Review Article

Cheng Chang, Saeed Rad*, Lei Gan*, Zitao Li, Junfeng Dai, and Asfandyar Shahab

Review of the sol–gel method in preparing nano TiO_2 for advanced oxidation process

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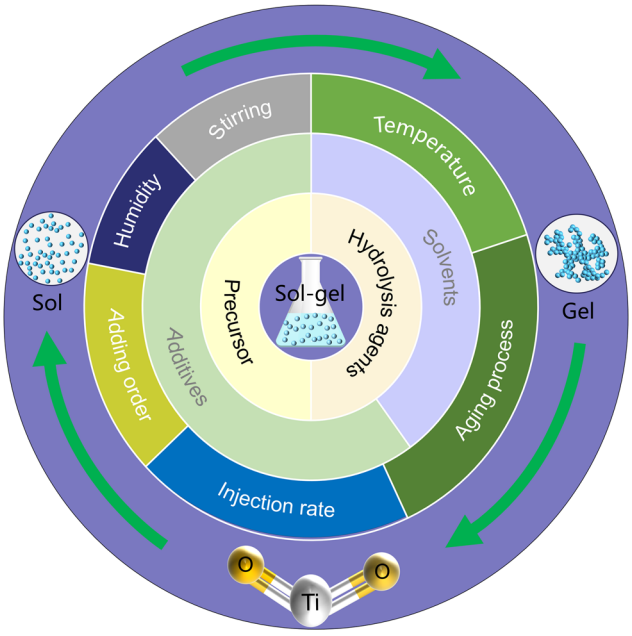
Abstract: Application of nano titanium dioxide (TiO_2) in various fields such as advanced oxidation process (AOP) has led to the development of its preparation technologies. The sol–gel process is a widely used chemical wet method for preparing nanoscale TiO_2 gels. This technique offers numerous advantages, such as the potential to produce large quantities of homogeneous materials with high purity, surface area, porosity, and reactivity, as well as being cost-effective, simple to implement, and capable of controlling the size and shape of the resulting particles. This review provides a comprehensive overview of the chemicals, reaction conditions, and procedures required for preparing nano TiO_2 using the sol–gel method. It covers the selection of necessary compounds, such as TiO_2 precursors, solvents, hydrolysis agents, and additives, along with their composition and sequences of adding, reaction order, and impact on the final product. Additionally, it provides detailed information on the routes of gel formation and ambient conditions, including temperature, humidity, stirring speed, injection rates of compounds, aging process, and storage conditions. This information serves as a basic reference for understanding the sol–gel process and the relative contribution rates of the influencing factors, which is essential for controlling the size, morphology, crystallinity, and other physicochemical properties of the resulting TiO_2 gel/powder for targeted applications.



Graphical abstract

Keywords: nano titanium dioxide, sol–gel method, TiO_2 preparation

*** Corresponding author: Saeed Rad,** College of Environmental Science and Engineering, Guilin University of Technology, Guilin 541004, Guangxi, China, e-mail: saeedrad1979@gmail.com, tel: +86-13517735068
*** Corresponding author: Lei Gan,** Guangxi Collaborative Innovation Center for Water Pollution Control and Water Safety in Karst Plot, Guilin University of Technology, Guilin 541004, China; Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guilin University of Technology, Guilin 541004, China,
e-mail: allen_gl2006@163.com, tel: +86-13557238256
Cheng Chang, Zitao Li, Asfandyar Shahab: College of Environmental Science and Engineering, Guilin University of Technology, Guilin 541004, Guangxi, China
Junfeng Dai: Guangxi Collaborative Innovation Center for Water Pollution Control and Water Safety in Karst Plot, Guilin University of Technology, Guilin 541004, China; Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guilin University of Technology, Guilin 541004, China

Abbreviations

AcAc	acetylacetone
DEA	diethanolamine
EDTA	ethylenediaminetetraacetic acid
HAD	hexadecylamine
HPC	hydroxypropyl cellulose
PEG	polyethylene glycol
PVA	polyvinyl alcohol
PVP	polyvinylpyrrolidone
$TiCl_3$	titanium trichloride
$TiCl_4$	titanium tetrachloride
TTB	titanium tetrabutoxide

TNBT titanium(IV) *n*-butoxide
TTE titanium tetraethoxide
TTIP titanium isopropoxide

1 Introduction

Nano titanium dioxide (TiO_2) has been extensively applied in various sectors such as in film coating industry [1,2], construction materials [3,4], electronic components [5,6], photocatalytic fuel generations [7], and degradation of pollutants [8,9], just to mention a few. Advanced oxidation process (AOP), on the other hand, is formulated to use various chemical compounds for the removal of organic/inorganic contaminants through the oxidation process [10,11]. Employing semiconductors for AOPs, especially TiO_2, has been among the most dynamic research areas [12,13]. This is due to its remarkable properties, including high photo-responsiveness, eco-friendliness, chemical stability, strong oxidizing property, and low cost [14–16]. It has emerged as a highly promising candidate for photocatalytic degradation of water and air pollutants [8,9,17,18], and a significant potential in environmental remediation [19,20]. Based on ISI's annual data analysis of papers related to AOP and TiO_2 (Figure 1), it is evident that research interest in AOP and nano-TiO_2 has experienced a notable surge since 2001. Furthermore, the research prominence of TiO_2 and AOP aligns closely with the overall upward trajectory in research interest. This compelling correlation underscores the intricate relationship between TiO_2 and the field of AOP research. Consequently, the development of nano TiO_2 preparation methods and material characterization technologies has received considerable attention, as it greatly contributes to the advancement of these applications. TiO_2-based products with different properties and applicability in specific fields have been the focus of many scholars' research efforts.

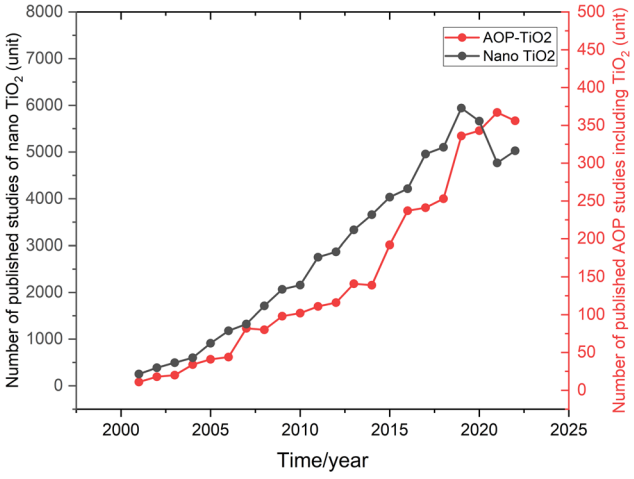


Figure 1: Number of publications per year on the topic of TiO_2 and AOP based on ISI web of science.

Numerous studies have reviewed various preparation technologies, synthesis principles, characterization techniques, modification methods, and applications of diverse types of TiO_2 in a large number of papers. Scholars have described the preparation methods and properties of TiO_2 nanoparticles with distinctive dimensions including zero-dimensional near spherical TiO_2 nanoparticles in organic chemistry, preparation methods of one-dimensional nanowires, nanorods, and nanobelts [21,22], two-dimensional and porous nanosheets as barrier films, building blocks, *etc.* [23], and three-dimensional nanocomposite for fast lithium storage [24]. Previous studies [25–27] have discussed the growth mechanism of nano-TiO_2 from the perspective of synthesis principles and the factors influencing the resulting material. In some work [28,29], the physicochemical properties of TiO_2 are comprehensively summarized across multiple dimensions, encompassing mechanical, optical, and catalytic aspects. This synthesis of information is aimed at fostering a profound understanding of TiO_2 properties, thereby enabling the optimization of their efficacy in chemical applications and facilitating the rational design of practical solid materials. Certain studies [30–33], driven by the ultimate objective of enhancing its overall properties and broadening its application scope, have undertaken extensive reviews on the doping of TiO_2 and other elements, with the explicit purpose of elucidating the resultant alterations in its properties. In addition, the applications of TiO_2 [6,29,33–35] in many fields such as building, information, and environmental science, have been widely reviewed.

Various synthesis techniques have been employed for the preparation of TiO_2 in different forms, such as powder, thin film, and doped complexes. These methods encompass a wide array of approaches, including hydrothermal synthesis to produce TiO_2 (B) nanowires with an exceptionally high surface area [36], the utilization of a low-temperature solvothermal process for the creation of fluorine–sulfur co-doped TiO_2 materials, particularly useful in photocatalytic dye degradation [37], the development of anatase TiO_2 supported on porous substrates through chemical vapor deposition [38], sol–gel synthesis for the fabrication of mixed TiO_2 composite photocatalysts tailored for environmental applications [39,40], the creation of nanostructured TiO_2-based nanotubes *via* template-assisted synthesis for environmental purposes [41], and the production of TiO_2- and ZnO-based photocatalysts using flame spray pyrolysis for water treatment [42]. Furthermore, innovative methods such as solvothermal microwave synthesis have been explored to generate doped-TiO_2 nanoparticles for the sustainable production of green hydrogen fuel, aimed at mitigating carbon

dioxide (CO_2) emissions [43]. These represent just a subset of the diverse procedures employed in TiO_2 synthesis and modification. Owing to its simple synthesis, homogeneity, low cost, and ease of control, the sol–gel method is extensively used [35,39,44,45]. Earlier studies have synthesized TiO_2 *via* modified sol–gel technique optimized by Plackett–Burman system design [2], Zn^{2+} doped TiO_2 catalyst with aqueous sol–gel process [46], nanocomposites of TiO_2-P25 (Degussa) using a peroxotitanic acid modified sol–gel [47], centrifugation and storage precipitation [48], and low-temperature sol–gel [49]. While researchers have conducted analyses on the synthesis methods of nano TiO_2 using the sol–gel approach and its subsequent applications in photocatalysis [50], equal attention has been devoted to the process of creating various forms of TiO_2 and its composites for environmental engineering purposes *via* the sol–gel method [40]. Additionally, the sol–gel processes applied in the production of TiO_2 thin films through dip coating have been explored with a particular emphasis on discerning the interplay between their microstructure and the optical properties of nano-crystalline materials [51]. Overall, the sol–gel method has the potential for large-scale synthesis of TiO_2 for AOP, especially in fields such as water treatment and environmental remediation.

However, even within a single method like sol–gel, the final TiO_2 product features can vary significantly depending on the experimental conditions and techniques applied. Therefore, generalizing the principles for preparing nanomaterials through this method is not feasible. Instead, it requires precise experimental protocols tailored to specific material requirements to achieve desired functions and properties. Especially, the morphology of TiO_2-based materials prepared by the sol–gel method is inseparable from the properties of the sols. Thus, the key to preparing the most suitable TiO_2 sol–gels lies in the experimental design. Nevertheless, relatively few scholars have focused on the sol–gel formulation mechanisms in detail. It is important to note that the choice of chemicals and preparation routes required for sol–gel, can greatly affect the properties of the targeted TiO_2 nanoparticles, which makes it difficult in the absence of a solid reference. Therefore, in this work, we have reviewed the TiO_2 sol–gel preparation mechanisms in-depth to show how the selection of TiO_2 precursors, solvents, hydrolysis agents, and additives during the process affects the gel properties. Moreover, how other influencing factors such as reaction temperature, humidity, stirring speed, aging time, and the sequences of adding and injection rate of chemicals, can determine the crystal types and morphology of the prepared TiO_2. Based on a total of 218 literature, this work offers a useful experimental guideline about the sol–gel process, which can also be a practical reference for researchers to prepare high-quality targeted nano TiO_2 materials *via* this method.

1.1 TiO_2 preparation *via* sol–gel in brief

Sol preparation is the first step of the sol–gel process to obtain any phase (such as anatase or rutile as presented in Figure 2) or type (such as dense film, powder form, *etc*.) of nano TiO_2 materials. To formulate the nano TiO_2 solution or the "sol," usually, TiO_2 precursor (titanium alkoxides such as titanium isopropoxide; TTIP, titanium(IV) *n*-butoxide; TNBT, *etc*.) is added into an alcohol-based solvent (such as ethanol or methanol) under continuous stirring, to be thoroughly mixed. Then, an appropriate amount of acid-mixed H_2O or H_2O-containing solution (*e.g*., HCl solution or acetic acid solution) will be added to the mixture, dropwise. After a certain time of hydrolysis-condensation reactions, TiO_2 sol is obtained. Finally, the sol will undergo an aging process to form the gel which can be later used for film coating or will be further dried to xerogel to obtain fiber, dense ceramic, or powder form of nano TiO_2. In this process, the addition of a pH-adjusted aqueous solution catalyzes the hydrolysis reaction. The hydrolysis-condensation rate in the solvating system can be regulated *via* different types and concentrations of these solutions. Considering the designed application of TiO_2 materials, various additives such as complexing agents (for adapting the hydrolysis process) and metal salts (to modify the TiO_2 sol) can be utilized to improve the properties of TiO_2 nanoparticles.

The general synthesis routes for the sol formation are schematically presented in Figure 3 [52]. As can be seen, titanium alkoxide, such as TTIP ($Ti(OR)_4$), reacts with water (H_2O) to form titanium hydroxide ($Ti(OH)_4$) and alcohol (ROH). This reaction is typically initiated by adding a small amount of acid or base as a catalyst. The resulting gel retains the shape of the container and contains a high

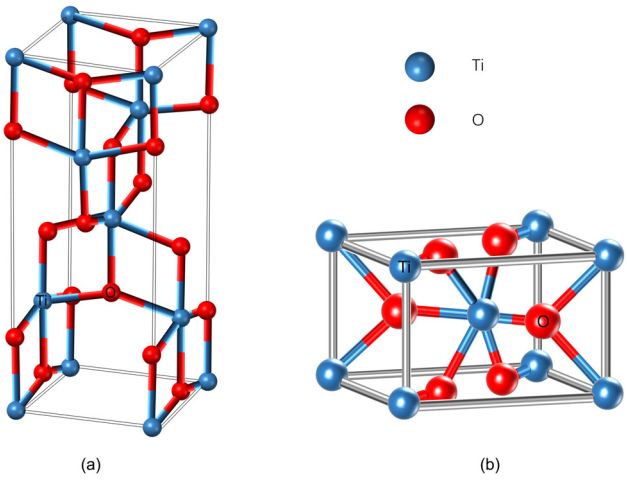


Figure 2: Anatase (a) and rutile (b) molecular 3D structures.

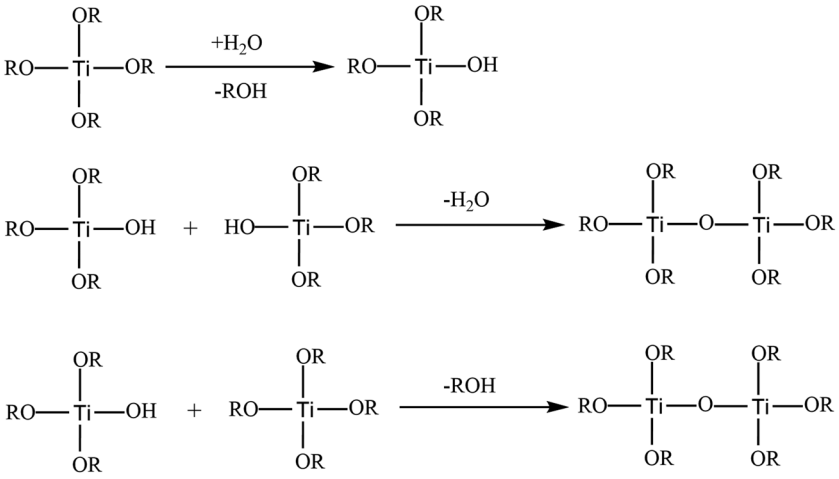


Figure 3: Hydrolysis-condensation reaction process of titanium alkoxide in sol–gel.

concentration of the metal oxide. The gelation involves the formation of a three-dimensional network structure through the interconnected Ti–O–Ti bonds. As the condensation reaction progresses, the gelation of the metal oxide network occurs. The gel is then subjected to aging or maturation, which allows further condensation reactions to occur and promotes the development of desired material characteristics. The aging process can range from hours to several days, depending on the specific requirements. Finally, the wet gel is dried to remove the remaining solvent or alcohol. Various methods such as evaporation, supercritical drying, or freeze-drying can be used to obtain a solid material, typically a xerogel or aerogel, with controlled porosity and high surface area.

In Sections 2 and 3, the effects and properties of the common chemicals required for the sol–gel as well as additives, the dosage used, and process sequences with the essential time in each step are introduced and exemplified. Also, the ambient condition for the preparation and storage of nano TiO_2 gel by the sol–gel method is illustrated. The related works are presented in Table 1 for reference.

