Preparation and integration of nanostructured titanium dioxide
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Titanium dioxide (TiO₂) is a chemically stable nontoxic transition-metal oxide associated with a wide range of existing chemical engineering processes. In this short review, recent research endeavors in preparation and integration of nanostructured TiO₂ materials system will be featured and discussed for their potential new applications. Because material development always plays pivotal roles in the progress of a particular engineering discipline, the reviewed subjects will provide useful information to stimulate nanoscale research of chemical engineering, linking established fundamentals with practical applications. Some critical issues and challenges regarding further development of this important functional material for nanotechnology will also be addressed.

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Introduction
Titanium dioxide (TiO₂) is a chemically stable nontoxic semiconducting material [1–5,6]. Over the past two decades, it has been considered probably to be the most studied transition metal oxide owing to its many extraordinary physical, chemical, electronic, electrochemical and photoactive properties, and unexceptionally, TiO₂ has also attracted vast interest in chemical engineering related research such as solar energy conversion via dye-sensitized and quantum-dot-sensitized solid-state solar cells, water splitting and general photocatalysis, lithium ion batteries and supercapacitors, chemical/gas sensing, controlled release, environmental remediation including indoor air purification, wastewater treatment, antifogging, self-cleaning, deodoration and deactivation of bacteria [1–5,6]. While there have been a great number of reports on the above research, nevertheless, the central key to fulfill the general requirement of a particular application is always placed on how to prepare an active phase of TiO₂ and how to integrate it into a desired materials system in order to extract its synergistic effects if any.

On the basis of recent advancements of TiO₂ research, the objective of this short review is to identify critical issues to gain good controllability over the crystal polymorph, surface termination, size and shape and overall morphology of TiO₂ products for the above technological applications. More importantly, fabrication of TiO₂ based materials system via integrative routes will also be reviewed. The identified topics as well as newly available processes and strategies may open up new frontiers for advanced chemical engineering research using this important functional material.

Methods of preparation
With the progress of colloidal science and synthetic chemistry, nanomaterials nowadays can be prepared with a greater degree of sophistication. A paradigm shift in general preparation has been made from polydisperse powders to monodisperse nanoparticles over the past two decades. In addition, size, shape, facets, polymorph, and composition of nanomaterials can now be controlled fairly routinely after certain study of the chemical processes involved. In line with this advancement, TiO₂ based nanomaterials can also be prepared more controllably with required specifications. In the following, salient features of representative studies in this area will be highlighted.

Aqueous solution routes for synthesis
The cost of solution-based synthesis is generally lower. For this reason, sol–gel methods with titanium containing inorganic salts and titanium alkoxides have been widely used for preparation of TiO₂ particle powder and thin films. Due to amorphous nature of xerogels, a separate heat-treatment step is required [7]. Under hydrothermal conditions, however, these titanium precursors can be directly transformed into crystalline products and the separate post-growth heat-treatment will then be omitted [8]. Using titanium halides (e.g. TiCl₄ and TiF₄) to react with water, formation temperature of TiO₂ can be significantly reduced to below 100°C, and in most cases, the final products are in metastable anatase TiO₂ phase which is often a more desirable polymorph for photocatalysis. For example, TiF₄ has been commonly used as a starting chemical due to its slow reaction rate with water (note that Ti–F bond is strong), where Ti(OH)Fₓ is considered as a hydrolysis intermediate in the TiO₂ formation process. Various TiO₂ products such as nanostructured films, submicron spheres and mesocrystals have been prepared.
Control of crystal plane termination
Among the different low Miller index surfaces of anatase, the \{001\} and \{100\} crystal planes have high surface energies due to high degree of unsaturated atomic bonding while the most thermodynamically stable planes are \{101\}. Over the past years, stabilizing the \{001\} planes has attracted great research attention; a continuous effort on planarization of the \{001\} surfaces has been evident [13,14,15,16,17,18], as depicted in Figure 1d. It is found that surface adspecies and growth environments have significant impacts on the crystal facet formation. For instance, fluorine ions have shown a greater ability to bond on the \{001\} surfaces than on the \{101\} [14,15]. Nevertheless, with the presence of surface adspecies, the nominal \{001\} surfaces of anatase may virtually become passivated and lose reactivity. It should be mentioned that for practical usages, the \{001\}-faceted anatase TiO2 crystals must have sufficient active surface sites and a large specific surface area. These two general criteria have been fulfilled progressively with some newer approaches [16,17,18]. Crystalline nanosheets of anatase TiO2 with nearly 100% of the \{001\} surfaces have been recently achieved [18]; these anatase TiO2 plates/sheets rich in the \{001\} planes have shown excellent photocatalytic and electrochemical activities, respectively [17,18].

