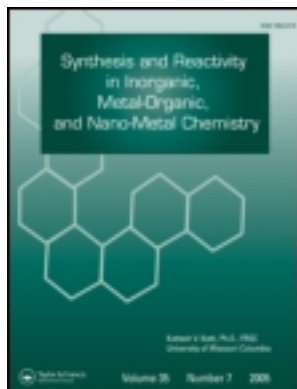


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Sol-Gel Synthesis of Inorganic Mesostructured Composite Photocatalyst for Water Purification: An Insight Into the Synthesis Fundamentals, Reaction, and Binding Mechanisms

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The paper discusses the sol-gel synthesis of an inorganic mesostructured composite photocatalyst for application in water purification. The fundamentals for each synthesis step on the final Ti-content, anatase-to-rutile composition, bonding structure and mechanism to kaolinite, shape, surface area, and size control were described. In addition, various advanced microscopic techniques were used to characterize and validate the physical and chemical properties of the composite photocatalyst. A hypothetical schematic for the fabrication of mesostructured composite photocatalyst was also presented to better illustrate the overall reaction and binding mechanism. The photocatalytic degradation of an aqueous dye solution was also investigated.

Keywords functional composites, nanomaterials, photocatalysts, sol-gel methods, water purification

INTRODUCTION

The sol-gel technique is a commonly used wet-chemical approach for the fabrication of porous materials of diverse chemical, thermal, mechanical and optical properties.^[1] This technique has been adopted in a wide range of production industries that encompasses building materials, personal care products and cosmetics, pharmaceuticals, biotechnology, and nanotechnology industries—with its synthesis procedures being constantly altered to meet the final product requirements. Among them,

sol-gel synthesis of nanosize titanium dioxide (TiO₂) is of increasing interest, owing to its potential applications in fog-proof and self-cleaning glass; anti-bacterial, anti-viral, or fungicidal agents; and water or air purification.^[2] Such a wide functionality of TiO₂ is being instigated by its multifaceted functional properties.

In recent years, the application trend of TiO₂ photocatalyst for water purification is escalating owing to the tighter environmental regulations and legislations on the final distributed water qualities. The benefits of using TiO₂ photocatalysis have been well documented, owing to its superiority in mineralizing a wide range of soluble refractory organic pollutants, inactivating water pathogens, and minimizing disinfection by-products formation.^[3] When TiO₂ photocatalyst is mixed with water under the co-irradiation of an UV source in a semiconductor reactor system, a series of redox reactions will be induced at the particle surface to generate different reactive oxygen species (ROS), such as hydroxyl radicals (OH·), superoxide radicals (O₂^{·-}), and hydrogen peroxide (H₂O₂).^[3] It was reported that all these ROS have their predominant or specific roles during the photocatalytic water purification process.^[4, 5] In this instance, nanosize TiO₂ photocatalyst promotes a higher photoactivity, owing to its better light opaqueness, higher surface area-to-volume ratio, and more efficient charge separation and trapping at the physical surface compared to its bulk equivalent.^[6–8] Giving all these benefits of nanosized TiO₂ photocatalyst, its application for water purification still poses a serious technical difficulty for the particle separation. In the worst-case scenario, the nanosize TiO₂ particle might penetrate through the water purification process to final water consumers.

In this work, we studied the sol-gel synthesis mechanisms of a novel inorganic mesostructured composite photocatalyst for water purification. Its distinctive, highly suitable and specific structure implications for water purification as a result of systematic sol-gel technique manipulation were addressed and elaborated in detail. The fundamentals for each sol-gel synthesis step on the final Ti-content, anatase-to-rutile composition,

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bonding structure and mechanism to kaolinite, shape, surface area, and size control were outlined and discussed further. We used various advanced microscopic characterization techniques to characterize and analyze the physical, chemical, and engineered properties of the composite photocatalyst. A hypothetical schematic for the formation of mesostructured composite photocatalyst was presented to better illustrate the overall reaction and binding mechanism. Kinetic results on the photocatalytic removal of organic dye from an aqueous solution were also presented, in order to probe the photoactivity of the prepared photocatalyst.

FUNDAMENTALS OF SOL-GEL SYNTHESIS

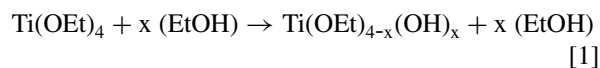
Overview on Sol-Gel Synthesis

Sol-gel synthesis is one of the basic and most constructive wet chemical methods used to fabricate an inorganic hybrid photocatalyst from its metal precursors. Its advantages include low processing temperatures, high molecular homogeneity, and ability to synthesis complex oxides.^[9] Hydrolysis and condensation of the metal precursors are the two major underlying principal reactions that dominate the end properties and characteristics of photocatalyst.^[11] The metal precursors used are usually of the metal alkoxide type, which are dissolved and reacted in a solvent controlled condition to yield clusters of metal oxide. In this instance, the extent of the reaction is determined by the stoichiometric ratio and solvents mixing conditions at the atomic and molecular levels. All these will have significant impacts on the final morphology, structure, and properties of the photocatalyst. The preliminary challenge in the synthesis of nanosize TiO₂ particle *via* the sol-gel route is to understand the effects of various stoichiometric and solvent mixing ratios on the hydrolysis and condensation rates, as well as on the metal cluster. If the effects of these mixing ratios are unknown, this may lead to a homocondensation phenomenon on the resultant sol where they can comprise multiple oxide phases instead of a single one.^[9]