2 Required chemicals

2.1 TiO_2 precursor

Precursor is the direct source of titanium applied in the sol–gel method, among which the most widely used type is titanium alkoxide. Alkyl groups in these alkoxides can either enhance or hinder the hydrolysis reaction of the alkoxide, with electron-withdrawing groups increasing reactivity and electron-donating groups decreasing reactivity [53–55]. Other inorganic titanium salts also have been applied as precursors to prepare TiO_2 materials by sol–gel methods, such as titanium tetrachloride ($TiCl_4$) [56,57], and titanium trichloride ($TiCl_3$) [58,59]. The most frequently used titanium alkoxides include ethyl titanate [60], isopropyl titanate [61–63], butyl titanate [64,65], and their isomeric chemicals [2,66,67]. The precursor type, concentration, and dosage can impact the crystalline structure, surface area, and pore size of the targeted TiO_2 produced through hydrolysis and condensation reactions of the alkoxides.

Several studies have explored the choice of precursor impacts on the properties of TiO_2 gels. For instance, Fröschl *et al.* [69] as well as Simonsen and Søgaard [68] have observed that the choice of precursor can significantly influence various characteristics, including particle size, morphology, crystallinity, and surface area. This influence arises from differences in the reactivity of the precursor's alkoxy group, with titanium tetraethoxide (TTE) being more reactive than titanium tetrabutoxide (TTB) and titanium tetraisoproxide (TTIP). In the context of their study, TiO_2 treated with TTIP exhibited the most noteworthy BET result (6 m^2/g) and the smallest particle size (3 nm), making it particularly conducive for AOP. Muthee and Dejene [70] delved into the impact of titanium precursor concentration on TiO_2 sol–gels and established that lower precursor concentrations (specifically, a volume ratio of 1:63 of TTIP to ethanol) resulted in a reduced anatase percentage (42.07%) compared to more optimal concentrations (1:9 or 1:7 of TTIP to ethanol volume ratios). In a similar study, Kwon *et al.* [60] prepared TiO_2 films using four different precursors, including TTIP titanium propoxide, titanium

Table 1: Common chemicals used in the sol–gel method to obtain nano TiO_2

#	Precursor	Solvent	Acidity modifier	Additive
1	Titanium tetrachloride ($TiCl_4$) [126]	Ethylene glycol ($C_2H_6O_2$) [126]		PVP ($(C_6H_9NO)_n$) [126]
2	TTIP ($C_{12}H_{28}O_4Ti$) [133]	Isopropanol (C_3H_8O) [133]		PEG ($HO(C_2H_2O)_nOH$) [133]
3	TTIP ($C_{12}H_{28}O_4Ti$) [175]	Ethanol (C_2H_6O) [175]	Hydrochloric acid (HCl) [175]	Methylcellulose ($C_{20}H_{38}O_{11}$) [175]
4	TTIP ($C_{12}H_{28}O_4Ti$) [141]	Ethanol (C_2H_6O) [141]		Oleic acid ($C_{18}H_{34}O_2$) [141]
5	TTIP ($C_{12}H_{28}O_4Ti$) [98]	Nitric acid (HNO_3) [98]	Ammonia solution (NH_5O) [98]	EDTA ($C_{10}H_{16}N_2O_8$) [98]
6	Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) [176]	Distilled water (H_2O) [176]	Ammonia solution (NH_5O) [176]	Citric acid ($C_6H_8O_7$) [176]
7	TTE ($C_8H_{20}O_4Ti$) [125]	Ethanol (C_2H_6O) [125]	Distilled water (H_2O) [125]	PVA ($[C_2H_4O]_n$) [125]
8	TTIP ($C_{12}H_{28}O_4Ti$) [177]	Ethanol (C_2H_6O) [177]	Acetic acid ($C_2H_4O_2$) [177]	Cetyltrimethyl ammonium bromide ($C_{19}H_{42}BrN$) [178]
9	TTIP ($C_{12}H_{28}O_4Ti$) [179]	Isopropyl alcohol (C_3H_8O) [179]	Nitric acid (HNO_3) [179]	HPC (C_3H_7O) [179]
10	Tetra-η-butyl titanat ($C_{16}H_{40}O_4Ti$) [180]	Ethanol (C_2H_6O) [180]	Distilled water (H_2O) [180]	Ethyl aceto acetate ($C_6H_{10}O_3$) [180]
11	TTIP ($C_{12}H_{28}O_4Ti$) [39]	Ethanol (C_2H_6O) [39]	Ammonia solution (NH_5O) [39]	Pluronic P123 ($C_{18}H_{36}O_5$) [39]
12	TTIP ($C_{12}H_{28}O_4Ti$) [82]	Propanol (C_3H_8O) [82]	Hydrochloric acid (HCl) [82]	AcAc ($C_5H_8O_2$) [82]
13	Titanium(IV) butoxide ($C_{16}H_{36}O_4Ti$) [181]	Ethanol (C_2H_6O) [181]	Nitric acid (HNO_3) [181]	Water-soluble chitosan ($C_6H_{11}NO_4X_2$) [181]
14	TiO_2 P25 [140]	Distilled water (H_2O) [140]	Ammonia solution (NH_5O) [140]	$([C_{12}mim]Br)_n$ ($C_{16}H_{31}BrN_2$) [140]
15	TTIP ($C_{12}H_{28}O_4Ti$) [136]	Ethanol (C_2H_6O) [136]	Ammonia solution (NH_5O) [136]	HDA ($C_{16}H_{35}N$) [136]
16	TTIP ($C_{12}H_{28}O_4Ti$) [127]	T-butanol ($C_4H_{10}O$) [127]	Distilled water (H_2O) [127]	DEA ($C_4H_{11}O_2N$) [127]
17	Titanium butoxide ($C_{16}H_{36}O_4Ti$) [182]	Distilled water (H_2O) [182]		Ethanolamine (C_2H_7ON) [182]
18	Tetrabutyl titanat ($C_{16}H_{40}O_4Ti$) [183]	Ethanol (C_2H_6O) [183]	Hydrochloric acid (HCl) [183]	Fluoroalkylsilane ($C_{16}H_{19}F_{17}O_3Si$) [183]
19	TTIP ($C_{12}H_{28}O_4Ti$) [61]		Nitric acid (HNO_3) [61]	Poly (diallyldimethylammonium) chloride ($C_{24}H_{54}Cl_3N_3X_2$) [61]
20	Titanium(IV) tert-butoxide ($C_{16}H_{36}O_4Ti$) [184]	Butanol ($C_4H_{10}O$) [184]	Formic acid (CH_2O_2) [184]	Polyethylenimine($H(C_2H_5N)_nNH_2$) [184]
21	TTIP ($C_{12}H_{28}O_4Ti$) [185]	Ethanol (C_2H_6O) [185]	Nitric acid (HNO_3) [185]	Triton X-100 (t-Oct-C_6H_4-$(OCH_2CH)x$OH, x = 9–10) [185]

ethoxide, and titanium butoxide. They found that the crystal size of the films made with the former three precursors was larger than that of the film made with titanium butoxide. This was due to the exchange rate of the alkoxy group in the precursors, which dominated the ratio of TiO_2 crystalline phases during the heat treatment and resulted in different grain sizes [70].

Another two types of frequently utilized precursor compounds for the synthesis of TiO_2 through hydrolysis are $TiCl_4$ and $TiCl_3$ in which $TiCl_3$ can also be synthesized from $TiCl_4$. However, the reduced purity of the produced titanium salt poses a significant drawback [71], which despite their lower cost, limits their potential and scalability in TiO_2 production. In particular, for large-scale manufacturing, the ease of control and higher purity achieved through the hydrolysis reaction of the titanium alkoxide make it a prominent choice based on literature [29,33,72]. While $TiO(OH)_2$, $Ti(SO_4)_2$, and titanium(4) bis-(ammonium lactate) dihydroxide ($C_6H_{18}N_2O_8Ti$) have also been employed as precursors in previous studies, however, due to their limited applicability they will not be further discussed here.

Furthermore, different precursors have various hydrolysis rates owing to their molecular structures, as pointed out by Kinoshita *et al.* [73]. A slower rate of hydrolysis-condensation promotes the formation of small colloidal clusters, which contributes to the formation of colloidal homogeneous sol. Nolan *et al.* [74] successfully accomplished the phase transformation of anatase to rutile (consisted of 77% rutile at 600°C and 95% rutile at 700°C) at relatively low temperatures for rutile (which is normally obtained about 13% at 700°C [74]) by employing TTIP as the precursor. This achievement serves as a valuable reference point for guiding the selection of the preferred crystalline phase orientation in TiO_2 materials. Ge *et al.* [75] used $TiOSO_4$ as the Ti precursor and ammonium hydroxide as a precipitating agent to generate $Ti(OH)_4$, an intermediate of TiO_2. Muthee and Dejene [70] used precursor solutions with different concentrations to organize TiO_2 nanoparticles and found that the percentage of anatase phase particles increased with the increase in precursor concentration, while the grain size showed a non-regular variation. The optimal precursor concentration for crystallinity was found to exist, beyond which the crystal size tended to decrease with the increase in the precursor concentration due to a lower number of reactive ions producing TiO_2. Finally, Bahloul *et al.* [72] investigated the mechanism by which TiO_2 production from precursors (TNBT) with different mass fractions was affected and found that the rate of hydrolysis-condensation reaction amplified with higher precursor mass fractions, resulting in a shorter time to generate TiO_2, decreased the precursor utilization efficiency. They also concluded that the higher mass fraction of the precursor is more sensitive to water, leading to a more violent reaction that can make the reaction less complete. Similarly, in our previous study (unpublished), we found that the use of a higher concentration of TiO_2 precursor solution can reduce the aging time for gel formation and result in a more viscous gel [76].

Overall, the sol–gel method for producing TiO_2 requires careful consideration of the precursor used in terms of type and dosage as it determines several properties of the final product. These properties include particle size, morphology, crystallinity, surface area, and pore size. The formation of colloidal homogeneous sols is facilitated by a slower rate of hydrolysis-condensation, which develops smaller colloidal clusters. Different types of precursors exhibit varying structures, sensitivity to water, as well as distinctive alkoxy exchange behavior. The hydrolysis rates of dissimilar precursors grow with their sensitivity to water during the sol–gel process, resulting in crystals of various sizes and types. Higher precursor concentrations lead to faster hydrolysis rates and more viscose gels, which can cause particle agglomeration and limit the effective sites on materials. Selecting appropriate precursors for TiO_2 material preparation allows for better control of the sol–gel reaction rate, leading to homogeneous sols, and enabling the subsequent production of diverse morphologies and material types, accordingly. Thus, the choice of the precursor is a critical factor in the sol–gel method for producing TiO_2 with specific desired properties.

2.2 Solvent

The primary function of a solvent in the sol–gel process is to dissolve the titanium alkoxide effectively and disperse the active components in the solution [77]. This will help to achieve more uniform hydrolysis and prevent the final product from agglomerating. Moreover, the selective use of solvents can introduce a spatial barrier effect that hinders the efficient hydrolysis of titanium alkoxides [78]. This approach also serves to stabilize the oligomers formed during the hydrolysis-condensation process of titanium alkoxides. Commonly used solvents include methanol [79,80], ethanol [70,81], propanol [82,83], butanol [83], and their isomers, such as ethylene glycol [84], 2-propanol [37], and glycerol [85]. The concentration and dosage of solvent used directly affect the hydrolysis-condensation reaction rate and the degree of reaction in the system, ultimately determining the properties of the resulting TiO_2 sol [86,87]. During the formation of TiO_2 gel, the evaporation of the

solvent, especially if heat treatment is applied, can have a significant impact on the crystallization and morphology of the material. For instance, in Jia and Jimmy's work [88], samples were subjected to a controlled evaporation process at 100°C within an oven for approximately 24 h in an air environment. This step effectively removed residual water and alcohol. Consequently, this solvent evaporation-induced crystallization method yielded nano-sized TiO_2 particles characterized by a bi-phase composition comprising anatase and brookite phases. Notably, these particles exhibited an impressive specific surface area of 265 m^2/g and a diminutive grain size of approximately 5 nm, all achieved at relatively low temperatures. The choice of the solvent type can also considerably impact the properties of the TiO_2 gel produced *via* the sol–gel process. This impact can be attributed to several factors, such as solvent polarity, acidity, basicity, and hydrogen bonding interactions between the solvent and the TiO_2 precursor [88]. However, it is also possible to produce a gel without the conventional use of solvents by directly adding the Ti precursor into acidic water [61,89]. It is crucial to highlight that the non-aqueous sol–gel method has emerged as a prominent technique for synthesizing TiO_2. This method entails dispersing Ti precursors in non-aqueous solvents, including organic solvents [90] and supercritical CO_2 [91] to produce gels that exhibit exceptional stability [92]. However, this technique is not considered practical for TiO_2 production due to its demanding safety requirements and high production costs [93]. Additionally, the use of organic and supercritical fluid solvents further contributes to its impracticality.

In a primary research work [81], three TiO_2 gels were synthesized by combining different solvents of ethanol, isopropyl alcohol, and 2-ethoxyethanol. It was found that the addition of isopropyl alcohol to the ethanol solvent increases the consistency of the gels. This is because the supplement of isopropyl alcohol gives a more monomeric structure to the complex formed by the solvent and TiO_2 precursor (TTIP) than with ethanol only, which helps to speed up the hydrolysis of the precursor. Polar solvents, like alcohol, are commonly applied in the sol–gel method, facilitating faster gel formation due to their polar functional groups. Nevertheless, low solvent amounts may prolong gelation time and result in a highly viscous gel, whereas high amounts may reduce the precursor solubility and cause incomplete hydrolysis. The viscosity of sol–gel is also influenced by the molecular structure of the solvent. Longer carbon chain solvents like octanol and hexanol intensify the viscosity, while smaller ones like methanol or ethanol decrease the viscosity due to their respective molecular weights and polarities [94]. Applying TiO_2 gels to silica glass plates using dip coating revealed that the thicker the gels, the greater the film thickness. This is explained by the fact that gels with higher viscosities have stronger adhesion due to the advanced toughness of the adhesive gel [95]. Nonetheless, the application of a thicker TiO_2 sol–gel coating may, at times, induce issues such as film detachment from the supporting substrate (Figure 4a *vs* Figure 4d) and the agglomeration of TiO_2 particles (Figure 4b and c compared to Figure 4e and f). This is primarily attributed to an excessive thickness of the

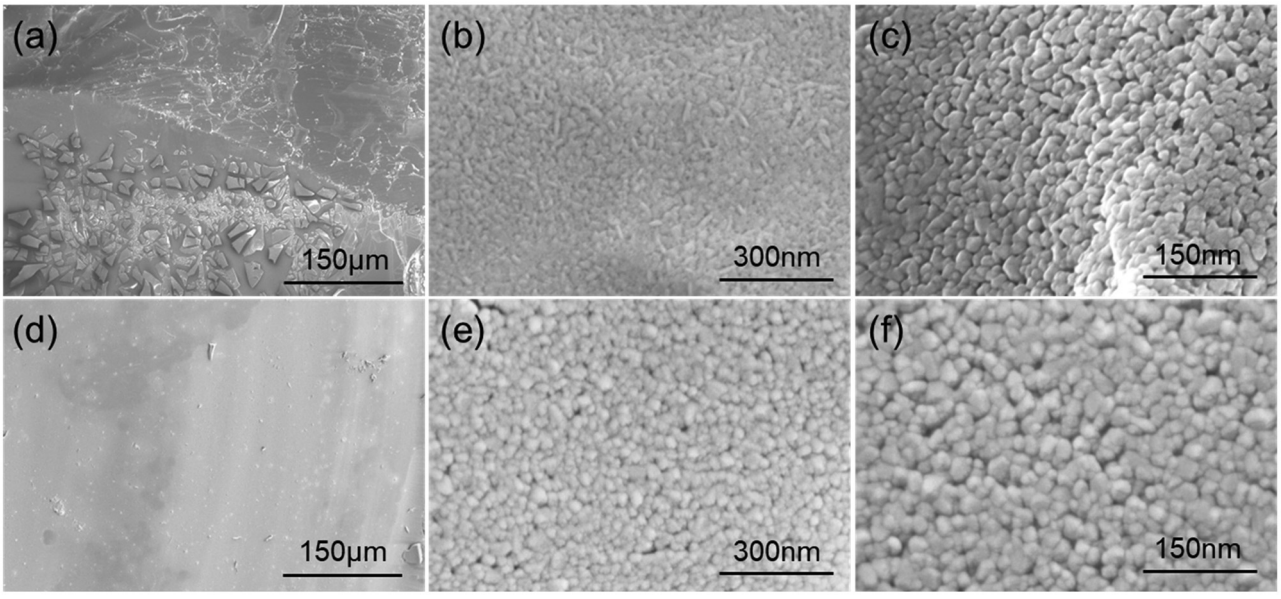


Figure 4: Morphology of TiO_2 films and particles prepared with a thicker gel (a)–(c) and a thin gel (d)–(f).

colloidal coating, which can lead to the uppermost layer drying more rapidly than the underlying ones, thereby causing stress disparities. Consequently, this drying incongruity can ultimately culminate in the formation of undesirable peelings [96].