Phase selection and manipulation
Although it is generally conceived that the photocatalytic efficiency of anatase TiO2 is higher [6], it has been recognized these days that simultaneous presence of other polymorphic phases may also be beneficial; commercial product P25 is in fact a mixture of both anatase and rutile. In this regard, rutile phase can be facilely added onto anatase phase through introduction of a small amount of surface or bulk dopants of metal ions [19]. In a recent investigation of anatase to rutile transformation, it is found that anatase nanoparticles are quite stable on the surface of rutile at elevated temperatures [20], as described in Figure 1e. The photocatalytic activity of TiO2 nanoparticles is directly related to the surface-phase structure. The phase junction between the surface anatase nanoparticles and rutile can enhance the photocatalytic activity for H2 production [20]. Illustrated in Figure 1f, quite similarly, it is also found that the \{001\} crystal planes of anatase and the \{100\} planes of TiO2 (B) (another polymorph of TiO2 with the monoclinic crystal system) can form a close stable phase interface and such a biphasic structure also exhibits strong enhancement in photocatalytic activity [21]. Apart from the elucidation of biphasic existence, rod-shaped TiO2 nanocrystals in brookite polymorph have been recently synthesized through a surfactant-assisted nonhydrolytic route [22], in which initially generated anatase seeds trigger heterogeneous nucleation of brookite and develop these anisotropic (brookite) nanocrystals with tunable aspect ratios in the subsequent growth described in Figure 1g.

Optical band gap engineering
As a stable and nontoxic metal oxide semiconductor, TiO2 has a large optical band-gap in the range of 3.0–3.2 eV; only less than 5% of the solar flux incident at the earth surface is able to excite this metal oxide. In order to extend its absorption ability to the visible spectral regime, the optical band gap energy of TiO2 has to be modified. Fortunately, nonmetal element doping has been widely used to red-shift the absorption spectrum of TiO2. For example, nitrogen, carbon, and sulfur have been investigated extensively over the past decade [23]. Compared to N, C, and S elements, boron (B) has been less studied, and the results are controversial. This subject has been recently investigated in greater detail [23]. It has been found that when the B doping is controlled at an optimal level (1.13 atom % B (nominal)), significant absorption of visible light and substantial photocatalytic activity can be attained, comparable to that of the well known N-doped TiO2 [23]. The preparation of B-doped TiO2 is a low cost process and it promises a large-scale preparation of this visible light absorbing material, though there are still many unknowns in the present stage of research for this less studied nonmetal dopant.

Methods of integration
Free-standing nanoparticles and nanostructures have limited applicability, due to their potential cytotoxicity and difficulty in separation and recovery after use. Furthermore, a practical functional materials system demands additional structural and compositional controls. To prepare larger and more complex TiO2 based systems, architectural aspects of design and integration need to be considered, because the ways of structural and compositional organizations in the final products will determine their ultimate performance. In this regard, a number of new integration strategies will be addressed in the following.

Mesocrystals, porous spheres, and hollow spheres
In addition to the preparation of free standing monodisperse TiO2 nanocrystals, it is highly desirable to prepare this class of materials into organized architectures and assemblages, such as ensembles of mesocrystals [12,24], mesoporous solids [18,25,26], stuffed intestines [27] or hollow spheres [28]. Such larger organized structures of nanomaterials will ease separation hassles after the use of nanostructured TiO2 in real applications. To prepare TiO2 into hollow spheres (or bubbles), hard-template methods, sol–gel process and micro-emulsion techniques are often used. Besides these common templating processes, TiO2 hollow spheres can also be prepared through matter relocation. In particular, light weight hollow
Nanostructured thin films and arrays

