

Cite this: *RSC Adv.*, 2017, 7, 4547

Room-temperature pulsed CVD-grown SiO₂ protective layer on TiO₂ particles for photocatalytic activity suppression

Jing Guo,^{ab} Shaojun Yuan,^a Yangyang Yu,^a J. Ruud van Ommen,^b Hao Van Bui^b and Bin Liang^{*a}

This work presents a novel chemical vapor deposition (CVD) approach that enables the deposition of ultrathin and conformal SiO₂ layers on TiO₂ anatase nanoparticles at room temperature using SiCl₄ and air containing water without the use of a catalyst. The morphology of the CVD-grown SiO₂ layers was found to be strongly dependent on the initial surface states of the TiO₂ nanopowders, which could be altered by applying a simple heat pretreatment. The deposition on untreated TiO₂ resulted in granular films, whereas on preheated TiO₂ highly uniform and conformal SiO₂ layers were obtained. By varying the SiCl₄ precursor dosing time and the number of CVD cycles, the thickness of the SiO₂ could be controlled at the nanometer level, which allowed us to investigate the influence of film thickness on the photocatalytic suppression ability. We found that a conformal SiO₂ layer with a thickness of 3 nm could sufficiently suppress the photocatalytic activity of anatase TiO₂ nanoparticles, which was demonstrated by the photodegradation of Rhodamine B. Our approach offers a simple, fast, feasible and low-temperature deposition method which can be directly applied to SiO₂ coating on nanoparticles in pigments and other fields, particularly heat-sensitive materials, and further developed for large-scale production.

Received 9th December 2016
Accepted 3rd January 2017

DOI: 10.1039/c6ra27976g

www.rsc.org/advances

1 Introduction

Nanoparticulate titanium dioxide (TiO₂) is the most commonly-used white pigment in the paint, plastic, and paper industries due to its high brightness, high refractive index and photostability.^{1,2} However, the high photocatalytic activity of TiO₂ facilitates the oxidation and decomposition of organic compounds, for instance, in the paint layer, which consequently changes the color and severely decreases the lifetime of the products.³ Therefore, in these practical applications, TiO₂ nanoparticles (NPs) are commonly coated with a thin insulating layer to suppress their photocatalytic activity. On the one hand, this coating layer is required to sufficiently block the transport of electrons and holes, which are generated in the TiO₂ particles under UV-light irradiation, to the surface that initiates the photocatalytic reactions with organic compounds. On the other hand, the coating layer must not affect the bulk optical properties of the TiO₂ pigment. Owing to their large band gap, high thermal and optical stabilities, and chemical inertness, ceramic oxides, such as Al₂O₃, SiO₂, CeO₂ and ZrO₂, have been popularly

used as coating materials on TiO₂ for photocatalytic suppression.^{4–14}

Various strategies have been developed to deposit thin metal oxide films on TiO₂ pigment particles. Among them, wet chemistry methods, such as sol-gel and precipitation, have been extensively used due to their simplicity, inexpensiveness and versatility in producing various materials with tunable properties.^{4–6,8,15,16} For instance, Ren *et al.* employed sol-gel method in the presence of 3-hydroxytyramine hydrochloride, poly(diallyldimethylammonium chloride), poly(sodium 4-styrenesulfonate), tetraethyl orthosilicate (TEOS) and solvents to fabricate TiO₂/SiO₂ core/shell particles.⁶ Upon exposure to UV radiation, a rattle-type structure with tunable catalytic/UV-shielding properties was obtained. The TiO₂/SiO₂ core/shell structure for UV radiation shielding can also be obtained by the conventional Stöber method using TEOS and solvents such as ethanol, NH₄OH and acetone.^{4,5} Binary Al₂O₃/SiO₂ coating layers have been deposited on TiO₂ nanoparticles using sol-gel and precipitation methods for enhanced brightness and whiteness of TiO₂.^{8,16} Moreover, wet chemistry methods enable the deposition of various ceramic and transition metal oxide materials such as ZrO₂, CeO₂, NiO and CoO on TiO₂ particles.¹⁵ Nevertheless, these methods have several shortcomings in controlling the coating thickness and conformality due to their high sensitivity to experimental parameters, such as precursor concentration, type and pH of the solvents, deposition time and temperature. In