Golobostanfard and Abdizadeh [79] prepared TiO_2 sols using methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, tert-butanol, and mixtures of them and analyzed their properties in terms of stability, gel transparency, gelation time, and other features. Among the gels produced, the 1-propanol-treated and 1-butanol-dominated-treated sols showed a longer gelation time (aging) and the best stability later, which was attributed to their higher order complexes, higher boiling points, and lower dipole moments. These were possibly through reducing the likelihood of TiO_2 particles aggregating, lowering the rate of solvent evaporation, and limiting the availability of reactive sites for gelation. The same justification was argued earlier in another work done by Hu *et al.* [81]. As an isomer of 1-butanol, the 2-butanol-treated sol has a very short gelation time and is less stable, which is supposed to be due to its smaller dipole moment and dielectric coefficient [97]. It is worth mentioning that the gel made with the mixed solvents neutralized its properties, compared with the gels from each one of the two solvents alone, which can be used as a reference for the choice of solvent type [79].

Mahyar *et al.* [80] found that the solvent type has an important contribution rate to the TiO_2 crystalline phase composition. The crystalline phase of TiO_2 nanoparticles synthesized with multiple solvents differed significantly (isopropanol-treated of 100 wt% anatase, methanol-treated of 55 wt% anatase and 45 wt%, ethanol-treated of 85 wt% anatase and 15 wt% rutile). This is because the TiO_2 particles, synthesized using isopropanol, have better thermal stability which can avoid the conversion of the anatase to the rutile phase during the annealing process at high temperatures (500°C and above [98]). The use of methanol and ethanol in this work resulted in larger TiO_2 grain sizes because their higher polarity and lower viscosity allowed for faster hydrolysis and diffusion of precursor. Han *et al.* [99] prepared TiO_2 films using four alcohol chemicals as solvents for TTIP, and their morphology and photocatalytic properties were investigated in response to methanol, ethanol, isopropanol, and 1-butanol. According to this literature, the TiO_2 films prepared using methanol (with the highest dielectric constant) as the solvent showed pronouncedly higher grain size and surface roughness with a lower specific surface area than the other solvent-dominated combinations. The dielectric constant of solvent on TiO_2 material morphology in this study was consistent with that reflected in the study by Lucky *et al.* [97]. This should be because solvents with high dielectric constant facilitate faster hydrolysis reactions of TiO_2 precursors, and the rapid growth of nanoparticles results in larger grain sizes, as does the surface roughness. A TiO_2 thin film with high roughness has more active sites, which helps to enhance its photocatalytic reaction efficiency.

In summary, selecting appropriate solvents is a highly influencing factor in producing TiO_2 materials with targeted shapes and crystalline phases. The differences in dielectric coefficient, viscosity, boiling point, and dipole moment among various solvents have a significant impact on the crystallinity, phase, and morphology of TiO_2 materials produced by the sol–gel process. These effects are not solely due to individual solvent properties, but rather a combination of them. The amount of solvent used is relative to the TiO_2 precursor. A lower precursor-to-solvent ratio not only leads to a more homogeneous solute, smaller crystal particles, and a larger specific surface area but also results in a lesser viscosity of gel and a reduced crystallinity of the final material, in general.

2.3 Hydrolysis

Hydrolysis reaction normally takes place *via* adding an adjusted pH water, dropwise, into the mixture of precursor and solvent. Water is necessary for hydrolysis reactions, while acidity modifiers act as catalysts in the sol–gel process, influencing both hydrolysis and polymerization reactions [100]. The commonly used acidity modifiers are hydrochloric [62,101], orthophosphoric [102], nitric [61], carboxylic [45], sulfuric [103], and perchloric acid [63]. Sodium chloride [58] and sodium hydroxide [104] also can mutually regulate the hydrolysis-condensation rate. TiO_2 particles of different sizes were prepared using several ratios of precursor to water by Li *et al.* [45]. They found that the TiO_2 particles with a TTIP to water volume ratio of 1:2.5 were the smallest and had the best effect in degrading the methyl orange dye. When either the water or precursor content was too high, it promoted the hydrolysis reaction rate resulting in larger particle size and agglomeration. The specific surface area of the material was also reduced and as a result, the photocatalytic efficiency of the final product was lower. Powders with low hydrolysis completion need higher temperatures for crystallization than the larger ones, due to smaller particle sizes which require more thermal energy for crystallization [105]. The powders with the most photocatalytic efficiency were produced with moderate water consumption (the molar ratio of water-to-TTIP was between 2 and 4) in this research. It means that there is an optimum value for

the complete degree of the reaction and that the amount of water is an effective control factor. Hafizah and Sopyan [86] investigated the effect of the hydrolysis reaction completion rate (adjusting the amount of water) on the properties of the TiO_2 powders formed. The powders with high hydrolysis completion were rod-shaped and had a low specific surface area, which was supposed to be due to the fast hydrolysis reaction leading to the agglomeration of nanoparticles.

The rate and extent of the hydrolysis reaction can be effectively regulated by selecting the type of acidity modifier [106], determining the appropriate amount of it [2,107], and controlling the quantity of water employed [45,49,86]. The selection of the acid type is crucial as it determines whether the introduced ions in the solution will or will not undergo unfavorable reactions with other ions during the hydrolysis-condensation process [108]. The introduction of acid serves to regulate pH and exerts a notable impact on both the reaction process and the resulting gel. In this context, it was observed that HNO_3 played a role in promoting the growth of brookite, whereas NH_4OH not only slowed down the phase transformation of TiO_2 powders from amorphous to anatase and anatase to rutile but also inhibited the growth of brookite. [109]. Furthermore, the characteristics of the TiO_2 gel generated through the sol–gel method are notably influenced by the quantity of water and its level of acidity. The findings suggest that achieving a sufficiently low pH, preferably around pH = 2, and employing a moderate excess of water, specifically with a water dosage ratio of at least 120 (the molar ratio of water to vanadium oxyacetyl acetonate-doped precursor of tetrabutyl titanate), are essential prerequisites for obtaining crystallized vanadium-doped TiO_2 at room temperature [110].

Lower pH values (1–5) lead to well-crystallized TiO_2 gel with a high degree of order [111,112], and the use of different acid types in the sol–gel process can impact TiO_2 gel properties [113]. In a word, the purpose of regulating the amount of water, pH, and acid types is to influence the properties of TiO_2 gels by controlling the degree of hydrolysis reaction [86]. Cruz *et al.* [62] prepared TiO_2 sols using HCl solution as an acidity modifier to adjust the solution pH to 1.5–1. According to the study, the density of TiO_2 sols increased (thick gel with lower viscosity) when decreasing the pH of the reaction solution (or increasing the dosage of acidic water) under a strongly acidic environment. They indicated that it may be due to this reason that the more acidic reaction conditions allowed the hydrolysis reaction to proceed faster and more completely, resulting in the production of denser TiO_2 gels. As shown in Figure 5a and b, using the same types and ratios of chemicals (3 mL TTIP, 30 mL ethanol, and HNO_3 solution at pH 1.2), two different viscosities of TiO_2 gel were obtained when various amounts of the acidic water (1–1.5 mL) were injected for hydrolysis during the same time of 38 min [76].

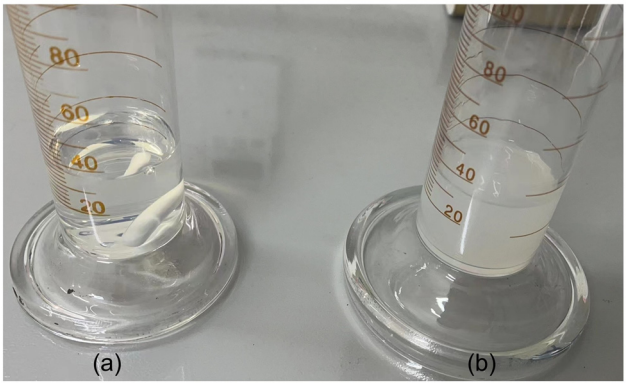


Figure 5: TiO_2 gels prepared *via* different amounts of acidic water: (a) 1 mL and (b) 1.5 mL.

In the research by Bai *et al.* [114], TiO_2 sols were obtained by adjusting the pH of the solution to 3, 4, 5, 7, 10, and 13 using NaOH solution to produce a powder form of TiO_2. It was found that as the pH increased, the particle size and agglomeration of TiO_2 powder gradually decreased and there was a shift in the shape, from dandelion-like (pH = 3–5) to nanorods (pH = 7 and 10), and to nanoparticles (pH = 13). This should be attributed to the fact that the increase in pH of the solution lowers the completion of the hydrolysis reaction, resulting in a gradual decrease in the amount of TiO_2 produced, and a decrease in powder agglomeration [115]. Analysis of the crystalline phase composition revealed that at low pH (pH = 3–5), only the rutile phase was presented in the TiO_2 grains, with the anatase phase appearing at pH = 7, and the highly crystalline anatase phase at pH = 10. Other studies have shown that acidic reaction conditions contribute to the formation of the rutile phase [114], but not essentially [116]. In contrast, Bano *et al.* [117] used HCl and NaOH to adjust the pH of the solution from 1 to 10 to obtain various types of Ag–TiO_2 nanocomposites and tested their surface morphology. They reported that the specific surface area of the composites shows an increase and then a decrease with the increase in the pH of the solution (the maximum value occurred at pH = 4). The smaller specific surface area implies agglomeration of nanoparticles, which should be related to the nucleation growth and photoreduction of AgCl (pH < 4) and Ag(OH) (pH > 9) precipitates, rather than the acidity affecting the hydrolysis reaction. In addition, pH can also influence the TiO_2 quantum confinement by regulating the rate and completion of the hydrolysis reaction. The crystallinity of TiO_2 can be controlled through hydrolysis, thereby influencing the optical band gap energy of the resulting material. Sridevi *et al.* [115] observed that

elevating the pH of the solution, indirectly reduces the TiO_2 band gap by affecting the crystallinity, leading to enhanced light utilization efficiency and improved photocatalytic activity.

In summary, the type of the acidity modifier applied, its dosage, the amount of water used, and the injection rate will impact the rate and completion of the hydrolysis-condensation reaction, resulting in diverse properties of the TiO_2 gels [49,118]. Therefore, the TiO_2 powders or thin films prepared *via* the same process may differ in their grain sizes, morphology, and optical properties. In general, a low pH (around 1–2 [62]), moderate amounts of water to precursor (molar ratio varies from 2 to 4 [86]), and slow injection rates (dropwise [119,120]), through slowing down of hydrolysis-condensation, are in favor of producing a desirable gel with acceptable transparency and optical properties, nano TiO_2 particle size, and photocatalytic efficiency. However, the selection of a suitable experimental protocol cannot be generalized and needs to be analyzed in light of practical needs.

2.4 Additives

In this review, TiO_2 precursor, solvent, and acidic water were defined as basic chemicals applied in the sol–gel method; while other compounds are introduced as additives that can modify the properties of TiO_2 when being added to the solution. Three main categories of additives including stabilizers, surfactants, and metal/nonmetal dopants are being extensively used in different research works for various purposes. Stabilizers are normally added to the solution to provide a more stable gel as the gel is an unstable structure by nature [121]. Surfactants are mainly used for surface modification and enhancing the adherence of the TiO_2 nanoparticles on the support surface *via* reducing surface tension and increasing the solubility of reactants [122]. And finally, nanoparticles, such as metal or metal oxides, can be applied as dopant additives to the sol which creates hybrid nanoparticles with TiO_2 that have superior properties (especially optical) [123]. These three categories are explained and exemplified further in the following subsections.

2.4.1 Stabilizers

The addition of stabilizers such as hydroxypropyl cellulose (HPC) [124], polyvinyl alcohol (PVA) [125], polyvinylpyrrolidone (PVP) [126], acetylacetone (AcAc) [118], and diethanolamine (or DEA which is also one of the most frequently used additives) [127] can boost the dispersion of TiO_2 nanoparticles in the sol [128]. This happens by providing steric and electrostatic repulsion to prevent particle agglomeration which provides a stable structure during the sol–gel process [129] as illustrated in Figure 6 [76]. Chelating agents, such as ethylenediaminetetraacetic acid (EDTA) [130] and citric acid [131] also can be added to control the stability and reactivity of the TiO_2 sol–gel solution [132]. Thompson *et al.* [2] used polypropylene glycol as a shape control agent to prepare TiO_2 thin films by sol–gel. The crystalline phase and grain size were investigated and it was found that increasing the dosage of polypropylene glycol resulted in larger grains due to more space for grain growth after heat treatment and solvent evaporation. Chen and Dionysiou [133] synthesized macroporous films using polyethylene glycol (PEG) as a porogenic agent in the sol–gel process; where PEG escapes during the heat treatment and leaves the pores.

In general, in the sol–gel process for TiO_2 synthesis, stabilizers serve the functions of regulating the properties of TiO_2 sol–gels, thus affecting particle size, preventing

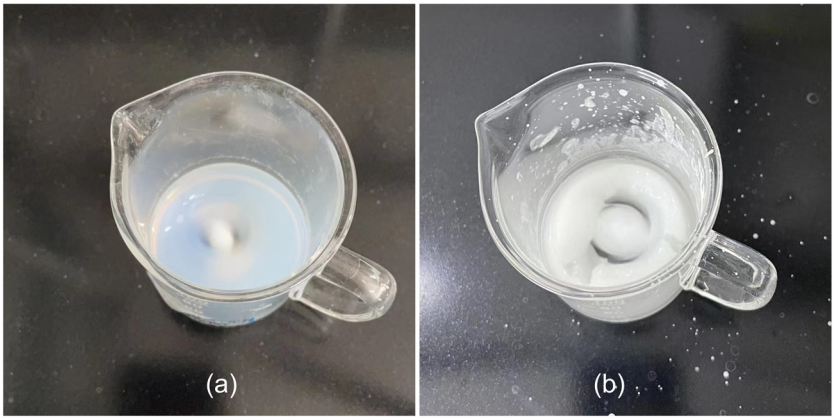


Figure 6: TiO_2 gels resulted with (a) and without (b) using DEA as stabilizer.

particle aggregation, and maintaining sol stability. They play a crucial role in achieving a controlled and consistent production of TiO_2 nanoparticles by overseeing aspects such as size, shape, and distribution. Stabilizers exercise control over the growth and clustering of particles, ensuring that the resulting material possesses the intended properties. Furthermore, they uphold the uniformity of the sol, avoiding premature gel formation, and promoting the even dispersion of nanoparticles within the gel precursor.

2.4.2 Surfactants

For the coating purpose, surfactants [134] act to reduce surface tension, increase the solubility of reactants, and serve as excellent media for surface directing agents, nucleation, and crystal growth [122], thus playing a crucial role in achieving the desirable size, shape, dispersion, and stability of TiO_2 nanoparticles formed *via* sol–gel [135]. Compounds, such as hexadecylamine (HDA) [136], PEG [133], and Triton X-100 [137] can be used to control the particle size and distribution of the TiO_2 nanoparticles. A proposed mechanism has been suggested for the formation of monodisperse precursor beads to illustrate the significant role of HDA in determining the morphology and monodispersity of TiO_2 during the sol–gel synthesis process in which HDA was used as a structure-directing agent to control the monodispersity of the resultant titania beads, along with the spherical shape, varying the amount of structure-directing agent involved in the sol–gel process [136]. Modifying the ammonia concentration (the molar ratio of HDA/TTIP = 0.33–1) in a mild solvothermal process gives rise to mesoporous anatase titania beads having controllable crystallite size (320–830 nm), specific surface area (from 89 to 120 m^2/g), and pore size distribution (from 14 to 23 nm). The resultant mesoporous titania materials are expected to have potential applications in areas of energy conversion and environmental cleanup. Nonionic surfactants like PEG [138], on the other hand, can enhance the dispersion and stability of TiO_2 nanoparticles within the gel. When adsorbed onto the surface of the particles, surfactants can create mesoporous structures, which increase the specific surface area of the particles and improve accessibility to active sites [139]. Wei *et al.* [59] utilized different mass concentrations of methylcellulose to induce the synthesis of micro-spherical TiO_2 powders. The concentration of methylcellulose affected the shape and phase of the synthesized particles and formed a three-dimensional network of high-density hydroxyl group-exposed methylcellulose molecules. Curcio *et al.* [44] added Triton X as a surfactant to improve the wettability of TiO_2 gels for film coating. Xin *et al.* [140] used $[C_{12}mim]Br$ as a surfactant to synthesize ionic liquid/TiO_2 composite films with good self-cleaning properties, where $[C_{12}mim]Br$ acted as lower surface tension material to enhance the hydrophobicity of the final product and improved its self-cleaning properties. Jin *et al.* [141] synthesized TiO_2 nanorods using oleic acid as a surfactant and 1-hexadecylamine as co-surfactant, which was found to be an effective substance to control the diameter of TiO_2 nanorods. Additionally, surfactants can promote the formation of highly crystalline mesoporous TiO_2, high surface area (245–300 m^2/g), and tunable mesopore diameter (2.2–3.8 nm) by means of anionic surfactant templating effects [142,143], which can enhance the photocatalytic activity of TiO_2 nanoparticles.