In order to increase the specific surface area and make fuller utilization of material, TiO₂ has been often prepared into thin films with a support. Sol–gel processes such as dip-coating or spin-coating had been well studied in the past. New challenges in this field are concerned with how to engineer TiO₂ nanostructures on thin film surfaces [31]. With photodeposition and electroless deposition of metals, nanostructured thin film photocatalysts of TiO₂, TiO₂:In₂O₃, TiO₂/Ag and TiO₂/Ag/Ni have been prepared on ceramic substrates [32]. Concerning their application in dye-sensitized solar cells (DSSC), assembly of single crystalline TiO₂ nanorods with vertical orientation to the substrate is highly desirable because of large surface area and less grain boundaries in single-crystal nanorods. Recently, oriented rutile TiO₂ nanorod arrays have been prepared on fluorine-doped tin dioxide substrate using a hydrothermal process [33*]. In particular, the diameter, length and density of the nanorods can

spheres of anatase TiO₂ can be obtained from spherical aggregates of crystallites after a prolonged aging in their preparative solutions [28*]. The underlying mechanism for this hollow process has been attributed to Ostwald ripening, during which large crystallites were grown at the expense of smaller ones; see Figure 2a–b. The interior space and shell textures of resultant hollow spheres can be tuned with a wide range of controlling parameters. The approach also shows high versatility for structural engineering of various targeted morphological products, including inner material refills [28*]. A great variety of metal oxides and inorganic compounds have been recently prepared into hollow spheres via this ripening process, including doped TiO₂ solids and noncrystalline silica [19]. These types of Ostwald-ripened derived TiO₂ hollow spheres have been designed as nanoreactors for photocatalysis [29*] and concurrent membrane water purification [30*], respectively, as presented in Figure 2c–d.

Illustrations of representative preparation methods and products: (a) mesocrystals assembled from small TiO₂ crystallites that share the same crystallographic orientations and provide intra-crystal porosity; (b) porous TiO₂ spheres; (c) hollow TiO₂ spheres; (d) normal crystal morphology of anatase TiO₂ (bi-pyramid faceted with the {1 0 1} surfaces) and planarization of the {0 0 1} planes; (e) small anatase TiO₂ particles stabilized on rutile TiO₂ support upon thermal transformation; (f) an interface between the {0 0 1} plane of anatase and the {1 0 0} plane of TiO₂ (B); and (g) a fast anatase (the purple particle attached) to brookite conversion through highly correlated atomic displacement pathways.
Illustrations of representative integration methods and products: (a) Ostwald ripening and creation of an interior space for a spherical aggregate of crystallites; (b) formation of yolk/shell structure via Ostwald ripening; (c) the Au@TiO₂ nanoreactor prepared through route (b); (d) porous TiO₂ spheres supported by cellulose acetate membrane for water purification; (e) a two-step anodization process: firstly, starting titanium metal foil; secondly, TiO₂ channels formed after the first anodization; thirdly, surface modification which makes a hydrophobic segment (purple lines) for the TiO₂ channels; and fourthly, the second anodization which creates a hydrophilic segment for the lower part of the channels; (f) anatase TiO₂ crystals grown on the two (0 0 1) ends of α-MoO₃ nanorod; (g) anatase TiO₂ crystal grown on the (0 0 0 1) end of ZnO nanorod; (h) amorphous TiO₂ shell deposited on the entire surface of ZnO nanorod; (i) ligand-assisted ‘impregnation’ of Au on TiO₂ hollow sphere; and (j) self-assembled complex nanocatalysts: firstly, TiO₂ nanoparticles adsorbed on carbon nanotube; secondly, a second type of nanoparticles adsorbed on the nanotube; thirdly, Au nanoparticles deposited on the TiO₂ nanoparticles with UV light excitation; fourthly, coating of TiO₂ on the surface of carbon nanotube via sol–gel method; and fifthly, ligand-assisted deposition of Au nanoparticles on the TiO₂ coated carbon nanotube.
be controlled through tuning growth parameters. Such nanorod thin films have demonstrated promising photochemical performance in DSSC application [33*]. Furthermore, using metallic titanium as a precursor, highly ordered self-organized anatase TiO₂ nanotube arrays have been prepared by electrochemical anodization technique. Apparently, the nanostructured tubular arrays yield higher photocatalytic activity (used for chemical oxygen demand determination in a thin-cell photovoltaic reactor) than conventional TiO₂ thin films [34]. Shown in Figure 2e, an amphiphilic TiO₂ nanotubular structure has also been synthesized through a two-step anodization process [35**], through which a hydrophobic segment can be made as a cap to prevent uncontrolled leaching of the hydrophilic drug into aqueous phase. On the other hand, this hydrophobic cap (or valve) can be photocatalytically removed (or opened) under UV light and a highly controlled drug release has been demonstrated [35**]. In addition to the UV light, scission of organics on TiO₂ surfaces can also be achieved by applied voltages. For instance, octadecylphosphonic-acid-grafted anatase TiO₂ nanotubular arrays show varying wettability upon different biased potentials, which is ascribed to chain scission reactions induced by a valence-band ionization mechanism when an external voltage is applied [36]. It should also be noted that anodic aluminum oxide membranes (AAO) have long been used for the preparation of various metals and metal-oxide nanotube arrays. This hard template can also help to grow three-dimensional networks of anatase TiO₂ nanorods inside the AAO channels with a pulsed chemical vapor deposition (CVD) process [37].