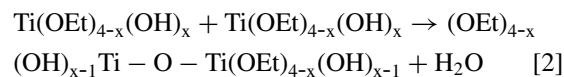
Experimental Sol-Gel Procedures

In our synthesis method, a two-step approach was adopted where an initial TiO₂ sol-gel synthesis was performed followed by a hetero-binding reaction with mesostructured inorganic kaolinite and calcination processing at elevated temperature conditions. During the first synthesis step, 25 mL aliquot of titanium (Ti) alkoxides precursor (namely titanium (IV) butoxide or tetrabutyl orthotitanate) was partially hydrolyzed with controlled absolute ethyl alcohol concentration of 30 mL under continuous stirring. This is to ensure that each solvent component is homogeneously mixed at the atomic and molecular levels. This was followed by condensation of the sol product under ambient conditions. Equations 1 and 2 show the respective chemical equations for hydrolysis and condensation reactions.

Hydrolysis:



Condensation:



A partial hydrolyzation state for Ti alkoxides needs to be achieved so as to provide non-hydrolyzable ligands of Ti after condensation reaction, for TiO₂ nanocluster growth. A subsequent acid-catalyzed reaction was employed to enable complete hydrolyzation of the initial sol product. This is the most important synthesis step, as the reactivity of partially hydrolyzed Ti sol product was suppressed to enable cluster-to-cluster growth. It is the synthesis-determining step, as the strength of cross-linked interaction formed between the metal clusters will set the porosity and particle size of eventual TiO₂ crystallites.

As for the following synthesis step, the complete hydrolyzed Ti sol was hetero-bound to inorganic kaolinite, which functioned as a mesostructured immobilization platform and an electro-stabilizer for the sol. The reason for using inorganic kaolinite is to ensure that the nanodimensionality and properties of TiO₂ crystallite is preserved, while allowing a structural rigid and stable support for ease of particle separation after water purification. In this instance, the inorganic kaolinite was pre-treated in order to remove surface and interstitial impurities that might be leached into and subsequently affect the photocatalyst properties. The pre-treated kaolinite was then reacted with the complete hydrolyzed Ti sol in a completely stirred flask, where the Ti sol was added dropwise into the kaolinite suspension. This hetero-binding process was conducted under constant temperature condition to minimize the temperature disturbances on the cross-linked interaction of Ti nanoclusters and the surface binding process. After an extended stirring period, the product was aged, filtered, and washed with deionized water to remove any excess ethyl alcohol or nitric acid. The final colloidal mesostructured TiO₂ composite particle was processed at an elevated temperature to tailor for the anticipated properties of Ti active phase ratio, porosity, particle size, and surface area. Further references to our sol-gel synthesis method can be made at our published works of Chong et al.^[10] and Vimonses et al.,^[11] respectively.

Pre-Treatments on Mesostructured Inorganic Kaolinite

As mentioned previously, the mesostructured inorganic kaolinite will be used as an immobilization substrate for the synthesis of composite photocatalyst. However, most natural clay materials contain impurities such as surface-bound water, zeolitic water, and other impurities that might affect the inter-layer pore space and effective surface area during TiO₂ sol-gel immobilization.^[10] If the clay is not being pre-treated properly, the chemical impurities might induce an internal reaction during

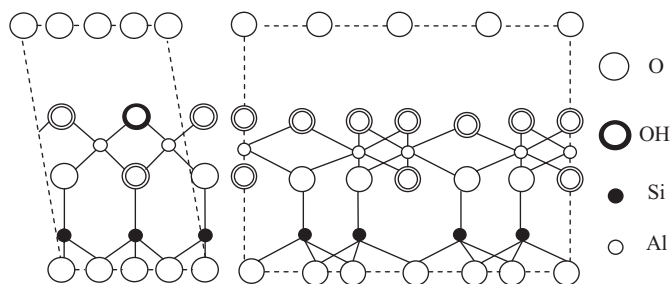


FIG. 1. The chemical structure of a mesostructured kaolinite substrate used for immobilization. Reproduction from Barrer.^[12]

calcination via a diffusional or leaching mechanism. Therefore, the impurities will leach into the eventual TiO_2 crystallite layer and affect its physical and chemical properties.