Surfactants function at the interfaces between liquids and either gases or other liquids to reduce surface tension and promote the dispersion of TiO_2 nanoparticles. Their main advantage lies in their ability to thwart particle aggregation and improve the uniform distribution of particles. This enhanced dispersion holds significant importance, particularly in applications such as coatings, where achieving uniform coverage is of utmost importance. Surfactants assume a central role in upholding the integrity of TiO_2 nanoparticles within the sol, diminishing the probability of particle clustering, and guaranteeing consistent properties of the end product.

2.4.3 Dopants

To modify the photocatalytic properties of TiO_2 nanoparticles, dopants like nitrogen [30,144], carbon [31,145], and transition metal ions [146] such as Fe can be used. Metal/nonmetal solutions have been investigated as additives in the sol–gel process to prepare TiO_2 composites for improved light utilization efficiency and wider applications in water treatment [147,148]. Transition metal dopants such as Fe, Co, and Ni can narrow the bandgap and increase visible light absorption [149], while nonmetal dopants such as N and C can introduce defect states and modify the electronic structure of TiO_2 [150,151]. The dopant concentration [152] and species [149] can affect the size, shape, crystallinity, and surface area of TiO_2 nanoparticles, thereby influencing their photocatalytic activity. For instance, Chen *et al.* [153] found that nitrogen-doped TiO_2 nanoparticles had higher photocatalytic activity than pure TiO_2. The incorporation of other elements such as Ag, Au, and ZnO can enhance the photocatalytic activity of TiO_2 by promoting charge separation and improving the light-harvesting efficiency [154].

Additionally, the integration of other nanoparticles with TiO_2 can modify the surface area, surface energy, and surface defects of TiO_2, which can enhance its photocatalytic performance [155]. For example, Fu and Zhang [156] reported that the addition of Au to the TiO_2 gel

improved its photocatalytic activity for the degradation of pollutants. Catalysts supplements such as noble and non-noble metals and metal oxides can promote the separation of electron-hole pairs and increase the surface area of TiO_2 nanoparticles, which supports their photocatalytic efficiency [157]. For instance, applying Pt, Pd, and Au as noble metal catalysts has reported to greatly enhance the photocatalytic activity of TiO_2 [158,159]. Moreover, metal oxides such as Fe_2O_3 and WO_3 have been utilized to boost the photodegradation ability of TiO_2 by acting as electron sinks [160,161].

Dopants are deliberately introduced into the TiO_2 matrix to bring about specific property modifications. These additives have the capacity to influence the electronic structure, optical characteristics, and reactivity of TiO_2, tailoring it for particular applications. For example, incorporating metals like Fe, N, or Pt as dopants can enhance the photocatalytic prowess of TiO_2 [32]. Dopants wield significant influence over TiO_2 properties; nitrogen (N) doping, for instance, can shift TiO_2's bandgap, rendering it responsive to visible light and thereby improving its photocatalytic performance [144]. Achieving the desired property adjustments necessitates careful control over the type and concentration of dopants.

In summary, incorporating suitable additives can enhance the properties or structural characteristics of TiO_2 nanomaterials when they fail to meet practical requirements, efficiently. The selection of additives depends on the intended application and desired properties of the final TiO_2 sol–gel product. Some additives can indirectly influence the sol–gel process by inducing and controlling chemical processes to prepare TiO_2 materials with specific structural features or properties. Chelating agents, for instance, affect the properties of TiO_2 sols and gel materials by influencing the rate and completion of hydrolysis, while shape control agents induce the corresponding shape of the generated TiO_2, thereby retrofitting the properties of nano TiO_2. Meanwhile, the addition of nanoparticles and metal/nonmetallic solutions will incorporate some properties of the additives, such as electrical conductivity and photosensitivity, directly into the TiO_2 gels. In either approach, the choice of additives aims to minimize any negative effects and maximize the efficiency of the targeted product.

2.5 Summary of chemical selection

The sol–gel method for the preparation of TiO_2 relies on the hydrolysis reaction, which requires Ti precursor, solvent, and water. However, some researchers have been able to achieve the desired results without the use of solvents [46,61], acidity modifiers [70,83], and additives [45,162]. The hydrolysis-condensation reaction in the sol–gel process is influenced by the selection of precursor type and its concentration, the amount of solvent used, acidity regulators, H_2O, and additives. However, due to the complexity of the chemical process, it is difficult to obtain the exact target material by solely controlling the use of chemicals in a specific manner, or even to replicate the identical product in the first attempt using the same process. Achieving control over the required molar ratio and the properties of the target product using a single chemical is also challenging and might require trial and error at the initial stages. In some cases, a combination of two or more chemicals (such as a mixture of solvents) and physical methods may be required to produce the desired convergent modification. Table 1 presents the different types of precursors, solvents, acids, and modifiers used in numerous studies done for producing nano TiO_2 *via* the sol–gel method.

3 Reaction conditions for the sol–gel process

Although not very complex, the preparation of TiO_2 sols is a process that requires accuracy in every step for successful chemical reactions. Each one of the steps and factors in this process plays a crucial role in formation of the final form of the gel. The properties of TiO_2 sol–gel can be influenced by factors like reaction temperature, humidity, stirring speed, the order of adding chemicals, the aging process, and injection rates of chemicals which are explained as follows.

3.1 Reaction temperature

The hydrolysis and condensation reaction rates in the sol–gel process are sensitive to temperature and time, which in turn affect the properties of the resulting TiO_2 gel. Specifically, the size, morphology, and crystallinity of TiO_2 particles can be impacted [163]. Higher temperatures during the gel-making process promote faster gelation, while longer times (aging) can result in increased crystallinity and larger particle sizes [164]. At lower temperatures, the hydrolysis and condensation reactions that form TiO_2 gel proceed more slowly, resulting in the formation of more amorphous TiO_2 due to a lower reaction rate and longer time for precursor molecules to form non-crystalline structures [121]. As temperature increases, the reaction rate accelerates, leading to the formation of crystalline structures due

to the higher energy state of the system [165]. The higher temperature also promotes the growth of TiO_2 crystals, which develops crystallinity [166]. Particle size is influenced by the rate of reactions, the concentration of precursor molecules, and the degree of agglomeration or sintering of particles. At higher temperatures, precursor molecules may hydrolyze and condense more rapidly, leading to the formation of larger particles [73]. Porosity is related to the degree of crosslinking between precursor molecules, with lower temperatures developing a highly porous structure due to the slower reaction rates and more uncross-linked chains [167]. Higher temperatures can lead to increased density and decreased porosity due to increased crosslinking and removal of solvents [168]. Surface area is related to both particle size and porosity, with lower temperatures leading to a greater surface area due to the formation of smaller particles and more porous structures [169]. However, higher temperatures can cause a denser structure with larger particles, resulting in a smaller surface area [86].

3.2 Humidity

Humidity affects both TiO_2 sol [170] and gel processes [171], causing changes in its surface area, pore structure [162], as well as crystallization [172]. Ti precursors are water-sensitive substances; thus, when the humidity of the experimental environment is high, the precursors will precipitate, which will destroy the hydrolysis reaction process. Therefore, the preparation of TiO_2 gel *via* the sol–gel method is recommended to be done under the air conditioner [173], if it is not in the glovebox. Slunecko *et al.* [174] found that samples prepared under different humidity conditions differed in their number of unhydrolyzed alkyl and rutile particles, indicating that increasing atmospheric relative humidity causes fewer water-soluble alkyl particles and larger rutile elements.

According to Barlier *et al.* [170], air humidity inhibits Ti $(OeCarb)_4$ hydrolysis activity when it comes to its environmental reactivity. Moreover, higher humidity levels result in a slower drying rate of TiO_2 gel [186], thereby affecting the crystallinity, formation of agglomerates, size, and shape of nanoparticles, and mechanical properties of TiO_2 gel. The rapid drying speed of TiO_2 gel can lead to uneven internal and external stresses, which can impact the morphology of the gel. If the drying process is too intense, the gel may even crack [187]. Matsuda *et al.* [172] found that under high temperatures and humidity, the structure of porous TiO_2–SiO_2 film is easy to be eroded by water vapor, resulting in the generation of more Ti–O–Ti bonds and anatase crystal phase. Generally, the TiO_2 films prepared at high room humidity (>75% RH) were rough and inhomogeneous, with significant differences compared to the uniform and more conductive films prepared at low RH (<15%) [188].

3.3 Stirring speed

The stirring rate is an important criterion in the preparation of TiO_2 *via* sol–gel, as it affects the subsequent product in multiple ways. Stirring at an appropriate rate helps to uniformly distribute the reactants, producing a more homogeneous and consistent sol–gel [189]. This, in turn, affects the size and morphology of the particles formed during the process [190], ultimately influencing the properties of the final TiO_2. Besides, the stirring rate can influence the gelation kinetics, accelerating the process, and developing a highly stable and mechanically solid gel [191]. Moderately increasing the stirring speed of a TiO_2 solution can decrease the particle size of the gel by applying a greater shear force to the solution, according to a study by Sun *et al.* [192]. Furthermore, increasing the stirring speed can lead to an increase in the specific surface area and crystallinity, a more homogeneous distribution of particles, and higher elastic modulus and hardness due to the densification of the gel network [193]. A stirring speed of 500 rpm is recommended for mixing the solution in the sol–gel method [194].

3.4 Sequences of adding chemicals

The order of adding chemicals during the preparation of TiO_2 sol–gel can significantly impact the properties and performance of the resulting material. It can affect the kinetics and thermodynamics of the hydrolysis and condensation reactions, the stability and colloidal behavior of the sol–gel precursor, the degree of agglomeration, and the surface area of the resulting TiO_2 material [195,196]. Hence, consideration of the chemicals' adding order is necessary to achieve the desired properties and performance of the TiO_2 material. During the preparation of TiO_2 *via* sol–gel, this order can impact the size and uniformity of TiO_2 particles. Adding water before acid can result in larger particles while adding acid before water can produce smaller particles. The reason for this is that the acid serves as a catalyst, preventing the hydrolysis of the precursor and ensuring that excessive hydrolysis does not occur, which can lead to the formation of smaller gel particles [180]. Incorporating a chelating agent before the titanium alkoxide precursor can lead to more uniform particles with smaller sizes [197]. A general order of adding chemicals is illustrated in Section 4 of this article.

3.5 Injection rate of chemicals in the solution

The injection rate or dropping speed of the chemicals during the sol–gel process can affect the properties of TiO_2 gel in various aspects. Tian *et al.* [120] found that a slower dropping speed of chemicals results in smaller particle size, higher crystallinity, porosity, surface area, photocatalytic activity, hardness, and elastic modulus, as well as a lighter color. When the chemicals are dropped slowly, the reaction between the precursors is allowed to proceed more gradually and uniformly, leading to a relatively controlled formation of the material [198,199]. This can cause smaller particle size, as the slower reaction kinetics allow for future homogeneous nucleation and growth of particles [200,201].

Additionally, lower injection rates can result in a higher degree of crystallinity, as the slower reaction kinetics allow for a complete conversion of the precursors to the crystalline form [202]. This can also lead to higher porosity and surface area, as the slower reaction kinetics provide a more thorough formation of voids and defects within the material [203]. The prolonged reaction kinetics can also result in higher photocatalytic activity, as the gentler formation process can allow for more effective integration of photoactive species [204]. Higher hardness and elastic modulus can also be derived from the more controlled formation process, as the gradual reaction kinetics can offer higher uniform packing and bonding of the material [205]. Hydrolysis is one of the most injection rate-sensitive steps in the sol–gel process which is normally recommended to be performed dropwise [206], and the dropping speed can be adjusted accordingly, considering the size of the experiment.

3.6 Aging process

The aging process, also known as maturation, is the last step in the preparation of TiO_2 sol–gel, and it can impact the resulting sol–gel from various points of view. First, aging promotes the hydrolysis and condensation of precursor molecules, which increases the cross-linking between TiO_2 particles, providing a more stable and mechanically robust sol–gel [207]. Second, aging can affect the size and morphology of TiO_2 particles through Ostwald ripening [208], which causes the smaller particles to dissolve while the larger particles continue to grow, thus increasing the average particle size. Third, aging can alter the surface chemistry of the TiO_2 particles, making them more hydrophobic and improving adhesion to hydrophobic substrates [209], and can impact photocatalytic properties. Moreover, aging can decrease the porosity of the gel, increase the density and mechanical strength, and decrease the surface area and reactivity [210]. Controlling the aging time and temperature can optimize the properties of the resulting sol–gel for its intended application.

Finally, aging time can affect the thermal stability of the TiO_2 gel too [211]. Panić *et al.* [212] found that aging led to improved thermal stability in TiO_2–SiO_2 composites. On the other hand, as aging time increases, particle aggregation can occur, causing a decrease in surface area [213]. Fajriati *et al.* [214] reported that increased crystallinity due to aging results in improved photocatalytic activity, while prolonged aging times can lead to decreased porosity and specific surface area due to larger TiO_2 particle formation [215]. Similarly, Venkatachalam *et al.* [164] reported that prolonged aging times decrease the TiO_2 nanoparticle size but increase the surface hydroxyl groups, improving the photocatalytic activity. Liu *et al.* [216] found that increasing the aging time can lead to a better TiO_2 gel cross-linking, resulting in improved mechanical strength and stability. Aging time can vary depending on the kind and dosage of chemicals used for the sol–gel. A thermal treatment process at low temperatures can shorten the required aging time. Some experiments have applied a 7 day aging (25°C) while using heat treatment (160–180°C) it can be reduced to 1 h [217]; however, this might impact the properties of the final product as mentioned above. Indeed, sometimes the gels might quickly become hard, even within 30 min at room temperature (22°C) [121], unless they are covered and stored in a refrigerator before hardening. Therefore, low-temperature storage (4°C in the refrigerator) is an effective way to avoid excessive aging of TiO_2 sol–gel and maintain its availability [2,218].

3.7 Summary of reaction conditions

Only through employing carefully controlled parameters such as temperature, humidity, stirring rate, sequences of chemical addition, injection rate, and aging time, the properties of TiO_2 sol–gel can be optimized. These are significant factors that influence the sol–gel process in TiO_2 preparation to achieve specific characteristics. Higher temperatures accelerate gelation, resulting in larger particles and increased crystallinity, while, lower temperatures yield slower reactions, causing a smaller, more amorphous particles. Humidity, on the other hand, affects the resulting gel's surface area, pore structure, and crystallization through the reaction completion of the sol–gel process. High humidity can deteriorate water-sensitive drugs, impacting sol–gel

reaction completion, and subsequent processes such as crystallization and molding. The lower stirring speed triggers the deposition of colloidal particles with larger sizes. Stirring speed is important in achieving uniform distribution of chemicals and influencing particle size, surface area, crystallinity, and mechanical properties of the resulting gel by affecting gelation kinetics. The sequence of adding chemicals during the sol–gel process affects hydrolysis, stability, and particle size due to variations in kinetics, thermodynamics, colloidal behavior, and agglomeration. The injection rate controls the severity of hydrolysis and the overall sol–gel process, impacting particle size, crystallinity, porosity, and mechanical properties. Aging the gel after its formation promotes stability and alters the surface chemistry. It affects the properties of TiO_2 sol–gel through ongoing hydrolysis, condensation, Ostwald ripening, and crystallization processes, over time. These processes influence particle size, morphology, crystallinity, and surface properties, ultimately impacting the overall characteristics of the sol–gel material. Therefore, adequate storage conditions must be maintained to prevent deterioration or alteration of the gel over time.