**Heterostructures and nanocomposites**

To prepare TiO₂-containing hetero-structures and nanocomposites, hydrothermal or solvothermal methods can also be used, in addition to more commonly employed processes such as CVD. In particular, the growths of these composite materials can be conducted using a simple ‘one-pot’ approach. In addition to the formation of crystal arrays [10,11], in Figure 2f, horseshoe-like TiO₂ nanocrystals have been grown on the two ends of (0 0 1)-propagated single-crystalline α-MoO₃ nanorods under hydrothermal conditions at 170°C [38]. However, the growth situation for the polar crystal materials is quite different. It is found that similar TiO₂ nanocrystals were grown selectively on the (0 0 0 1) end of ZnO nanorods under solvothermal conditions at 180°C [39], as depicted in Figure 2g. This is because wurtzite-type ZnO has a polar crystalline structure that consists of Zn-terminated (0 0 0 1) and O-terminated (0 0 0 −1) ends along the c-axis. Obviously, the polarity of the ZnO (0 0 0 1) surface plays an important role in the formation of ZnO/TiO₂ heterostructures. Besides the ‘one-pot’ synthesis, heterostructures and nanocomposites can also be fabricated in a step-by-step manner (i.e. ‘multi-pot’ synthesis). For instance, under hydrothermal conditions, ZnO nanorod arrays can be added onto the external surfaces of one-dimensional anatase TiO₂ crystals, giving rise to generation of hairy ZnO–TiO₂ nanocomposites [40]. Atomic layer deposition (ALD) technique can precisely manipulate the thickness of surface coating. Recently this technique was employed to deposit TiO₂ on ZnO or CuO nanorod or nanowire templates, producing ZnO@TiO₂ or CuO@TiO₂ core/shell composites [41]; see Figure 2h. Interestingly, the central cores of ZnO or CuO can be removed through a photocatalytic process under UV-irradiation. In both cases, protons which were generated from the reaction between water and photoexcited holes (i.e., water splitting reaction) are believed to be the cause for the elimination of core-templates [41].