Figure 1 shows the chemical structure of the mesostructured kaolinite used for nanosize TiO_2 immobilization. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) belongs to the kandites mineral group, and is a layered silicate mineral with one octahedral layer that reacts with one sheet of $(\text{Si}_2)_3(\text{OH})_2$.^[12] To thermally pre-treat the kaolinite, we have conducted the differential thermal analysis and thermogravimetric analysis (DTA-TG). Results indicate that the maximum applicable temperature before causing an irreversible disruption to the kaolinite structure is 985°C . Prior to this maximum temperature, it was identified that there exists an endothermic peak at 503°C due to the dehydroxylation of the single water layer between each pair of silicate sheets. Thus, the appropriate temperature for kaolinite pre-treatment lies between 503 and 985°C . Simultaneously, we also monitored the change in BET surface area to confirm the applicability of the chosen pre-treatment temperature. From the BET measurements, we found that the pre-treatment temperature of up to 750°C is suitable and only results in a slight decrease in specific surface area from 15.24 to 14.54 m^2/g . When the pre-treated kaolinite was examined using X-ray diffraction (XRD), it was found that the c-spacing within the kaolinite structure shrank from 10 to 7.2 \AA and this corresponds to the distance of a single layer of water molecules being driven off as also examined by the DTA-TG method. Barrer^[12] found that such dehydroxylation impedes the pore tunnels and only allows small polar molecules to replace the single zeolitic water molecules layer. With this thermal pre-treatment, it was deduced that the mesostructured kaolinite (with an average size of 3.5 μm) can present a rigid and stable immobilization platform that can withstand any intrastructure reaction, leaching of impurities, and diffusional problems. The mesostructured kaolinite was further treated with chemical base treatment. The major aim of such chemical base treatment is to alter the isoelectric point of kaolinite to basic pH regime in order to enhance the subsequent chemical binding with positively charged TiO_2 sol-gel. Further details on the pre-treatment methodology can be found in Chong et al.^[10] and Vimonses et al.^[11]

IMPACTS OF SOL-GEL SYNTHESIS STEPS

Hydrolyzation Reaction

In our synthesis method, the hydrolysis of Ti alkoxide precursors is the primary step to fabricate the mesostructured composite photocatalyst. Within this synthesis step, we have investigated the effect of concentrations of ethyl alcohol to a constant volume (25 mL) of Ti precursor. The Ti contents can only be controlled via the addition or reduction in effective reaction volume rather than its concentration, owing to the high chemical susceptibility of Ti alkoxides to dilution. Results show that the Ti cluster-to-cluster growth only occurs over a narrow range of ethyl alcohol concentrations used. In this instance, the thickness of the colloidal Ti dispersion was seen to increase with ethyl alcohol concentration up to a saturation threshold and thereafter it became resulted in too hard solid gel or no gelation at all. The nucleation rate for TiO_2 nuclei formation was relatively low at the lower ethyl alcohol concentration range. This has caused a significant induction time to mark the TiO_2 nuclei using the electron microscope approach.

As mentioned previously, a partial hydrolysis state for the Ti precursor was targeted in order to provide non-hydrolysable ligands and a better molecular homogeneity at the lower-end ethyl alcohol concentration ranges. Owing to the functionality of ethyl alcohol over only a narrow concentration range, the extent of hydrolysis reaction is better manipulated via the following acid catalyzed reaction. It can be concluded that a minimum amount of ethyl alcohol is required for the partial hydrolysis reaction, and usually a supplementary stoichiometric allowance needs to be included to compensate for the evaporation loss of ethyl alcohol during experimental handling.

Acid-Catalyzed Reaction

The acid-catalyzed reaction is an important step in the synthesis of Ti sol-gel through our bottom-up molecular chemistry approach. The rationale of this reaction is to retard the reactivity of Ti alkoxides, allowing the metal clusters to slowly align between each other and thus, facilitating the cross-linked interaction to form a strong TiO_2 sol-gel. A schematic diagram is presented in Figure 2 to illustrate the mechanism of nanocluster

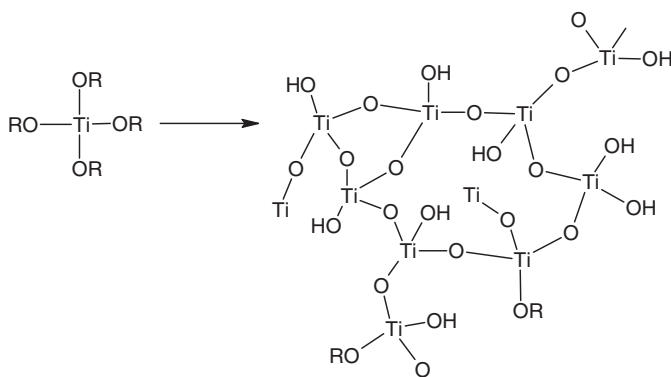


FIG. 2. A schematic for the Ti nanoclusters growth mechanism.