4 A practical example of TiO_2 gel preparation

The following example provides a better understanding of the routes' selection and ambient conditions for gel formation. To prepare 275 mL of gel [62,165], use 25 mL ethanol as a solvent in a beaker. While the solvent is stirred at 500 rpm, drop 1.25 mL of TTIP for 10 min and continue stirring for an hour. If additives such as stabilizers are required, they can be added at this stage (DEA:TTIP molar ratio R = 1 to 2 [127]). In the next step, the hydrolysis takes place by adding 250 mL of acid-mixed water (at pH 1.5) using a dropping funnel, dropwise during 240 min while stirring. Continue stirring the mixture overnight until a viscose transparent (or slightly translucent) gel is formed. In case the gel has not formed yet, an aging process can take place by leaving the sol undisturbed at room temperature. This step can be shorter if a low-temperature heat (at 30–60°C) is used (it will cause evaporation of some components). After the gelation, the final product can be kept at 4°C for around a month. The general order of adding chemicals is roughly depicted in Figure 7.

The justifications behind the choice of chemicals in the abovementioned example are interpreted as follows. TTIP is a commonly used Ti precursor with ethanol chosen as the solvent since its relatively high polarity and low viscosity help the rapid diffusion of TTIP and avoid causing colloidal agglomeration of colloidal particles. Moreover, ethanol itself is a chemical with more daily exposure, increasing the convenience of its storage and use. HNO_3, as an inorganic acid, has solution ions that do not conflict significantly with the other chemicals used and do not generate additional reactions (*e.g.*, precipitation reactions) that might make the process less efficient [75].

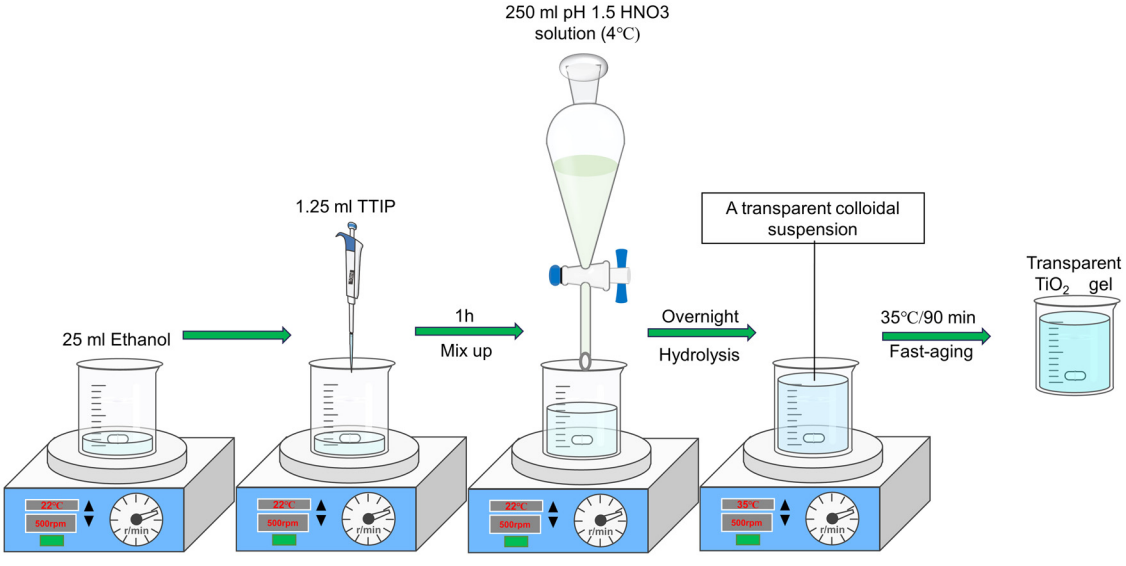


Figure 7: Schematic sol–gel process to prepare 275 mL of TiO_2 gel.

5 Concluding remarks and future perspectives

The preparation of TiO_2 gels *via* the sol–gel is a process that requires careful selection of chemicals, precise reaction conditions, and appropriate procedures. This method offers numerous advantages over others, including the ability to produce nanoscale TiO_2 gels with controlled properties. The choice of precursors, solvents, acid, and additive types and concentrations, as well as the reaction conditions, all play crucial roles in the final product properties including the size, morphology, crystalline phase of the nanoparticles, and various physical and chemical characteristics of the resulting TiO_2 gels. Proper control of these parameters is essential for an optimized preparation of TiO_2 gels for various applications, including catalysis, energy storage, environmental remediation, *etc*.

In the future, the preparation of TiO_2 *via* the sol–gel process is expected to continue as an active area of research. One future trend is the use of novel TiO_2 precursors and additives to tailor the properties of the resulting gels for specific applications. Another trend is the development of new reaction conditions that can enhance the efficiency and reproducibility of the sol–gel process, such as the use of microwave heating or continuous flow reactors. Additionally, the integration of TiO_2 with other materials, such as graphene or metal nanoparticles, is expected to accelerate the development of new composite materials with enhanced properties. The application of TiO_2 gels in fields such as AOP, photocatalysis, and biomedical engineering is also likely to expand in the future. Overall, the continued exploration and optimization of the sol–gel process for TiO_2 preparation is predicted to result in the development of new materials with significant applicability in numerous fields.

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References

[1] Mesgari M, Aalami AH, Sahebkar A. Antimicrobial activities of chitosan/titanium dioxide composites as a biological nanolayer for food preservation: A review. Int J Biol Macromol. 2021;176:530–9. doi: 10.1016/j.ijbiomac.2021.02.099.

[2] Thompson WA, Perier C, Maroto-Valer MM. Systematic study of sol-gel parameters on TiO_2 coating for CO_2 photoreduction. Appl Catal B-Environ. 2018;238:136–46. doi: 10.1016/j.apcatb.2018.07.018.

[3] Rad S, Shamsudin S, Taha MR, Shahid S. Tropical stormwater nutrient degradation using nano-TiO_2 in photocatalytic reactor detention pond. Water Sci Technol. 2016;73(2):405–13. doi: 10.2166/wst.2015.465.

[4] Chen X, Rad S, Lei G, Junfeng D, Shahab A, You S, et al. Photocatalytic reactor and detention pond integration: a novel technique for surface water quality enhancement via nano-TiO_2. Env Earth Sci. 2019;78:1–12. doi: 10.1007/s12665-019-8577-5.

[5] Kapilashrami M, Zhang Y, Liu Y-S, Hagfeldt A, Guo J. Probing the optical property and electronic structure of TiO_2 nanomaterials for renewable energy applications. Chem Rev. 2014;114(19):9662–707. doi: 10.1021/cr5000893.

[6] Bai J, Zhou B. Titanium dioxide nanomaterials for sensor applications. Chem Rev. 2014;114(19):10131–76. doi: 10.1021/cr400625j.

[7] Ma Y, Wang X, Jia Y, Chen X, Han H, Li C. Titanium dioxide-based nanomaterials for photocatalytic fuel generations. Chem Rev. 2014;114(19):9987–10043. doi: 10.1021/cr500008u.

[8] Rengifo-Herrera JA, Osorio-Vargas P, Pulgarin C. A critical review on N-modified TiO_2 limits to treat chemical and biological contaminants in water. Evidence that enhanced visible light absorption does not lead to higher degradation rates under whole solar light. J Hazard Mater. 2022;425:127979. doi: 10.1016/j.jhazmat.2021.127979.

[9] Guizhen Z, Yingying Y, Yi T, Yang L, Jintao H, Xiaochun Y, et al. Preparation of reusable UHMWPE/TiO_2 photocatalytic microporous membrane reactors for efficient degradation of organic pollutants in water. Sep Purif Technol. 2023;305:122515. doi: 10.1016/j.seppur.2022.122515.

[10] Tufail A, Price WE, Hai FI. A critical review on advanced oxidation processes for the removal of trace organic contaminants: A voyage from individual to integrated processes. Chemosphere. 2020;260:127460. doi: 10.1016/j.chemosphere.2020.127460.

[11] Amor C, Marchão L, Lucas MS, Peres JA. Application of advanced oxidation processes for the treatment of recalcitrant agro-industrial wastewater: A review. Water. 2019;11(2):205. doi: 10.3390/w11020205.

[12] Suzuki H, Araki S, Yamamoto H. Evaluation of advanced oxidation processes (AOP) using O3, UV, and TiO2 for the degradation of phenol in water. J Water Process Eng. 2015;7:54–60. doi: 10.1016/j.jwpe.2015.04.011.

[13] Černigoj U, Štangar UL, Trebše P. Degradation of neonicotinoid insecticides by different advanced oxidation processes and

studying the effect of ozone on TiO_2 photocatalysis. Appl Catal B-Environ. 2007;75(3-4):229–38. doi: 10.1016/j.apcatb.2007.04.014.
[14] Linsebigler AL, Lu GQ, Yates JT. Photocatalysis on TiO_2 surfaces - principles, mechanisms, and selected results. Chem Rev. 1995;95(3):735–58. doi: 10.1021/cr00035a013.
[15] Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiuchi Y, Anpo M, et al. Understanding TiO_2 photocatalysis: mechanisms and materials. Chem Rev. 2014;114(19):9919–86. doi: 10.1021/cr5001892.
[16] Bai W, Krishna V, Wang J, Moudgil B, Koopman B. Enhancement of nano titanium dioxide photocatalysis in transparent coatings by polyhydroxy fullerene. Appl Catal B-Environ. 2012;125:128–35. doi: 10.1016/j.apcatb.2012.05.026.
[17] Santhosh C, Velmurugan V, Jacob G, Jeong SK, Grace AN, Bhatnagar A. Role of nanomaterials in water treatment applications: A review. Chem Eng J. 2016;306:1116–37. doi: 10.1016/j.cej.2016.08.053.
[18] Puddu V, Choi H, Dionysiou DD, Puma GL. TiO_2 photocatalyst for indoor air remediation: Influence of crystallinity, crystal phase, and UV radiation intensity on trichloroethylene degradation. Appl Catal B-Environ. 2010;94(3–4):211–8. doi: 10.1016/j.apcatb.2009.08.003.
[19] Paola AD, García-López E, Marcì G, Palmisano L. A survey of photocatalytic materials for environmental remediation. J Hazard Mater. 2012;211–12:3–29. doi: 10.1016/j.jhazmat.2011.11.050.
[20] Wee-Jun O, Lling-Lling T, Siang-Piao C, Siek-Ting Y, Rahman MA. Facet-dependent photocatalytic properties of TiO_2 -based composites for energy conversion and environmental remediation. Chemsuschem. 2014;7(3):690–719. doi: 10.1002/cssc.201300924.
[21] Wang X, Li Z, Shi J, Yu Y. One-dimensional titanium dioxide nanomaterials: nanowires, nanorods, and nanobelts. Chem Rev. 2014;114(19):9346–84. doi: 10.1021/cr400633s.
[22] Wang L, Sasaki T. Titanium oxide nanosheets: graphene analogues with versatile functionalities. Chem Rev. 2014;114(19):9455–86. doi: 10.1021/cr400627u.
[23] Fattakhova-Rohlfing D, Zaleska A, Bein T. Three-dimensional titanium dioxide nanomaterials. Chem Rev. 2014;114(19):9487–558. doi: 10.1021/cr500201c.
[24] Shen L, Zhang X, Li H, Yuan C, Cao G. Design and tailoring of a three-dimensional TiO_2–graphene–carbon nanotube nanocomposite for fast lithium storage. J Phys Chem Lett. 2011;2(24):3096–101. doi: 10.1021/jz201456p.
[25] De Angelis F, Di Valentin C, Fantacci S, Vittadini A, Selloni A. Theoretical studies on anatase and less common TiO_2 phases: bulk, surfaces, and nanomaterials. Chem Rev. 2014;114(19):9708–53. doi: 10.1021/cr500055q.
[26] Zhang H, Banfield JF. Structural characteristics and mechanical and thermodynamic properties of nanocrystalline TiO_2. Chem Rev. 2014;114(19):9613–44. doi: 10.1021/cr500072j.
[27] Liu L, Chen X. Titanium dioxide nanomaterials: self-structural modifications. Chem Rev. 2014;114(19):9890–918. doi: 10.1021/cr400624r.
[28] Coppens P, Chen Y, Trzop E. Crystallography and properties of polyoxotitanate nanoclusters. Chem Rev. 2014;114(19):9645–61. doi: 10.1021/cr400724e.
[29] Chen X, Mao SS. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. Chem Rev. 2007;107(7):2891–959. doi: 10.1021/cr0500535.
[30] Asahi R, Morikawa T, Irie H, Ohwaki T. Nitrogen-doped titanium dioxide as visible-light-sensitive photocatalyst: designs, developments, and prospects. Chem Rev. 2014;114(19):9824–52. doi: 10.1021/cr5000738.
[31] Nasirian M, Lin Y, Bustillo-Lecompte C, Mehrvar M. Enhancement of photocatalytic activity of titanium dioxide using non-metal doping methods under visible light: a review. Int J Env Sci Te. 2018;15:2009–32. doi: 10.1007/s13762-017-1618-2.
[32] Teh CM, Mohamed AR. 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 Alloy Compd. 2011;509(5):1648–60. doi: 10.1016/j.jallcom.2010.10.181.
[33] Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, Kontos AG, et al. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl Catal B-Environ. 2012;125:331–49. doi: 10.1016/j.apcatb.2012.05.036.
[34] Bai Y, Mora-Sero I, De Angelis F, Bisquert J, Wang P. Titanium dioxide nanomaterials for photovoltaic applications. Chem Rev. 2014;114(19):10095–130. doi: 10.1021/cr400606n.
[35] Pant B, Park M, Park SJ. Recent advances in TiO_2 films prepared by sol-gel methods for photocatalytic degradation of organic pollutants and antibacterial activities. Coatings. 2019;9(10):613. doi: 10.3390/coatings9100613.
[36] Li J, Wan W, Zhou H, Li J, Xu D. Hydrothermal synthesis of TiO_2(B) nanowires with ultrahigh surface area and their fast charging and discharging properties in Li ion batteries. Chem Commun (Camb). 2011;47(12):3439–41. doi: 10.1039/c0cc04634e.
[37] Yang G, Jiang Z, Shi H, Jones MO, Xiao T, Edwards PP, et al. Study on the photocatalysis of F–S co-doped TiO_2 prepared using solvothermal method. Appl Catal B-Environ. 2010;96(3):458–65. doi: 10.1016/j.apcatb.2010.03.004.
[38] Ding Z, Hu X, Yue PL, Lu GQ, Greenfield PF. Synthesis of anatase TiO_2 supported on porous solids by chemical vapor deposition. Catal Today. 2001;68(1):233–42. doi: 10.1016/S0920-5861(01)00298-X.
[39] Palanisamy B, Babu CM, Sundaravel B, Anandan S, Murugesan V. Sol-gel synthesis of mesoporous mixed Fe_2O_3/TiO_2 photocatalyst: application for degradation of 4-chlorophenol. J Hazard Mater. 2013;252–253:233–42. doi: 10.1016/j.jhazmat.2013.02.060.
[40] Wang Y, He Y, Lai Q, Fan M. Review of the progress in preparing nano TiO_2: An important environmental engineering material. J Env Sci. 2014;26(11):2139–77. doi: 10.1016/j.jes.2014.09.023.
[41] Pang YL, Lim S, Ong HC, Chong WT. A critical review on the recent progress of synthesizing techniques and fabrication of TiO_2-based nanotubes photocatalysts. Appl Catal A-Gen. 2014;481:127–42. doi: 10.1016/j.apcata.2014.05.007.
[42] Wetchakun K, Wetchakun N, Sakulsermsuk S. An overview of solar/visible light-driven heterogeneous photocatalysis for water purification: TiO_2-and ZnO-based photocatalysts used in suspension photoreactors. J Ind Eng Chem. 2019;71:19–49. doi: 10.1016/j.jiec.2018.11.025.
[43] Ismael M. A review and recent advances in solar-to-hydrogen energy conversion based on photocatalytic water splitting over doped-TiO_2 nanoparticles. Sol Energy. 2020;211:522–46. doi: 10.1016/j.solener.2020.09.073.
[44] Curcio MS, Oliveira MP, Waldman WR, Sanchez B, Canela MC. TiO_2 sol-gel for formaldehyde photodegradation using polymeric support: photocatalysis efficiency versus material stability. Env Sci Pollut Res Int. 2015;22(2):800–9. doi: 10.1007/s11356-014-2683-4.
[45] Li S, Chen G, Qiang S, Yin Z, Zhang Z, Chen Y. Synthesis and evaluation of highly dispersible and efficient photocatalytic TiO_2/

