/10.1016/j.jtice.2018.05.035>

1876-1070/© 2018 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Please cite this article as: C. Lai et al., A review of titanium dioxide and its highlighted application in molecular imprinting technology in environment, Journal of the Taiwan Institute of Chemical Engineers (2018), <https://doi.org/10.1016/j.jtice.2018.05.035>

In the early 2000s, scientists have focused on the utilization of surface modification via coating a thin layer of molecular imprinting polymers (MIPs) on TiO_2 to selectively detect and photo-degrade contaminants such as heavy metals, organics, pesticide, antibiotics, and then obtain remarkable achievements. The study of TiO_2 -based MIT is a hotspot so that lots of articles updated every year. Nevertheless, a summary of current development of TiO_2 -based MIT has been few reviewed. Accordingly, we focus on researches published during the past 20 years, especially within the last 10 years, aiming to provide a clearer understanding of their origins, characteristics, affecting factors, and up-to-date development.

Moreover, TiO_2 -based MIPs have faced many challenges in improving their working efficiency, which restricted their advanced application in environment remediation. Herein, we especially concern on the existing problems (e.g., low utilization of visible-light, fast recombination of photo-generated electrons-hole pairs, leakage of template, etc.) and some appealing strategies to those challenges (e.g., physical or chemical modifications, surface modification, different imprinting methods, etc.). Furthermore, majority of TiO_2 -based MIPs in researches are with the size ranging from 1 to 100 nm, and their nanostructures exhibit novel properties that are different from bulk-sized materials. Unfortunately, the extensive use of nano-sized TiO_2 -based MIPs can deteriorate environmental quality. Simultaneously, the substrate TiO_2 of TiO_2 -based MIPs can cause oxidative damage to DNA, apoptosis and inflammation to organisms in environment. Moreover, the great quantity of emission of organics and the risk of leakage of template molecules in the process of imprinting also can result in some negative and irreversible influence on ecosystem and human [16]. Herein, we especially have discussed the potential fates and behaviors of TiO_2 -based MIPs nanomaterials (NMs) discharged into the environment and their toxicity on environment and human health.

2. TiO_2 and improvement of selectivity

Before the “photo-catalyst” terminology is defined, TiO_2 powders are noted as white pigment in the world. Until the photo-activity of TiO_2 under UV light is observed from the flaking of paints, photo-bleaching of dyes and degradation of fabrics incorporating TiO_2 , TiO_2 has attracted limited scientists' attentions as a photo-sensitizer. Subsequently, the firstly proposed possibility of photo-electrolysis of water on a single crystal TiO_2 (rutile) electrode in 1969 [17] and an efficient hydrogen (H_2) production from water-splitting on TiO_2 electrode published in Nature in 1972 [18], marked the start of the remarkable development of utilizing TiO_2 as the most popular wide band gap semiconductor material. Additionally, the test of decomposition of cyanide in the presence of TiO_2 [19] attracted widely concern on the utilization of strong photo-produced oxidation power to decompose pollutants. Subsequently, its appealing characteristics of stability, non-corrosion, and low cost have attracted not only the attention of electrochemists but also the scientists in broad fields, such as H_2 production, photo-catalytic antibacterial activity, self-cleaning (i.e., exterior tiles, glass, aluminum walls, and PVC fabric) and anti-fogging materials (i.e., glass products, mirrors, eyeglasses, etc.). The historical development of TiO_2 is shown in Fig. 1. Additionally, with the shape-dependent” physicochemical properties of TiO_2 , we especially introduce its crystal phase and surface structure.

2.1. Crystal phase and surface structure of TiO_2

Besides three commonly known polymorphs of TiO_2 (anatase, rutile and brookite) occurred in nature, there are still at least 11 reported bulk and/or nano-crystalline TiO_2 phases and at least 3 reported non-crystalline phases [20], shown in Fig. 2. All crystal

phases of TiO_2 can be regard as constructed by different numbers of edges, corners, and/or faces-sharing Ti-O polyhedra. Anatase exhibits edges-sharing configurations, while rutile and brookite consists of edges and corners-sharing TiO_6 octahedra. Simultaneously, the numbers of edges-sharing for rutile, brookite and anatase are 2, 3, and 4 out of the 12 edges per octahedron, respectively.