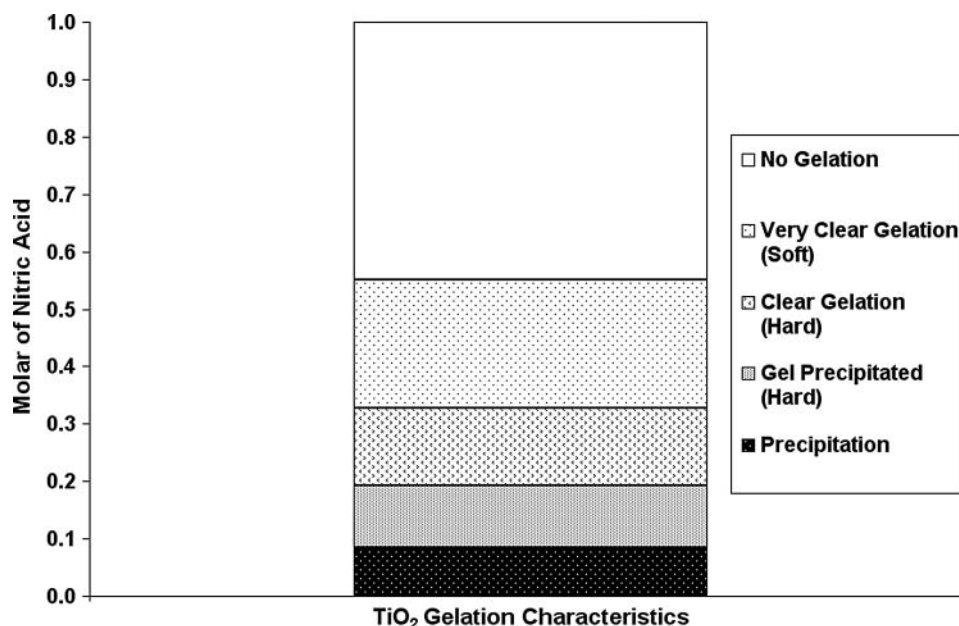


FIG. 3. Various fluid and gelation characteristics of TiO₂ sol-gel under different HNO₃ concentration regimes.

growth during acid catalyzed reaction. Owing to the different chemical reactivities of solvents used, the acid concentration required a systematic investigation for its possible impacts on the physical and chemical properties of the final TiO₂ sol-gel. Suh et al.^[13] previously reported that the onset concentration for gelation of TiO₂ sol only occurs in a narrow range of acid concentration and thus its impacts should be investigated accordingly. In their study, they found that an optimum nitric acid (HNO₃) concentration of 1 M can produce a strong cross-linked Ti aerogel.

In our study, we have investigated the impacts of different HNO₃ concentration ranging from 0.05 to 1 M. We found that the final TiO₂ sol-gel produced under the studied HNO₃ concentration will exhibit four distinct fluid and gelation characteristics. Figure 3 shows the various fluid and gelation characteristics of TiO₂ sol-gel formed under different HNO₃ concentration regimes. Results show that the transparent TiO₂ sol-gel was not formed using 1 M HNO₃. Instead, the TiO₂ sol-gel exhibits an extended degree of fluidity after the completion of acid-catalyzed reaction at 1 M HNO₃. This is because the high HNO₃ concentration used could retard the condensation process and further affect the Ti cluster-to-cluster growth to form Ti-O-Ti polymeric gel network. The optimum HNO₃ concentration was found to lie within the range of 0.25–0.30 M, where it yields a strong clear transparent hard TiO₂ sol-gel. At the optimum HNO₃ concentration, it was noted that the acid effect contributes not only to the formation of suitable homogeneous transparent TiO₂ sol-gel (*i.e.*, no precipitation) but also its corresponding gelation behavior and textural properties. When a lower HNO₃ concentration was used, it was observed that the gelation rate increased to an extent where rapid solid precipi-

tation occurred. The occurrence of gel precipitation was due to the presence of precipitates in the polymeric gel network. This precipitated gel exhibits a lower degree of fluidity and thus conveys a negative impact on the subsequent hetero-binding process with the mesostructured inorganic kaolinite.

In addition, a paired pH effect on acid-catalyzed reaction was also measured and investigated to detail its impact on the polymeric gel network. Previously, Robert et al.^[14] found that the optimum pH for the TiO₂ sol-gel was pH 3 for better photoactivity. However, we found that the pH value at the current optimum HNO₃ concentration corresponds to pH 1.80. When the pH value was adjusted to pH 3 using 1 M of sodium hydroxide solution, large dense TiO₂ crystallites were obtained after the calcination process. This was evidenced from the XRD measurements by overlapping the extent of peak broadening with the original peak signal. The reason for the formation of dense TiO₂ crystallite is due to the few rigid clusters within the Ti-O-Ti polymeric network. Although the actual formation mechanism of dense TiO₂ crystallites remain ambiguous, it can be concluded that the overall of HNO₃ concentration and pH will have a significant impact on the formation structures of the Ti-O-Ti polymeric gel network and their associated porous and adsorptive characteristics.

Hetero-Binding of TiO₂ Sol-Gel to Mesostructured Inorganic Kaolinite

Metal nanocluster constituents that exist in the TiO₂ sol-gel usually hold a high surface free energy due to the large surface area-to-volume ratio. Such an implicit characteristic usually creates a strong tendency for the crystallized nanosize TiO₂ particles to agglomerate under the influence of Brownian motion.^[15]

This is one predominant reason why the application of nanosize TiO_2 will impair its real-world implementation for water purification in a surplus to the solid separation issue. In this study, we utilized the pre-treated mesostructured kaolinite as a binding support to suppress nanosize TiO_2 particle agglomeration and further enhance its downstream separation. In addition, the mesostructured kaolinite also serves as a perfect charge neutralizer for electrosteric stabilization of TiO_2 sol-gel from the acid-catalyzed reaction. The TiO_2 sol-gel possesses a positively charged surface due to the existence of Ti(IV) valency, while the pre-treated mesostructured kaolinite is negatively charged owing to the chemical base treatment for an effective blending.