poly lactic acid nanocomposite films via sol-gel and casting processes. Int J Food Microbiol. 2020;331:108763. doi: 10.1016/j.ijfoodmicro.2020.108763.
[46] Malengreaux CM, Pirard SL, Bartlett JR, Heinrichs B. Kinetic study of 4-nitrophenol photocatalytic degradation over a Zn^{2+} doped TiO_2 catalyst prepared through an environmentally friendly aqueous sol–gel process. Chem Eng J. 2014;245:180–90. doi: 10.1016/j.cej.2014.01.068.
[47] Oshani F, Marandi R, Rasouli S, Farhoud MK. Photocatalytic investigations of TiO_2–P25 nanocomposite thin films prepared by peroxotitanic acid modified sol–gel method. Appl Surf Sci. 2014;311:308–13. doi: 10.1016/j.apsusc.2014.05.059.
[48] Yahaya MZ, Abdullah MZ, Mohamad AA. Centrifuge and storage precipitation of TiO_2 nanoparticles by the sol–gel method. J Alloy Compd. 2015;651:557–64. doi: 10.1016/j.jallcom.2015.08.110.
[49] Chen Z, Zhao G, Li H. Effects of water amount and ph on the crystal behavior of a TiO_2 nanocrystalline derived from a sol-gel process at a low temperature. J Am Ceram Soc. 2009;92(5):1024–9. doi: 10.1111/j.1551-2916.2009.03047.x.
[50] Macwan DP, Dave PN, Chaturvedi S. A review on nano-TiO_2 sol–gel type syntheses and its applications. J Mater Sci. 2011;46(11):3669–86. doi: 10.1007/s10853-011-5378-y.
[51] Mechiakh R, Sedrine NB, Chtourou R, Bensaha R. Correlation between microstructure and optical properties of nano-crystalline TiO_2 thin films prepared by sol–gel dip coating. Appl Surf Sci. 2010;257(3):670–6. doi: 10.1016/j.apsusc.2010.08.008.
[52] Trino LD, Bronze-Uhle ES, George A, Mathew MT, Lisboa-Filho PN. Surface physicochemical and structural analysis of functionalized titanium dioxide films. Colloid Surf A. 2018;546:168–78. doi: 10.1016/j.colsurfa.2018.03.019.
[53] Yoldas BE. Hydrolysis of titanium alkoxide and effects of hydrolytic polycondensation parameters. J Mater Sci. 1986;21:1087–92. doi: 10.1007/bf01117399.
[54] Danks AE, Hall SR, Schnepp Z. The evolution of 'sol–gel' chemistry as a technique for materials synthesis. Mater Horiz. 2016;3(2):91–112. doi: 10.1039/C5MH00260E.
[55] Guglielmi M, Carturan G. Precursors for sol-gel preparations. J Non-Cryst Solids. 1988;100(1–3):16–30. doi: 10.1016/0022-3093(88)90004-X.
[56] Suárez S, Jansson I, Ohtani B, Sánchez B. From titania nanoparticles to decahedral anatase particles: Photocatalytic activity of TiO_2/zeolite hybrids for VOCs oxidation. Catal Today. 2019;326:2–7. doi: 10.1016/j.cattod.2018.09.004.
[57] Yuan Z, Zhang J, Li B, Li J. Effect of metal ion dopants on photochemical properties of anatase TiO_2 films synthesized by a modified sol-gel method. Thin Solid Films. 2007;515(18):7091–5. doi: 10.1016/j.tsf.2007.02.101.
[58] Feng X, Zhai J, Jiang L. The fabrication and switchable superhydrophobicity of TiO_2 nanorod films. Angew Chem. 2005;117:5245–8. doi: 10.1002/ange.200501337.
[59] Wei J, Yao J, Zhang X, Zhu W, Wang H, Rhodes MJ. Hydrothermal growth of titania nanostructures with tunable phase and shape. Mater Lett. 2007;61:4610–3. doi: 10.1016/j.matlet.2007.02.070.
[60] Kwon CH, Shin H, Kim JH, Choi WS, Yoon KH. Degradation of methylene blue via photocatalysis of titanium dioxide. Mater Chem Phys. 2004;86(1):78–82. doi: 10.1016/j.matchemphys.2004.02.024.
[61] Cámara RM, Portela R, Gutiérrez-Martín F, Sánchez B. Photocatalytic activity of TiO_2 films prepared by surfactant-mediated sol–gel methods over commercial polymer substrates. Chem Eng J. 2016;283:535–43. doi: 10.1016/j.cej.2015.07.080.
[62] Cruz NKO, Semblante GU, Senoro DB, You S-J, Lu S-C. Dye degradation and antifouling properties of polyvinylidene fluoride/titanium oxide membrane prepared by sol–gel method. J Taiwan Inst Chem E. 2014;45(1):192–201. doi: 10.1016/j.jtice.2013.04.011.
[63] Hou J, Dong G, Ye Y, Chen V. Enzymatic degradation of bisphenol-A with immobilized laccase on TiO_2 sol–gel coated PVDF membrane. J Membr Sci. 2014;469:19–30. doi: 10.1016/j.memsci.2014.06.027.
[64] Mu Q, Li Y, Wang H, Zhang Q. Self-organized TiO_2 nanorod arrays on glass substrate for self-cleaning antireflection coatings. J Colloid Interf Sci. 2012;365:308–13. doi: 10.1016/j.jcis.2011.09.027.
[65] Arıer ÜÖA, Tepehan FZ. Influence of heat treatment on the particle size of nanobrookite TiO_2 thin films produced by sol–gel method. Surf Coat Tech. 2011;206:37–42. doi: 10.1016/j.surfcoat.2011.06.039.
[66] Sirirerkratana K, Kemacheevakul P, Chuangchote S. Color removal from wastewater by photocatalytic process using titanium dioxide-coated glass, ceramic tile, and stainless steel sheets. J Clean Prod. 2019;215:123–30. doi: 10.1016/j.jclepro.2019.01.037.
[67] Yamazaki S, Sonoda K, Maruoka K, Yamazaki Y, Naragino H, Honda K, et al. Porous TiO_2 adsorbed with squaraine dye as visible-light-responsive photocatalyst. J Photoch Photobio A. 2021;421:113543. doi: 10.1016/j.jphotochem.2021.113543.
[68] Simonsen ME, Søgaard EG. Sol–gel reactions of titanium alkoxides and water: influence of pH and alkoxy group on cluster formation and properties of the resulting products. J Sol-Gel Sci Techn. 2010;53:485–97. doi: 10.1007/s10971-009-2121-0.
[69] Fröschl T, Hörmann U, Kubiak P, Kučerová G, Pfanzelt M, Weiss CK, et al. High surface area crystalline titanium dioxide: potential and limits in electrochemical energy storage and catalysis. Chem Soc Rev. 2012;41(15):5313–60. doi: 10.1039/C2CS35013K水.
[70] Muthee DK, Dejene BF. The effect of tetra isopropyl orthotitanate (TIP) concentration on structural, and luminescence properties of titanium dioxide nanoparticles prepared by sol-gel method. Mat Sci Semicon Proc. 2020;106:104783. doi: 10.1016/j.mssp.2019.104783.
[71] Kuzin E, Krutchinina N. Hydrolysis and chemical activity of aqueous $TiCl_4$ solutions. Inorg Mater. 2019;55:834–7. doi: 10.1134/s0020168519080065.
[72] Bahloul W, Oddes O, Bounor-Legaré V, Mélis F, Cassagnau P, Vergnes B. Reactive extrusion processing of polypropylene/TiO_2 nanocomposites by in situ synthesis of the nanofillers: Experiments and modeling. Aiche J. 2011;57(8):2174–84. doi: 10.1002/aic.12425.
[73] Kinoshita M, Kamizato T, Shimoyama Y. Effect of precursor structure on mixed-crystal phase titanium oxide synthesized by sol-gel reaction in supercritical carbon dioxide. J Supercrit Fluids. 2018;138:193–9. doi: 10.1016/j.supflu.2018.04.017.
[74] Nolan NT, Seery MK, Pillai SC. Spectroscopic investigation of the anatase-to-rutile transformation of sol− gel-synthesized TiO_2 photocatalysts. J Phys Chem C. 2009;113(36):16151–7. doi: 10.1021/jp904358g.
[75] Ge L, Xu M, Fang H, Sun M. Preparation of TiO_2 thin films from autoclaved sol containing needle-like anatase crystals. Appl Surf Sci. 2006;253(2):720–5. doi: 10.1016/j.apsusc.2005.12.162.
[76] Cheng C, Rad S. Preparation of nano TiO_2 filmcoated crushed glass via sol-gel method for the removal of biodegradable contaminants (unpublished).
[77] Kajitvichyanukul P, Ananpattarachai J, Pongpom S. Sol–gel preparation and properties study of TiO_2 thin film for photocatalytic

reduction of chromium(VI) in photocatalysis process. Sci Technol Adv Mat. 2005;6(3–4):352. doi: 10.1016/j.stam.2005.02.014.
[78] Chen H-S, Kumar RV. Sol–gel TiO_2 in self-organization process: Growth, ripening and sintering. RSC Adv. 2012;2(6):2294–301. doi: 10.1039/c2ra00782g.
[79] Golobostanfard MR, Abdizadeh H. Effect of mixed solvent on structural, morphological, and optoelectrical properties of spin-coated TiO_2 thin films. Ceram Int. 2012;38(7):5843–51. doi: 10.1016/j.ceramint.2012.04.034.
[80] Mahyar A, Amani-Ghadim AR. Influence of solvent type on the characteristics and photocatalytic activity of TiO_2 nanoparticles prepared by the sol-gel method. Micro Nano Lett. 2011;6(4):244–8. doi: 10.1049/mnl.2011.0058.
[81] Hu L, Yoko T, Kozuka H, Sakka S. Effects of solvent on properties of sol—gel-derived TiO_2 coating films. Thin Solid Films. 1992;219(1–2):18–23. doi: 10.1016/0040-6090(92)90718-Q.
[82] Naumenko A, Gnatiuk I, Smirnova N, Eremenko A. Characterization of sol–gel derived TiO_2/ZrO_2 films and powders by Raman spectroscopy. Thin Solid Films. 2012;520(14):4541–6. doi: 10.1016/j.tsf.2011.10.189.
[83] Sievers NV, Pollo LD, Corção G, Medeiros, Cardozo NS. In situ synthesis of nanosized TiO_2 in polypropylene solution for the production of films with antibacterial activity. Mater Chem Phys. 2020;246:122824. doi: 10.1016/j.matchemphys.2020.122824.
[84] Zhang L, Bai H, Liu L, Sun DD. Dimension induced intrinsic physio-electrical effects of nanostructured TiO_2 on its antibacterial properties. Chem Eng J. 2018;334:1309–15. doi: 10.1016/j.cej.2017.11.075.
[85] Wang C, Cai X, Chen Y, Cheng Z, Luo X, Mo S, et al. Improved hydrogen production from glycerol photoreforming over sol-gel derived TiO_2 coupled with metal oxides. Chem Eng J. 2017;317:522–32. doi: 10.1016/j.cej.2017.02.033.
[86] Hafizah N, Sopyan I. Nanosized TiO_2 photocatalyst powder via sol-gel method: effect of hydrolysis degree on powder properties. Int J Photoenergy. 2009;2009:962783. doi: 10.1155/2009/962783.
[87] Roevens A, Van Dijck JG, Tassi M, D'Haen J, Carleer R, Adriaensens P, et al. Revealing the influence of the solvent in combination with temperature, concentration and pH on the modification of TiO_2 with 3PA. Mater Chem Phys. 2016;184:324–34. doi: 10.1016/j.matchemphys.2016.09.059.
[88] Seisenbaeva GA, Daniel G, Nedelec J-M, Kessler VG. Solution equilibrium behind the room-temperature synthesis of nano-crystalline titanium dioxide. Nanoscale. 2013;5(8):3330–6. doi: 10.1039/c3nr34068f.
[89] Tashiro K, Tanimura T, Yamazaki S. Photocatalytic degradation of gaseous trichloroethylene on porous titanium dioxide pellets modified with copper(II) under visible light irradiation. J Photoch Photobio A. 2019;377:228–35. doi: 10.1016/j.jphotochem.2019.03.037.
[90] Malengreaux CM, Timmermans A, Pirard SL, Lambert SD, Pirard J-P, Poelman D, et al. Optimized deposition of TiO_2 thin films produced by a non-aqueous sol–gel method and quantification of their photocatalytic activity. Chem Eng J. 2012;195:347–58. doi: 10.1016/j.cej.2012.04.076.
[91] Boujday S, Wünsch F, Portes P, Bocquet J-F, Colbeau-Justin C. Photocatalytic and electronic properties of TiO_2 powders elaborated by sol–gel route and supercritical drying. Sol Energ Mat Sol C. 2004;83(4):421–33. doi: 10.1016/j.solmat.2004.02.035.
[92] Avci N, Smet PF, Poelman H, Van de Velde N, De Buysser K, Van Driessche I, et al. Characterization of TiO_2 powders and thin films prepared by non-aqueous sol–gel techniques. J Sol-Gel Sci Techn. 2009;52:424–31. doi: 10.1007/s10971-009-2028-9.
[93] Jia F, Zhang L, Shang X, Yang Y. Non-aqueous sol–gel approach towards the controllable synthesis of nickel nanospheres, nanowires, and nanoflowers. Adv Mater. 2008;20(5):1050–4. doi: 10.1002/adma.200702159.
[94] Agafonov A, Davydova O, Krayev A, Ivanova O, Evdokimova O, Gerasimova T, et al. Unexpected effects of activator molecules' polarity on the electroreological activity of titanium dioxide nanopowders. J Phys Chem B. 2017;121(27):6732–8. doi: 10.1021/acs.jpcb.7b04131.
[95] Shan AY, Ghazi TIM, Rashid SA. Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review. Appl Catal A-Gen. 2010;389(1–2):1–8. doi: 10.1016/j.apcata.2010.08.053.
[96] Singh KB, Tirumkudulu MS. Cracking in drying colloidal films. Phys Rev Lett. 2007;98(21):218302. doi: 10.1103/PhysRevLett.98.218302.
[97] Lucky RA, Sui R, Lo JMH, Charpentier PA. Effect of solvent on the crystal growth of one-dimensional ZrO_2–TiO_2 nanostructures. Cryst Growth Des. 2010;10:1598–604. doi: 10.1021/cg901145d.
[98] Wetchakun N, Incessungvorn B, Wetchakun K, Phanichphant S. Influence of calcination temperature on anatase to rutile phase transformation in TiO_2 nanoparticles synthesized by the modified sol–gel method. Mater Lett. 2012;82:195–8. doi: 10.1016/j.matlet.2012.05.092.
[99] Han C, Andersen J, Likodimos V, Falaras P, Linkugel J, Dionysiou DD. The effect of solvent in the sol–gel synthesis of visible light-activated, sulfur-doped TiO_2 nanostructured porous films for water treatment. Catal Today. 2014;224:132–9. doi: 10.1016/j.cattod.2013.11.052.
[100] Rahmani-Azad M, Najafi A, Rahmani-Azad N, Khalaj G. Improvement of ZrB_2 nanopowder synthesis by sol-gel method via zirconium alkoxide/boric acid precursors. J Sol-Gel Sci Techn. 2022;103(1):87–96. doi: 10.1007/s10971-022-05788-y.
[101] Lewkowicz A, Synak A, Grobelna B, Bojarski P, Bogdanowicz R, Karczewski J, et al. Thickness and structure change of titanium(IV) oxide thin films synthesized by the sol–gel spin coating method. Opt Mater. 2014;36(10):1739–44. doi: 10.1016/j.optmat.2014.02.033.
[102] Ortiz-Islas E, López T, Gomez R, Navarrete J. Effect of phosphate ions in the properties of titania sol-gel. J Sol-Gel Sci Techn. 2006;37:165–8. doi: 10.1007/s10971-005-6622-1.
[103] Verma R, Singh S, Dalai MK, Saravanan M, Agrawal VV, Srivastava AK. Photocatalytic degradation of polypropylene film using TiO2-based nanomaterials under solar irradiation. Mater Des. 2017;133:10–8. doi: 10.1016/j.matdes.2017.07.042.
[104] Cassaignon S, Koelsch M, Jolivet J-P. From $TiCl_3$ to TiO_2 nanoparticles (anatase, brookite and rutile): Thermohydrolysis and oxidation in aqueous medium. J Phys Chem Solids. 2007;68(5–6):695–700. doi: 10.1016/j.jpcs.2007.02.020.
[105] Wahi RK, Liu Y, Falkner JC, Colvin VL. Solvothermal synthesis and characterization of anatase TiO_2 nanocrystals with ultrahigh surface area. J Colloid Interf Sci. 2006;302(2):530–6. doi: 10.1016/j.jcis.2006.07.003.
[106] Bakre PV, Volvoikar PS, Vernekar AA, Tilve SG. Influence of acid chain length on the properties of TiO_2 prepared by sol-gel method and LC-MS studies of methylene blue photodegradation. J Colloid Interf Sci. 2016;474:58–67. doi: 10.1016/j.jcis.2016.04.011.