**Self-assembled nanohybrids and nanocatalysts**

Self-assembly is a powerful approach to integrate the TiO₂ phase with others. Very recently, aggregative nanoparticles of anatase TiO₂ have served as templates for polymerization of aniline, which results in organic–inorganic nanohybrids of poly(aniline)-wrapped TiO₂ [42]. By tuning synthetic parameters, linear or spherical assemblages and three-dimensional networks of these nanohybrids can be obtained [42]. It should be pointed out that van der Waals force generated from the organic surfactants anchored on the TiO₂ nanoparticles is responsible for this self-assembly. Different roles of self-assembled TiO₂ nanoparticles have been further explored for the synthesis of poly(aniline)-wrapped TiO₂ hollow spheres and other nanocatalysts [43*]. For the integration of metal/TiO₂ catalysts, on the other hand, redox reactions between metal cations and oxidizable titanium containing compounds can be utilized. For example, in making M/TiO₂ (M = Pt, Au, Ru, and PtRu) nanocatalysts, noble metal gold nanoparticles were deposited on TiO₂ phase through redox reactions between Ti³⁺ (from TiCl₄) and related noble metal salts [44*]. Furthermore, in Figure 2i, better size and loading control of active metal nanoparticles have been achieved by the ‘impregnation’ of pre-synthesized monodisperse Au nanoparticles onto TiO₂ supports, in which bi-dentate organic ligands provide additional bonding to bring the metal nanoparticles and TiO₂ substrate together in the self-assembled nanocatalysts [45*]. In view of their good electrical conductivity and adsorption capacity, carbon nanotubes (CNTs) can be physically mixed with TiO₂ nanoparticles to enhance photocatalytic degradation of organic pollutants [46]. A general self-assembly method has been developed to introduce TiO₂ (and other metal oxides) nanoparticles onto CNTs and form binary catalytic composites of TiO₂/CNTs [47], as explained in Figure 2. The combination of two assembling phases can be described as a partial replacement of carboxylic ends of surface-capping on TiO₂ nanoparticles with the carboxylate groups of CNTs [47]. Meanwhile, the long alkane chain of surfactant
molecules can also noncovalently associate with the surface of CNTs and therefore bring the two assembling phases together [48]. Under UV irradiation, moreover, Au(III) precursor can be photocatalytically reduced (by photogenerated electrons) to Au nanoparticles, giving rise to tertiary Au/TiO2/CNTs [47]. Similarly, presynthesized Au nanoparticles can also be loaded directly onto the TiO2/CNTs via adsorptive self-assembly [49] (also refer to Figure 2).

Concluding remarks: bridging the materials development and chemical engineering applications

We have witnessed a significant advancement in titanium dioxide materials research over the past two decades, especially over the past 10 years. This progress may provide a new platform for next level of chemical engineering applications of these materials. Before this can be actually achieved, nevertheless, a number of critical issues must be considered: firstly, better controllability of synthesis, preferably via solution routes, must be attained; secondly, newer and greener chemical synthetic routes should be devised, ideally through water medium at low reaction temperatures, as many existing processes use toxic organic solvents and surfactants; and thirdly, scale up methodologies and processes for large-scale production must be further developed. While it will take more time to tackle all these challenges, perhaps it is time for researchers of chemical engineering to adopt a multidisciplinary approach and work more closely with chemists and materials scientists for their engineering problems. With the present stage of accomplishments, definitely, nanoscale chemical engineering fundamentals can be investigated in greater depths by employing these tailor-made TiO2 materials.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:
• of special interest
•• of outstanding interest


This paper examines fundamental aspects of adsorption of water molecules on the (1 0 0) crystal planes of anatase TiO2. The references therein also give a general introduction of TiO2 as well as the present status of research on this material.


This work theoretically demonstrates the importance of surface chemistry that dictates the stability of TiO2 crystal planes and phases and therefore the resultant crystal structure and morphology.


This paper reports a very interesting stabilization of the 0 0 1 facets of anatase TiO2 single crystals with assistance of fluorine adsorption; the observation was successfully verified by theoretical calculations.


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28. Li J, Zeng HC: Size tuning, functionalization, and reactivation of Au in TiO₂ nanoreactors. Angew Chem Int Ed 2005, 44:4342-4345. From the function of membrane, the TiO₂ shells of nanoreactors also work as both a catalyst and a light energy harvester for the energy required in photocatalytic reactions.

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32. Liu B, Aydil ES: Growth of oriented single-crystalline rutile TiO₂ nanorods on transparent conducting substrates for dye-sensitized solar cells. J Am Chem Soc 2009, 131:3885-3890. This paper established a hydrothermal route for the synthesis of large area arrays of oriented rutile TiO₂ nanorods on conducting oxide substrates. The applications of the nanorod arrays can definitely go beyond the field of DSSC. It is desirable to gain additional polymeric control over other TiO₂ phases with further development of this method.


34. Song YY, Schmidt-Stehn F, Bauer S, Schmuki P: Amphiphilic TiO₂ nanotube arrays: an actively controllable drug delivery system. J Am Chem Soc 2009, 131:4230-4232. The excellent flexibility of anodization method for fabricating TiO₂ related complex nanotube arrays was illustrated in this work. Along the same line, it is anticipated that additional anodization processes can also be carried out to prepare even more complicated delivery devices or systems in other types of applications.