We investigated on the different weight fraction of kaolinite in a fixed volume suspension (100 mL) required for chemical binding reaction. The TiO_2 sol-gel is added dropwise into a continuously stirred flask that contained the aqueous kaolinite suspension. The rationale is to promote uniform distribution and binding of the TiO_2 onto the vast kaolinite structures. However, the uncontrolled binding reaction will result in the formation

of a double layer around kaolinite particle. This is due to the excessive addition of either TiO_2 sol-gel or underestimation on the kaolinite suspension used for the binding reaction. Within our study, three different kaolinite mass loadings of 5%, 10%, and 15% (w/v) were investigated. It was found that the kaolinite particles settled at the bottom of the reaction flask is independent of the amount being held up in the aqueous suspension.

At a lower kaolinite mass loading of 5% (w/v), it was found that there is no individual precipitation of the composite particle after aging. This indicated that the TiO_2 sol-gel was fully bound to kaolinite loads. When the composite particle was examined under the transmission electron microscopy (TEM) after calcination, a number of distinct TiO_2 crystallite structures with relatively thick and inconsistent layers were observed and as shown in Figure 4. At a higher kaolinite mass loading of 10% (w/v), however, it was observed that the resultant thickness of TiO_2 crystallites was relatively uniform and well dispersed. TEM examination revealed that an average TiO_2 crystallites size distribution of 7 nm was bound onto the mesostructured kaolinite.