[107] Bahloul W, Bounor-Legaré V, David L, Cassagnau P. Morphology and viscoelasticity of PP/TiO_2nanocomposites prepared by in situ sol-gel method. J Polym Sci Pol Phys. 2010;48:1213–22. doi: 10.1002/polb.22012.

[108] Xiaoming F. Synthesis and optical absorpition properies of anatase TiO_2 nanoparticles via a hydrothermal hydrolysis method. Rare Met Mat Eng. 2015;44:1067–70. doi: 10.1016/s1875-5372(15)30068-0.

[109] Yu J, Jimmy CY, Leung MK-P, Ho W, Cheng B, Zhao X, et al. Effects of acidic and basic hydrolysis catalysts on the photocatalytic activity and microstructures of bimodal mesoporous titania. J Catal. 2003;217(1):69–78. doi: 10.1016/S0021-9517(03)00034-4.

[110] Zhao G, Li H, Zhang J, Chen Z, Han G, Song B. Effects of preparation parameters on room temperature formation of vanadium-doped TiO_2 nanocrystalline powder. J Am Ceram Soc. 2011;94(1):71–6. doi: 10.1111/j.1551-2916.2010.04033.x.

[111] Chen Y-F, Lee C-Y, Yeng M-Y, Chiu H-T. The effect of calcination temperature on the crystallinity of TiO_2 nanopowders. J Cryst Growth. 2003;247(3–4):363–70. doi: 10.1016/S0022-0248(02)01938-3.

[112] Jimmy CY, Yu J, Zhao J. Enhanced photocatalytic activity of mesoporous and ordinary TiO_2 thin films by sulfuric acid treatment. Appl Catal B-Environ. 2002;36(1):31–43. doi: 10.1016/S0926-3373(01)00277-6.

[113] Wang Z, Xia D, Chen G, Yang T, Chen Y. The effects of different acids on the preparation of TiO_2 nanostructure in liquid media at low temperature. Mater Chem Phys. 2008;111(2-3):313–6. doi: 10.1016/j.matchemphys.2008.04.015.

[114] Bai X, Xie B, Pan N, Wang X, Wang H. Novel three-dimensional dandelion-like TiO_2 structure with high photocatalytic activity. J Solid State Chem. 2008;181(3):450–6. doi: 10.1016/j.jssc.2007.12.019.

[115] Sridevi DV, Ramya Devi KT, Jayakumar N. pH dependent synthesis of TiO_2 nanoparticles exerts its effect on bacterial growth inhibition and osteoblasts proliferation. Aip Adv. 2020;10(9):095119. doi: 10.1063/5.0020029.

[116] Behnajady MA, Eskandarloo H. Preparation of TiO_2 nanoparticles by the sol–gel method under different pH conditions and modeling of photocatalytic activity by artificial neural network. Res Chem Intermediat. 2015;41(4):2001–17. doi: 10.1007/s11164-013-1327-5.

[117] Bano I, Kumar RV, Hameed A. Influence of pH on the preparation of dispersed Ag–TiO_2 nanocomposite. Ionics. 2012;18(3):307–13. doi: 10.1007/s11581-011-0625-4.

[118] Sun R, Chen Z, Peng J, Zheng T. The effect mechanisms of pH, complexant and calcination temperature on the hydrophilicity of TiO_2 films prepared by the sol-gel method. Appl Surf Sci. 2018;462:480–8. doi: 10.1016/j.apsusc.2018.08.163.

[119] Chen W, Shen H, Zhu X, Xing Z, Zhang S. Effect of citric acid on structure and photochromic properties of WO_3–TiO_2–ZnO composite films prepared by a sol–gel method. Ceram Int. 2015;41(10):12638–43. doi: 10.1016/j.ceramint.2015.06.093.

[120] Tian G, Fu H, Jing L, Tian C. Synthesis and photocatalytic activity of stable nanocrystalline TiO_2 with high crystallinity and large surface area. J Hazard Mater. 2009;161(2–3):1122–30. doi: 10.1016/j.jhazmat.2008.04.065.

[121] Kment Š, Gregora I, Kmentová H, Novotná P, Hubička Z, Krýsa J, et al. Raman spectroscopy of dip-coated and spin-coated sol–gel TiO_2 thin films on different types of glass substrate. J Sol-Gel Sci Techn. 2012;63(3):294–306. doi: 10.1007/s10971-012-2787-6.

[122] Ravishankar T, Vaz MdO, Teixeira S. The effects of surfactant in the sol–gel synthesis of CuO/TiO_2 nanocomposites on its photocatalytic activities under UV-visible and visible light illuminations. N J Chem. 2020;44(5):1888–904. doi: 10.1039/c9nj05246a.

[123] Parsa SM, Yazdani A, Dhahad H, Alawee WH, Hesabi S, Norozpour F, et al. Effect of Ag, Au, TiO2 metallic/metal oxide nanoparticles in double-slope solar stills via thermodynamic and environmental analysis. J Clean Prod. 2021;311:127689. doi: 10.1016/j.jclepro.2021.127689.

[124] Sarker S, Nath N, Rahman MM, Lim SS, Ahammad A, Choi WY, et al. TiO2 paste formulation for crack-free mesoporous nanocrystalline film of dye-sensitized solar cells. J Nanosci Nanotechnol. 2012;12(7):5361–6. doi: 10.1166/jnn.2012.6398.

[125] Jaseela P, Garvasis J, Joseph A. Selective adsorption of methylene blue (MB) dye from aqueous mixture of MB and methyl orange (MO) using mesoporous titania (TiO_2)–poly vinyl alcohol (PVA) nanocomposite. J Mol Liq. 2019;286:110908. doi: 10.1016/j.molliq.2019.110908.

[126] Liu T, Chen W, Liu X, Zhu J, Lu L. Well-dispersed ultrafine nitrogen-doped TiO_2 with polyvinylpyrrolidone (PVP) acted as N-source and stabilizer for water splitting. J Energy Chem. 2016;25(1):1–9. doi: 10.1016/j.jechem.2015.11.009.

[127] Takahashi Y, Matsuoka Y. Dip-coating of TiO_2 films using a sol derived from Ti (O-i-Pr)$_4$-diethanolamine-H_2O-i-PrOH system. J Mater Sci. 1988;23:2259–66. doi: 10.1007/bf01115798.

[128] Faure B, Salazar-Alvarez G, Ahniyaz A, Villaluenga I, Berriozabal G, De Miguel YR, et al. Dispersion and surface functionalization of oxide nanoparticles for transparent photocatalytic and UV-protecting coatings and sunscreens. Sci Technol Adv Mat. 2013;14(2):023001. doi: 10.1088/1468-6996/14/2/023001.

[129] Deiss JL, Anizan P, El Hadigui S, Wecker C. Steric stability of TiO_2 nanoparticles in aqueous dispersions. Colloid Surf A. 1996;106(1):59–62. doi: 10.1016/0927-7757(95)03353-x.

[130] Chaúque EF, Adelodun AA, Dlamini LN, Greyling CJ, Ray SC, Ngila JC. Synthesis and photocatalytic application of TiO_2 nanoparticles immobilized on polyacrylonitrile nanofibers using EDTA chelating agents. Mater Chem Phys. 2017;192:108–24. doi: 10.1016/j.matchemphys.2017.01.016.

[131] Meichtry JM, Brusa M, Mailhot G, Grela MA, Litter MI. Heterogeneous photocatalysis of Cr(VI) in the presence of citric acid over TiO_2 particles: relevance of Cr(V)–citrate complexes. Appl Catal B-Environ. 2007;71(1–2):101–7. doi: 10.1016/j.apcatb.2006.09.002.

[132] Kurajica S. A Brief Review on the Use of Chelation Agents in Sol-gel Synthesis with Emphasis on β-Diketones and β-Ketoesters. Chem Biochem Eng Q. 2019;33(3):295–301. doi: 10.15255/CABEQ.2018.1566.

[133] Chen Y, Dionysiou DD. A comparative study on physicochemical properties and photocatalytic behavior of macroporous TiO_2 -P25 composite films and macroporous TiO_2 films coated on stainless steel substrate. Appl Catal A-Gen. 2006;317(1):64–72. doi: 10.1016/j.apcata.2006.10.025.

[134] Pénard A-L, Gacoin T, Boilot J-P. Functionalized sol–gel coatings for optical applications. Accounts Chem Res. 2007;40(9):895–902. doi: 10.1021/ar600025j.

[135] Díaz-García ME, Laínño RB. Molecular imprinting in sol-gel materials: Recent developments and applications. Microchim Acta. 2005;149:19–36. doi: 10.1007/s00604-004-0274-7.

[136] Chen D, Cao L, Huang F, Imperia P, Cheng Y-B, Caruso RA. Synthesis of monodisperse mesoporous titania beads with controllable diameter, high surface areas, and variable pore

diameters (14– 23 nm). J Am Chem Soc. 2010;132(12):4438–44. doi: 10.1021/ja100040p.
[137] Liu J, Han R, Wang H, Zhao Y, Chu Z, Wu H. Photoassisted degradation of pentachlorophenol in a simulated soil washing system containing nonionic surfactant Triton X-100 with La–B codoped TiO_2 under visible and solar light irradiation. Appl Catal B-Environ. 2011;103(3–4):470–8. doi: 10.1016/j.apcatb.2011.02.013.
[138] G-y Huang, S-m Xu, L-y Li, X-j Wang. Effect of surfactants on dispersion property and morphology of nano-sized nickel powders. T Nonferr Met Soc. 2014;24(11):3739–46. doi: 10.1016/S1003-6326(14)63523-8.
[139] Ren T-Z, Yuan Z-Y, Su B-L. Surfactant-assisted preparation of hollow microspheres of mesoporous TiO_2. Chem Phys Lett. 2003;374(1–2):170–5. doi: 10.1016/S0009-2614(03)00722-X.
[140] Xin B, Wang L, Jia C. Stably superhydrophobic (IL/TiO_2) hybrid films: Intelligent self-cleaning materials. Appl Surf Sci. 2015;357:2248–54. doi: 10.1016/j.apsusc.2015.09.218.
[141] Jin J, Gu KS, Taekyung Y, Min C, Jinwoo L, Jeyong Y, et al. Large-scale synthesis of TiO_2 nanorods via nonhydrolytic sol-gel ester elimination reaction and their application to photocatalytic inactivation of E. coli. J Phys Chem B. 2005;109(32):15297–302. doi: 10.1021/jp052458z.
[142] Noorimotlagh Z, Kazeminezhad I, Jaafarzadeh N, Ahmadi M, Ramezani Z. Improved performance of immobilized TiO_2 under visible light for the commercial surfactant degradation: Role of carbon doped TiO_2 and anatase/rutile ratio. Catal Today. 2020;348:277–89. doi: 10.1016/j.cattod.2019.08.051.
[143] Wang D, Choi D, Yang Z, Viswanathan VV, Nie Z, Wang C, et al. Synthesis and Li-ion insertion properties of highly crystalline mesoporous rutile TiO_2. Chem Mater. 2008;20(10):3435–42. doi: 10.1021/cm8002589.
[144] Ananpattarachai J, Kajitvichyanukul P, Seraphin S. Visible light absorption ability and photocatalytic oxidation activity of various interstitial N-doped TiO_2 prepared from different nitrogen dopants. J Hazard Mater. 2009;168(1):253–61. doi: 10.1016/j.jhazmat.2009.02.036.
[145] Park Y, Kim W, Park H, Tachikawa T, Majima T, Choi W. Carbon-doped TiO_2 photocatalyst synthesized without using an external carbon precursor and the visible light activity. Appl Catal B-Environ. 2009;91(1–2):355–61. doi: 10.1016/j.apcatb.2009.06.001.
[146] Ghasemi S, Rahimnejad S, Setayesh SR, Rohani S, Gholami M. Transition metal ions effect on the properties and photocatalytic activity of nanocrystalline TiO_2 prepared in an ionic liquid. J Hazard Mater. 2009;172(2–3):1573–8. doi: 10.1016/j.jhazmat.2009.08.029.
[147] Wu S, Shen L, Lin Y, Yin K, Yang C. Sulfite-based advanced oxidation and reduction processes for water treatment. Chem Eng J. 2021;414:128872. doi: 10.1016/j.cej.2021.128872.
[148] Diban N, Pacuła A, Kumakiri I, Barquín C, Rivero MJ, Urtiaga A, et al. TiO_2–zeolite metal composites for photocatalytic degradation of organic pollutants in water. Catalysts. 2021;11(11):1367. doi: 10.3390/catal11111367.
[149] Chand R, Obuchi E, Katoh K, Luitel HN, Nakano K. Effect of transition metal doping under reducing calcination atmosphere on photocatalytic property of TiO_2 immobilized on SiO_2 beads. J Env Sci. 2013;25(7):1419–23. doi: 10.1016/S1001-0742(12)60211-3.
[150] Di Valentin C, Pacchioni G. Trends in non-metal doping of anatase TiO_2: B, C, N and F. Catal Today. 2013;206:12–8. doi: 10.1016/j.cattod.2011.11.030.
[151] Sharifi F, Mahmoodi Z, Abbasi SM, Najafi A, Khalaj G. Synthesis and characterization of mesoporous TiC nanopowder/nanowhisker with low residual carbon processed by sol–gel method. J Mater Res Technol. 2023;22:2462–72. doi: 10.1016/j.jmrt.2022.12.097.
[152] Mou P, Pal U, Jiménez J, Pérez-Rodríguez F. Effects of crystallization and dopant concentration on the emission behavior of TiO_2:Eu nanophosphors. Nanoscale Res Lett. 2012;7(1):1–6. doi: 10.1186/1556-276X-7-1.
[153] Chen D, Jiang Z, Geng J, Wang Q, Yang D. Carbon and nitrogen co-doped TiO_2 with enhanced visible-light photocatalytic activity. Ind Eng Chem Res. 2007;46(9):2741–6. doi: 10.1021/ie061491k.
[154] Opoku F, Govender KK, van Sittert CG, Govender PP. Understanding the mechanism of enhanced charge separation and visible light photocatalytic activity of modified wurtzite ZnO with nanoclusters of ZnS and graphene oxide: from a hybrid density functional study. N J Chem. 2017;41:8140. doi: 10.1039/c7nj01942d.
[155] Misra R, Fu BX, Morgan SE. Surface energetics, dispersion, and nanotribomechanical behavior of POSS/PP hybrid nanocomposites. J Polym Sci Pol Phys. 2010;45(17):2441–55. doi: 10.1002/polb.21261.
[156] Fu P, Zhang P. Uniform dispersion of Au nanoparticles on TiO_2 film via electrostatic self-assembly for photocatalytic degradation of bisphenol A. Appl Catal B-Environ. 2010;96(1–2):176–84. doi: 10.1016/j.apcatb.2010.02.017.
[157] Lei XF, Zhang ZN, Wu ZX, Piao YJ, Chen C, Li X, et al. Synthesis and characterization of Fe, N and C tri-doped polymorphic TiO_2 and the visible light photocatalytic reduction of Cr(VI). Sep Purif Technol. 2017;174:66–74. doi: 10.1016/j.seppur.2016.09.039.
[158] Trin J, Nagahiro S, Mali H. Photoinduced glycerol oxidation over plasmonic Au and AuM (M = Pt, Pd and Bi) nanoparticle-decorated TiO_2 photocatalysts. Nanomaterials-Basel. 2018;8(4):269. doi: 10.3390/nano8040269.
[159] Huang S, Yu Y, Yan Y, Yuan J, Cao Y. Enhanced photocatalytic activity of TiO_2 activated by doping Zr and modifying Pd. Rsc Adv. 2016;6(36):29950–7. doi: 10.1039/c6ra03275c.
[160] Peng L, Xie T, Lu Y, Fan H, Wang D. Synthesis, photoelectric properties and photocatalytic activity of the Fe_2O_3/TiO_2 heterogeneous photocatalysts. Phys Chem Chem Phys. 2010;12(28):8033–41. doi: 10.1039/c002460k.
[161] Ramos-Delgado NA, Gracia-Pinilla MA, Maya-Trevino L, Hinojosa-Reyes L, Guzman-Mar JL, Hernández-Ramírez A. Solar photocatalytic activity of TiO_2 modified with WO_3 on the degradation of an organophosphorus pesticide. J Hazard Mater. 2013;263(Pt 1):36–44. doi: 10.1016/j.jhazmat.2013.07.058.
[162] Johari ND, Rosli ZM, Juoi JM, Yazid SA. Comparison on the TiO_2 crystalline phases deposited via dip and spin coating using green sol–gel route. J Mater Res Technol. 2019;8(2):2350–8. doi: 10.1016/j.jmrt.2019.04.018.
[163] Najafi A, Sharifi F, Mesgari-Abbasi S, Khalaj G. Influence of pH and temperature parameters on the sol-gel synthesis process of meso porous ZrC nanopowder. Ceram Int. 2022;48(18):26725–31. doi: 10.1016/j.ceramint.2022.05.367.
[164] Venkatachalam N, Palanichamy M, Murugesan V. Sol–gel preparation and characterization of nanosize TiO_2: Its photocatalytic performance. Mater Chem Phys. 2007;104(2–3):454–9. doi: 10.1016/j.matchemphys.2007.04.003.
[165] Kim SH, Kwak S-Y, Sohn B-H, Park TH. Design of TiO_2 nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem. J Membr Sci. 2003;211(1):157–65. doi: 10.1016/s0376-7388(02)00418-0.