In bulk form, rutile is the only stable phase, whereas the metastable phase (anatase and brookite) can transform irreversibly to rutile upon heating. In phase transformation, anatase is transformed faster to rutile than brookite, attributing to their smaller crystallite size and aggregate state. While in anatase–brookite mixture, anatase is firstly transformed into brookite, and then both of them can be transformed into rutile [21,22], due to required activation energy in phase transformation of anatase to brookite is small (11.9 kJ mol^{-1}). Differently, during the phase transformation of brookite to rutile, anatase is observed as transitory phase with surface stabilization phenomena. The main reason is probably that anatase, brookite differs in the stacking arrangement of similar structural layers. The phase stability is “size-dependent”. Their bulk phase stability is rutile > brookite > anatase, whereas phase stability can be changed at the nanoscale structures [22]. A review of anatase to rutile phase transformation has been reported by Hanaor in 2011, he concluded the thermodynamics and affecting factors of the phase transformation, especially comprehensively analyst of the effect of dopants and the work mechanisms [23].

For surface structure, generally, anatase TiO_2 is constructed by two facets on the top and bottom and eight (101) facets on sides. The (101) facets of anatase TiO_2 are considered to be less reactive and more thermodynamically stable than (001) facets, and it accounts for almost 90% of the total exposed surface of the anatase TiO_2 occurred in nature [24]. Nowadays, to optimize the performance of TiO_2 , controlling TiO_2 crystal facets has spurred a tremendous amount of researches, due to their fascinating “shape-dependent” physicochemical properties. Lu et al. [25] make an important breakthrough to synthesis of one high percentage of exposed (001) facets anatase TiO_2 single crystals by using F^- as stabilizing agent. Afterward, in 2014, Yu et al. [26] for the first time investigated the photo-catalytic CO_2 -reduction performance of anatase with different ratios of exposed (101) and (001) facets. The formed “surface heterojunction” on coexposed (101) and (001) facets is beneficial for the transfer of photo-generated electrons and holes.

In rutile TiO_2 , (110) facets are the most thermodynamically stable surface and are also relatively easy to prepare, thus, (110) facets have been extensively studied in the past. Nevertheless, the rarely reported (011) facets, exhibiting a higher photo-reactivity than other surfaces, have attracted considerable attention for catalytic reaction recently. After continuously proposing new ideas and experimental verification, the long-term researches of structure models of rutile TiO_2 suffer from bulk terminated “ TiO_2 (011)-(1 × 1) model”, zigzag “titanyl (Ti=O) double bond model” [27], “micro-faceting missing-row structural models” [28] and then to “brookite (001)-like model” [29]. Interestingly, the recent researches are mainly focused on the strong different adsorption and reaction of acetic acid [30], H_2 [31] on rutile (011)-(2 × 1) versus (110) surfaces, or the interaction of formic acid, formaldehyde and formamide on rutile (011)-(2 × 1) versus terminated (1 × 1) surfaces [32].

Compared to the comprehensively studied anatase and rutile, brookite is the least investigated due to the challenges in acquiring its pure form, selective control of exposed crystal faces especially the high energy facets, and the controversial cognition of photo-catalytic reactivity of brookite TiO_2 . Since the controversial researches of the degradation efficiency of dyes exhibited on brookite by Li and Gray [33] and Li et al. [34] in 2007, more detailed study about brookite TiO_2 is necessary in the catalytic

Download English Version:

<https://daneshyari.com/en/article/10226220>

Download Persian Version:

<https://daneshyari.com/article/10226220>

[Daneshyari.com](https://daneshyari.com)