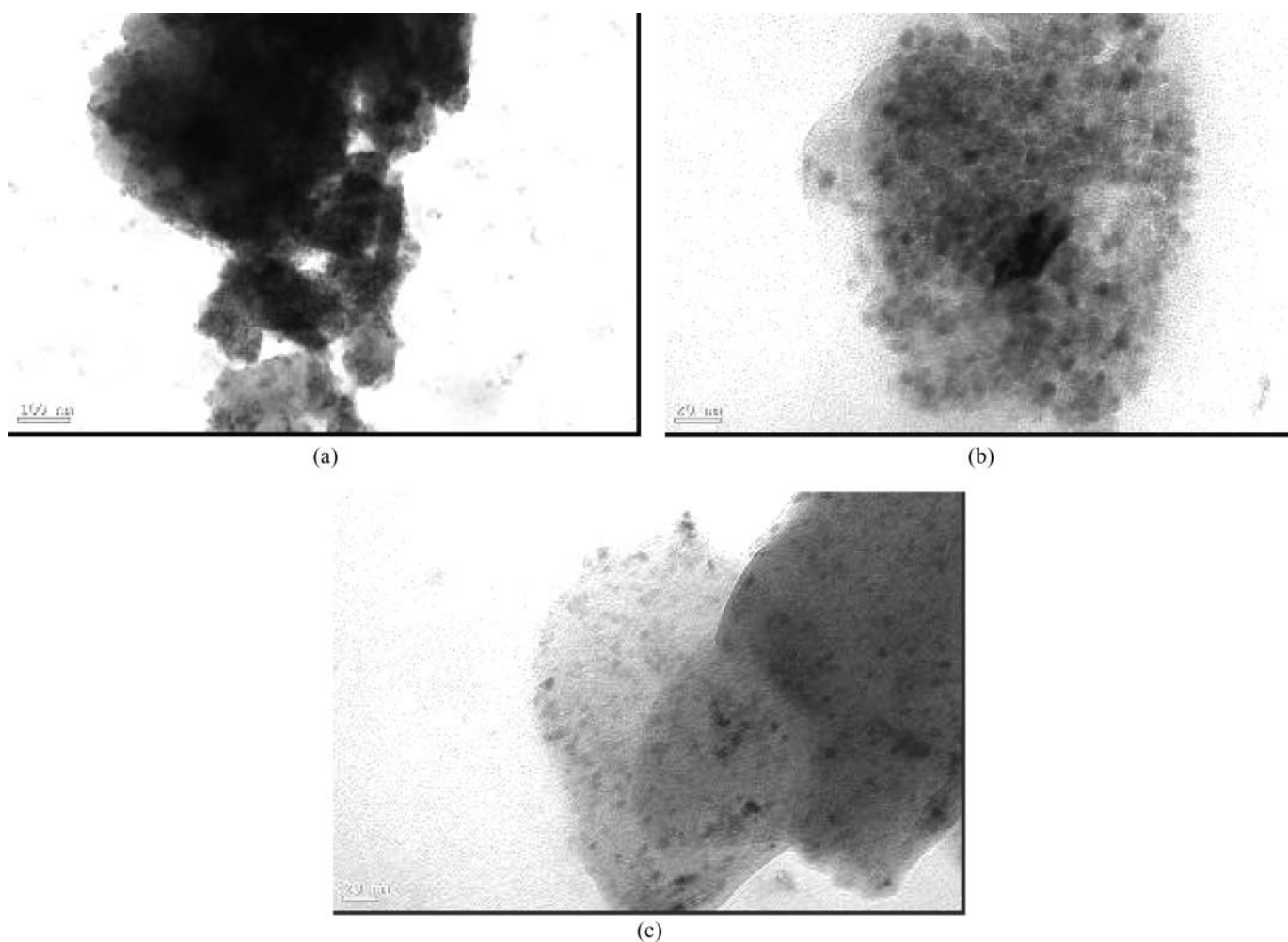


FIG. 4. TEM images for different mass loadings of mesostructured kaolinite substrate (a) 5% (w/v), (b) 10% (w/v), (c) 15% (w/v).

The final TiO₂ crystallite size showed a strong function of the calcination temperature. For the kaolinite mass loadings of 15% (w/v), a relatively distant dispersion of TiO₂ crystallites was found after calcination. This was explained by an increase in the total nucleation sites from 10% to 15% (w/v) that superseded the fixed volume of TiO₂ sol-gel. Therefore, the optimum kaolinite loading for chemical binding with TiO₂ sol-gel was determined to be 10% (w/v).

Aging Time

Aging of the bounded colloidal TiO₂ particle is an extension to the gelation during the acid-catalyzed reaction, in which the binding interaction formed during the preceding step can be reinforced. It was deduced that the condensation and polymerization reactions continue to occur at a slower pace, yielding a more cross-linked Ti-O-Ti polymeric gel network. Thus, the variation in aging time will contribute to different physical and chemical properties such as particle size, porosity, and mechanical strength of the chemical binding.

In our study, we found that the eventual TiO₂ crystallinity increases with aging time. During the initiation of aging period, it was found that the composite particle exists in amorphous state before calcination. However, the TiO₂ crystallites layer grew with increasing aging time. Such an observation was in agreement with the earlier notion that the condensation process still occurs during aging period to further reinforced the polymeric Ti-O-Ti gel network. Hsiang et al.^[16] reported a similar observation where the TiO₂ crystallinity increased after an aging period of 12–48 hr.

At a short aging time, we examined that the TiO₂ crystallite formed was small, rigid, and had a low porosity characteristic. This owes to the calcination process where the amorphous TiO₂ sol-gel was transformed into crystalline structure. When the amorphous TiO₂ sol-gel was calcined at elevated temperature, the polymeric Ti-O-Ti gel network slowly shrank to form a final TiO₂ crystalline structure. However, the gel shrinkage is highly dependent on the extent and strength of the polymeric network. It was examined that the polymeric gel network that found within 2 h of aging is relatively weak and constantly collapses for small and rigid TiO₂ crystallites. Effectively the optimum aging time was determined after a series of iterative physical and chemical characterizations. It was found that the optimum aging time for polymeric Ti-O-Ti gel network is 13–16 h that yields the best corresponding physical and chemical properties.

Calcination Temperature

Generally, the aged colloidal TiO₂ composite mixture is a dilute solution that consists of a small proportion of Ti metal nanoclusters to a large volume proportion of inorganic solvents used. When this colloidal mixture is subjected to calcination at elevated temperature, this will enhance the removal of excess solvents used and result in the shrinkage of the polymeric Ti-O-

Ti gel network. If the calcination temperature is uncontrolled, the worst-case scenario is that there will be a severe cracking on the derived TiO₂ crystallite films on kaolinite. Such a cracking will physically impose some limitation on forming TiO₂ crystallite size of smaller than a micron.^[9] Thus, the major challenge is to control the calcination temperature, which not only alters the size, shape, and structural formation but also the degree of crystallinity and composition of anatase-to-rutile photoactive phase. Different calcination temperatures can contribute to various photoactive phases such as anatase, rutile, brookite, or any combination between them. Beydoun et al.^[17] reported that different photoactive phases of TiO₂ will lead to dissimilar photoreactivities. To date, the most highly regarded Degussa P-25 TiO₂ photocatalyst for water purification has a combination of anatase (70–80) to rutile (20–30).

In our study, we investigated for the best calcination temperature to yield the optimum physical and chemical properties for the composite photocatalyst. Figure 5 shows the correlation between the TiO₂ crystallite size, BET surface area, and calcination temperature. The result from Figure 5 reveals that the TiO₂ crystallite size formed on the mesostructured kaolinite was strongly affected by the calcination temperature. The TiO₂ crystallite size was seen to grow from 6 to 18 nm when the calcination temperature varied between 500 and 700°C. This is owing to the formation of agglomerates and accompanying crystal growth, as evidenced from the peak broadening scenario in XRD and scanning electron microscopy (SEM; results not shown). The crystal growth will also lead to a reduction in the BET surface area. Figure 5 shows that the BET surface area dropped slightly when the calcination temperature increased from 500 to 600°C. However, a radical decline in BET surface area was observed when the calcination temperature increased to 650°C with simultaneous transformation in photoactive phase from anatase to rutile. The phase transformation of anatase to rutile was examined to involve by the simultaneous rupture of Ti-O bonds,^[17] as well as the Ti-O-Si bonds.