[166] Lee I, Zaera F. Use of Au@Void@TiO_2 yolk-shell nanostructures to probe the influence of oxide crystallinity on catalytic activity for low-temperature oxidations. J Chem Phy. 2019;151(23):234706. doi: 10.1063/1.5132715.
[167] Moscato S, Cascone MG, Lazzeri L, Danti S, Mattii L, Dolfi A, et al. Morphological features of ovine embryonic lung fibroblasts cultured on different bioactive scaffolds. J Biomed Mater Res A. 2006;76(1):214–21. doi: 10.1002/jbm.a.30538.
[168] Jia-Guo Y, Jimmy CY. Low Temperature Solvent Evaporation – Induced Crystallization Synthesis of Nanocrystalline TiO2 Photocatalyst. Chin J Chem. 2003;21(8):994–7. doi: 10.1002/cjoc.20030210803.
[169] Yoshida K, Makihara M, Tanaka N, Aoyagi S, Nishibori E, Sakata M, et al. Specific surface area and three-dimensional nanostructure measurements of porous Titania photocatalysts by electron tomography and their relation to photocatalytic activity. Microsc Microanal. 2011;17(2):264–73. doi: 10.1017/S1431927610094419.
[170] Barlier V, Léonard D, Boiteux G, Davenas J, Boisson F, Bounor-Legaré V. New TiO_2 precursor for TiO_2: poly (N-vinylcarbazole) (PVK) thin film: Synthesis and reactivity to hydrolysis of titanium tetrakis (9H-carbazole-9-yl-ethyl-oxy). J Non-Cryst Solids. 2009;355(6):386–92. doi: 10.1016/j.jnoncrysol.2008.12.007.
[171] Kumar K, Zaspalis VT, Keizer K, Burggraaf AJ. Drying process in the formation of sol-gel-derived TiO_2 ceramic membrane. J Non-Cryst Solids. 1993;147–148(147):375–81. doi: 10.1016/S0022-3093(05)80646-5.
[172] Matsuda A, Kogure T, Matsuno Y, Katayama S, Tsuno T, Tohge N, et al. Structural changes of sol–gel-derived TiO_2–SiO_2 coatings in an environment of high temperature and high humidity. J Am Ceram Soc. 1993;76(11):2899–903. doi: 10.1111/j.1151-2916.1993.tb04034.x.
[173] Ahmed MI, Ahamed JU. TiO2 nanolubricant: An approach for performance improvement in a domestic air conditioner. Res Mater. 2022;13:100255. doi: 10.1016/j.rinma.2022.100255.
[174] Slunecko J, Kosec M, Holc J, Drazic G, Orel B. Morphology and crystallization behavior of sol–gel-derived titania. J Am Ceram Soc. 1998;81(5):1121–4. doi: 10.1111/j.1151-2916.1998.tb02458.x.
[175] Habibi MH, Nasr-Esfahani M, Egerton TA. Preparation, characterization and photocatalytic activity of TiO_2/methylcellulose nanocomposite films derived from nanopowder TiO_2 and modified sol–gel titania. J Mater Sci. 2007;42:6027–35. doi: 10.1007/s10853-006-1149-6.
[176] Liu G, Liu Y, Yang G, Li S, Zu Y, Zhang W, et al. Preparation of titania–silica mixed oxides by a sol– gel route in the presence of citric acid. J Phys Chem C. 2009;113(21):9345–51. doi: 10.1021/jp900577c.
[177] Arconada N, Castro Y, Durán A. Photocatalytic properties in aqueous solution of porous TiO_2-anatase films prepared by sol–gel process. Appl Catal A-Gen. 2010;385(1–2):101–7. doi: 10.1016/j.apcata.2010.06.051.
[178] Zolgharnein J, Bagtash M, Asanjarani N. Hybrid central composite design approach for simultaneous optimization of removal of alizarin red S and indigo carmine dyes using cetyltrimethylammonium bromide-modified TiO_2 nanoparticles. J Env Chem Eng. 2014;2(2):988–1000. doi: 10.1016/j.jece.2014.03.017.
[179] Habibi S, Jamshidi M. Sol–gel synthesis of carbon-doped TiO_2 nanoparticles based on microcrystalline cellulose for efficient photocatalytic degradation of methylene blue under visible light. Env Technol. 2020;41:3233–47. doi: 10.1080/09593330.2019.1604815.
[180] Barati N, Sani MF, Ghasemi H, Sadeghian Z, Mirhoseini S. Preparation of uniform TiO_2 nanostructure film on 316L stainless steel by sol–gel dip coating. Appl Surf Sci. 2009;255(20):8328–33. doi: 10.1016/j.apsusc.2009.05.048.
[181] Wang X, Shi F, Gao X, Fan C, Huang W, Feng X. A sol–gel dip/spin coating method to prepare titanium oxide films. Thin Solid Films. 2013;548:34–9. doi: 10.1016/j.tsf.2013.08.056.
[182] Gao S-A, Xian A-P, Cao L-H, Xie R-C, Shang J-K. Influence of calcining temperature on photoresponse of TiO_2 film under nitrogen and oxygen in room temperature. Sens Actuat B-Chem. 2008;134(2):718–26. doi: 10.1016/j.snb.2008.06.017.
[183] Ji G, Shi Z, Zhang W, Zhao G. Tribological properties of titania nanofilms coated on glass surface by the sol–gel method. Ceram Int. 2014;40(3):4655–62. doi: 10.1016/j.ceramint.2013.09.006.
[184] Mathumba P, Kuvarega AT, Dlamini LN, Malinga SP. Synthesis and characterisation of titanium dioxide nanoparticles prepared within hyperbranched polyethylenimine polymer template using a modified sol–gel method. Mater Lett. 2017;195:172–7. doi: 10.1016/j.matlet.2017.02.108.
[185] Bamne J, Taiwade K, Sharma P, Haque FZ, editors. Effect of calcination temperature on the growth of TiO_2 nanoparticle prepared via sol-gel method using triton X-100 as surfactant. Aip Conference Proceedings. AIP Publishing; 2018;2039:020076.
[186] Samie L, Beitollahi A, Faal-Nazari N, Nejad M, Akbar M, Vinu A. Effect of humidity treatment on the structure and photocatalytic properties of titania mesoporous powder. J Mater Sci. 2011;22:273–80. doi: 10.1007/s10854-010-0127-6.
[187] Ji H, Li X, Chen D. Cymbiola nobilis shell: Toughening mechanisms in a crossed-lamellar structure. Sci Rep-UK. 2017;7:40043. doi: 10.1038/srep40043.
[188] Bu T, Wen M, Zou H, Wu J, Zhou P, Li W, et al. Humidity controlled sol-gel Zr/TiO_2 with optimized band alignment for efficient planar perovskite solar cells. Sol Energy. 2016;139:290–6. doi: 10.1016/j.solener.2016.10.003.
[189] Yang J, Xu JJ. Nonaqueous sol-gel synthesis of high-performance $LiFePO_4$. Electrochem Solid-State Lett. 2004;7(12):A515. doi: 10.1149/1.1819893.
[190] Latibari ST, Mehrali M, Mehrali M, Mahlia TMI, Metselaar HSC. Synthesis, characterization and thermal properties of nanoencapsulated phase change materials via sol–gel method. Energy. 2013;61:664–72. doi: 10.1016/j.energy.2013.09.012.
[191] Pirzada T, Ashrafi Z, Xie W, Khan SA. Cellulose silica hybrid nanofiber aerogels: from sol–gel electrospun nanofibers to multifunctional aerogels. Adv Funct Mater. 2020;30(5):1907359. doi: 10.1002/adfm.201907359.
[192] Sun W, Ma J, Xi Z, Lin Y, Wang B, Hao C. Titanium oxide-coated titanium-loaded metal organic framework (MOF-Ti) nanoparticles show improved electrorheological performance. Soft Matter. 2020;16(40):9292–305. doi: 10.1039/d0sm01147a.
[193] Pinto D, Bernardo L, Amaro A, Lopes S. Mechanical properties of epoxy nanocomposites using titanium dioxide as reinforcement–a review. Constr Build Mater. 2015;95:506–24. doi: 10.4028/www.scientific.net/JNanoR.30.9.
[194] Sayilkan F, Asiltürk M, Sayilkan H, Önal Y, Akarsu M, Arpaç E. Characterization of TiO_2 synthesized in alcohol by a sol-gel process: the effects of annealing temperature and acid catalyst. Turk J Chem. 2005;29(6):697–706.
[195] Šefčík J, McCormick AV. Kinetic and thermodynamic issues in the early stages of sol-gel processes using silicon alkoxides. Catal Today. 1997;35(3):205–23. doi: 10.1016/S0920-5861(96)00158-7.

[196] Chang S-M, Doong R-A. Characterization of Zr-doped TiO_2 nanocrystals prepared by a nonhydrolytic sol–gel method at high temperatures. J Phys Chem B. 2006;110(42):20808–14. doi: 10.1021/jp0626566.

[197] Siwińska-Stefańska K, Zdarta J, Paukszta D, Jesionowski T. The influence of addition of a catalyst and chelating agent on the properties of titanium dioxide synthesized via the sol–gel method. J Sol-Gel Sci Techn. 2015;75:264–78. doi: 10.1007/s10971-015-3696-2.

[198] Wang X, Li Y, Wei J, De, Groot K. Development of biomimetic nanohydroxyapatite/poly (hexamethylene adipamide) composites. Biomaterials. 2002;23(24):4787–91. doi: 10.1016/S0142-9612(02)00229-6.

[199] Xu P, Zheng M, Chen N, Wu Z, Xu N, Tang J, et al. Uniform magnetic chitosan microspheres with radially oriented channels by electrostatic droplets method for efficient removal of Acid Blue. J Taiwan Inst Chem E. 2019;104:210–8. doi: 10.1016/j.jtice.2019.09.016.

[200] Forgacs A, Moldovan K, Herman P, Baranyai E, Fabian I, Lente GB, et al. Kinetic model for hydrolytic nucleation and growth of TiO_2 nanoparticles. J Phys Chem C. 2018;122(33):19161–70. doi: 10.1021/acs.jpcc.8b04227.

[201] Charbonneau C, Gauvin R, Demopoulos G. Nucleation and growth of self-assembled nanofibre-structured rutile (TiO_2) particles via controlled forced hydrolysis of titanium tetrachloride solution. J Cryst Growth. 2009;312(1):86–94. doi: 10.1016/j.jcrysgro.2009.09.033.

[202] Regonini D, Bowen CR, Jaroenworaluck A, Stevens R. A review of growth mechanism, structure and crystallinity of anodized TiO_2 nanotubes. Mater Sci Eng R Rep. 2013;74(12):377–406. doi: 10.1016/j.mser.2013.10.001.

[203] Alexander D, Schwandt C, Fray D. Microstructural kinetics of phase transformations during electrochemical reduction of titanium dioxide in molten calcium chloride. Acta Mater. 2006;54(11):2933–44. doi: 10.1016/j.actamat.2006.02.049.

[204] Sakthivel S, Neppolian B, Shankar M, Arabindoo B, Palanichamy M, Murugesan V. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2. Sol Energ Mat Sol C. 2003;77(1):65–82. doi: 10.1016/S0927-0248(02)00255-6.

[205] Crawford G, Chawla N, Das K, Bose S, Bandyopadhyay A. Microstructure and deformation behavior of biocompatible TiO_2 nanotubes on titanium substrate. Acta Biomater. 2007;3(3):359–67. doi: 10.1016/j.actbio.2006.08.004.

[206] Lirong Y, Guoxing Y. TiO_2-SiO_2 monolithic glass formation from sol-gel. J Non-Cryst Solids. 1988;100(1–3):309–15. doi: 10.1016/0022-3093(88)90038-5.

[207] Konishi J, Fujita K, Nakanishi K, Hirao K. Monolithic TiO_2 with controlled multiscale porosity via a template-free sol– gel process accompanied by phase separation. Chem Mater. 2006;18(25):6069–74. doi: 10.1021/cm0617485.

[208] Wan Q, Hu S, Dai J, Chen C, Li W-X. Influence of crystal facet and phase of titanium dioxide on Ostwald ripening of supported Pt nanoparticles from first-principles kinetics. J Phys Chem C. 2019;123(17):11020–31. doi: 10.1021/acs.jpcc.9b01942.

[209] Qu L, Rahimi S, Qian J, He L, He Z, Yi S. Preparation and characterization of hydrophobic coatings on wood surfaces by a sol-gel method and post-aging heat treatment. Polym Degrad Stabil. 2021;183:109429. doi: 10.1016/j.polymdegradstab.2020.109429.

[210] Jena S, Tokas R, Thakur S, Udupa D. Study of aging effects on optical properties and residual stress of HfO_2 thin film. Optik. 2019;185:71–81. doi: 10.1016/j.ijleo.2019.03.084.

[211] Choi H, Kim YJ, Varma RS, Dionysiou DD. Thermally stable nanocrystalline TiO_2 photocatalysts synthesized via sol–gel methods modified with ionic liquid and surfactant molecules. Chem Mater. 2006;18(22):5377–84. doi: 10.1021/cm0615626.

[212] Panić V, Dekanski A, Milonjić S, Atanasoski R, Nikolić B. The influence of the aging time of RuO_2 and TiO_2 sols on the electrochemical properties and behavior for the chlorine evolution reaction of activated titanium anodes obtained by the sol-gel procedure. Electrochim Acta. 2000;46(2–3):415–21. doi: 10.1016/s0013-4686(00)00600-9.

[213] Hwang K-J, Lee J-W, Shim W-G, Jang HD, Lee S-I, Yoo S-J. Adsorption and photocatalysis of nanocrystalline TiO_2 particles prepared by sol–gel method for methylene blue degradation. Adv Powder Technol. 2012;23(3):414–8. doi: 10.1016/j.apt.2011.05.010.

[214] Fajriati I, Mudasir M, Wahyuni ET. The effect of pH and aging time on the synthesis of TiO_2–Chitosan nanocomposites as photocatalyst by sol-gel method at room temperature. molekul. 2017;12(2):117–25. doi: 10.20884/1.jm.2017.12.2.324.

[215] Panić VV, Nikolic BZ. Electrocatalytic properties and stability of titanium anodes activated by the inorganic sol-gel procedure. J Serb Chem Soc. 2008;73(11):1083–112. doi: 10.2298/JSC0811083P.

[216] Liu J, Yu Q, Yu M, Li S, Zhao K, Xue B, et al. Silane modification of titanium dioxide-decorated graphene oxide nanocomposite for enhancing anticorrosion performance of epoxy coatings on AA-2024. J Alloy Compd. 2018;744:728–39. doi: 10.1016/j.jallcom.2018.01.267.

[217] Wang HW, Kuo CH, Lin HC, Kuo IT, Cheng CF. Rapid formation of active mesoporous TiO_2 photocatalysts via micelle in a microwave hydrothermal process. J Am Ceram Soc. 2006;89(11):3388–92. doi: 10.1111/j.1551-2916.2006.01251.x.

[218] Hidalgo MC, Sakthivel S, Bahnemann D. Highly photoactive and stable TiO_2 coatings on sintered glass. Appl Catal A-Gen. 2004;277(1–2):183–9. doi: 10.1016/j.apcata.2004.09.011.