During the calcination process, we propose a binding mechanism that the polymeric Ti-O-Ti gel network could shrink and collapse onto the mesostructured kaolinite particle. In this instance, the Ti-O side of the polymeric network could be attached to the siliceous side of kaolinite structure that presents a surface of oxygen molecules. When this attachment is subjected to calcination, both the water and oxygen molecules will evolve as a result of the Ti-O-Si bonding formation. Figure 6 shows the binding mechanism for the entire physical processes that occurred during the calcination process. Gates and Knozinger^[15] discussed that the existence of Ti-O-Si bonding is highly beneficial for environmental catalysis application due to its intense stability. Thus, it can be concluded that the optimum calcination temperature for our mesostructured composite photocatalyst is 600°C. With this optimum calcination temperature, the optimum TiO₂ crystallite size, porosity, BET surface area, and anatase photoactive phase were attained.

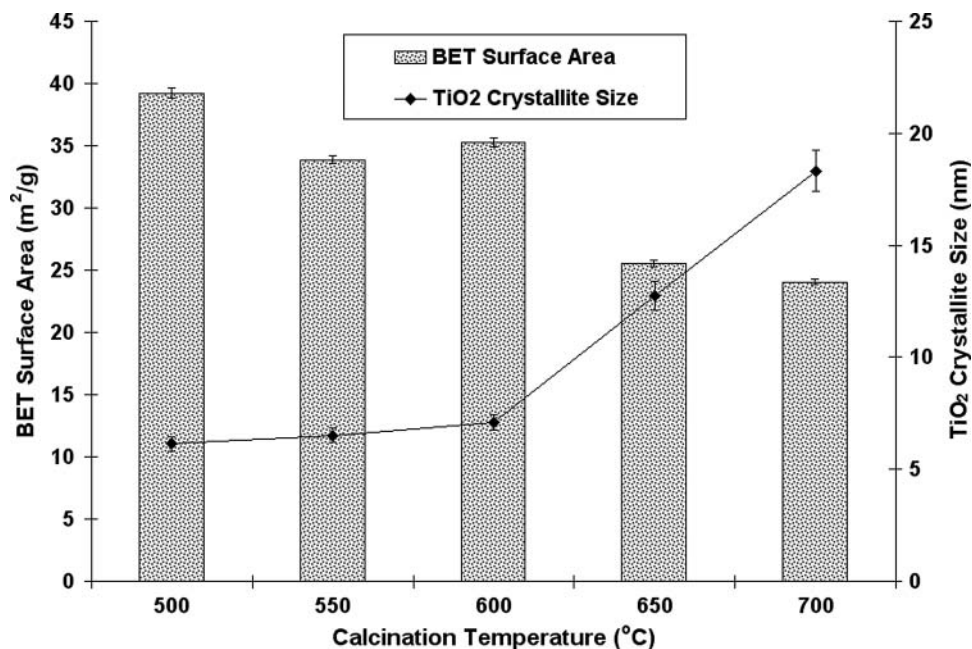


FIG. 5. Correlation between TiO₂ crystallite size, BET surface area, and calcination temperature.^[10]

Photocatalytic Degradation of Aqueous Dye Solution

The photocatalytic degradation of an aqueous synthetic dye solution of Congo red (IUPAC name: sodium 3,3-(1E,1'E)-biphenyl-4,4'-diylbis(diazene-2,1-diyl)bis(4-aminonaphthalene-1-sulfonate)) was used as a surrogate reaction for the photoactivity probing of our new composite photocatalyst. In this study, we monitored the photocatalytic degradation of 40 mg/L of Congo red through the UV-Vis

spectrophotometer absorbance measurement at 496.5 nm. Figure 7 shows that the Congo red was first adsorbed onto the photocatalyst before the subsequent photocatalytic reaction. When the kinetic isotherm was classified into adsorption and photocatalysis regimes, it can be observed that there exists a high adsorption enhancement factor and this was deduced to be due to the mesostructured kaolinite support (as compared with similar controlled experiment using bare TiO₂

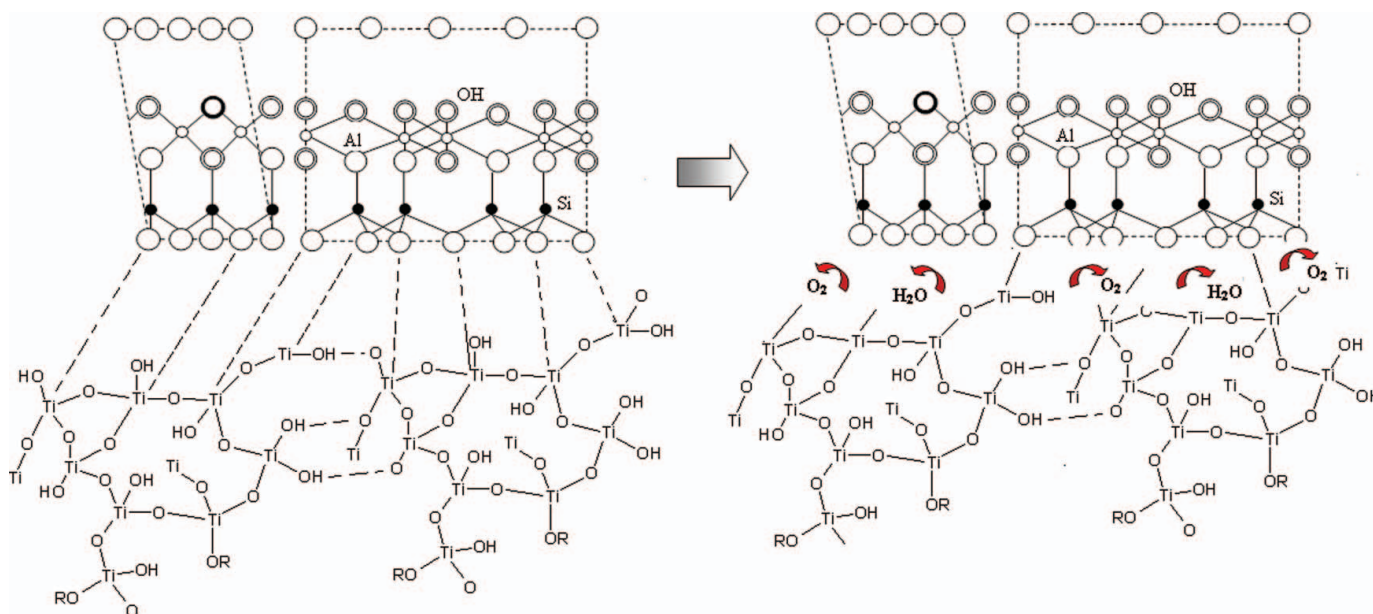


FIG. 6. Binding mechanism of TiO₂ colloidal sol to mesostructured inorganic kaolinite (color figure available online).

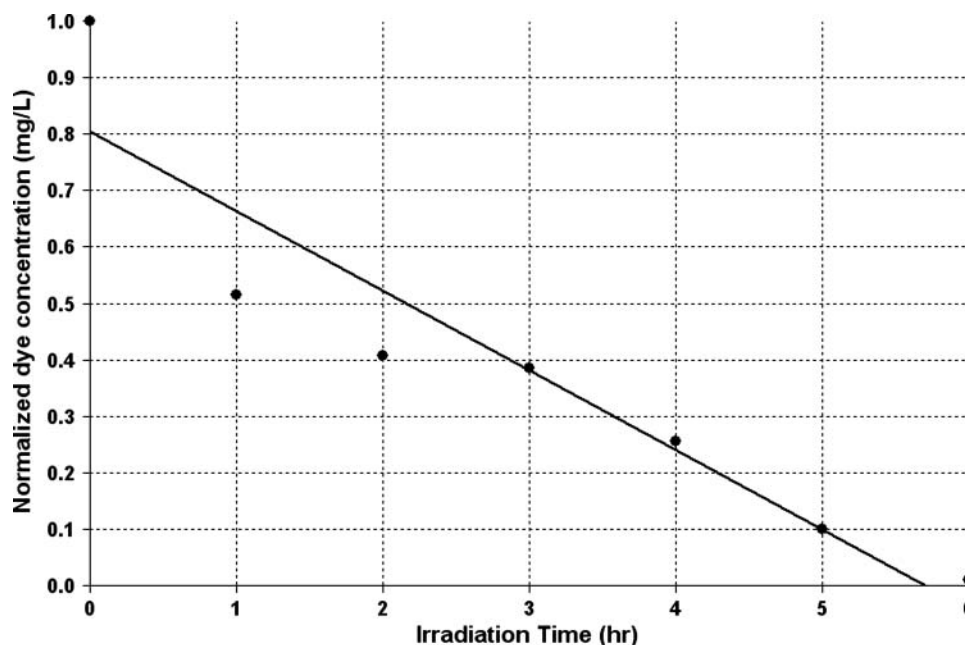


FIG. 7. Photocatalytic degradation of aqueous dye solution using new composite photocatalyst.

crystallites). The results suggested that the mesostructured kaolinite has an important contribution not only for a separable photocatalyst, but also enhancing the adsorptive removal of organic compounds in water. Further engineering determination on the settling velocity of this composite photocatalyst can be found in Vimonses et al.^[11]

CONCLUSION

This article highlights the fundamental insights into the synthesis of a novel inorganic mesostructured composite photocatalyst for water purification. It was proven to be essential to understand the theory behind each sol-gel synthesis step before the physical and chemical properties can be manipulated for specific end uses. In addition, this study also presented a hypothetical binding reaction during the calcination process to yield a composite photocatalyst with a robust Ti-O-Si bonding. It is anticipated that the knowledge gained from this synthesis methodology could be transferred across other sol-gel applications for better fabrication of functional nanomaterials in the future.

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