^aMulti-phase Mass Transfer & Reaction Engineering Lab, College of Chemical Engineering, Sichuan University, Chengdu 610065, China. E-mail: liangbin@scu.edu.cn; Fax: +86-28-85460556; Tel: +86-28-85460556

^bDepartment of Chemical Engineering, Delft University of Technology, Delft, The Netherlands

addition, these methods are time consuming and normally require post-treatment processes, for instance, high temperature treatment, washing, drying, and separation to eliminate impurities that arise from the residual solvent and reaction byproducts.^{5,6} These disadvantages hinder the applicability of wet chemistry in the syntheses of metal oxide layers on TiO₂ in practical applications. It is therefore of importance to search for a facile, low-cost, and efficient approach for deposition of metal oxide layers on the TiO₂ particles.

Gas-phase deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been attractive alternatives in recent years. ALD is based on the sequential exposures of the support/substrate to precursors in the gas phase. This enables self-limiting surface reactions and provides the ability to control the amount of depositing materials down to atomic level with high uniformity and conformality in many applications.^{17,18} ALD has also been applied for coating Al₂O₃ and SiO₂ films on TiO₂ nanoparticles for catalytic suppression.^{12–14} With ALD, ultrathin and conformal SiO₂ and Al₂O₃ layers with a thickness of several nanometers can be achieved, showing excellent stability and high efficiency in suppressing the catalytic properties of TiO₂ nanoparticles.^{12,13} Molecular layer deposition (MLD), the organic counterpart of ALD, has also been applied for depositing aluminum alkoxide (*i.e.*, alucone) using trimethylaluminum and ethylene glycol as precursors. This alucone layer can reduce the undesired color change of the white pigment TiO₂, which was observed for the TiO₂ coated with SiO₂ and Al₂O₃ layers by ALD.¹⁴

CVD of SiO₂ thin films has been extensively investigated over the past decades.^{10,11,19–25} TEOS, silane (SiH₄), dichlorosilane (SiCl₂H₂) and silicon tetrachloride (SiCl₄) are among the most popularly used precursors in conjunction with H₂O or O₂ as oxidizing agent. This has been used to deposit thin SiO₂ layers on TiO₂ micro- and nanoparticles.^{10,23,26,27} Powell *et al.* demonstrated CVD of SiO₂ films at a temperature in the range of 1300–1500 °C employing the SiCl₄/O₂ chemistry, and found that the film surface was smoother at a higher temperature and in the absence of water.^{11,26,27} Using the same SiCl₄/O₂ chemistry, Simpson *et al.* reported that ultrathin and continuous SiO₂ layers with a thickness of 1–2 nm could be obtained at 1000 °C.¹⁰ By replacing O₂ with H₂O as the oxidizing agent, Tsapatsis and Gavalas demonstrated that the deposition temperature of SiO₂ CVD could be significantly reduced to approximately 600 °C.²³ It can be concluded that CVD of SiO₂ generally requires an elevated temperature. Remarkably, Klaus and George found that the use of NH₃ as catalyst for the SiCl₄/H₂O CVD process could enable the deposition of SiO₂ at room temperature.²⁴ To the best of our knowledge, this is so far the only room-temperature SiO₂ CVD process using SiCl₄ precursor reported in literature.

Accordingly, the main aim of this work is to develop a novel approach that enables the room-temperature CVD (RTCVD) of SiO₂. We demonstrate that ultrathin and conformal SiO₂ layers on TiO₂ nanoparticles can be deposited at room temperature using SiCl₄ and air containing water without the use of catalysts. As SiCl₄ can react robustly with H₂O, the use of air containing water is to decelerate the reaction kinetics and achieve a better control of deposition rate. Therefore, the thickness of coating layers can

be controlled at nanometer scale by varying the SiCl₄ dosing time and the number of CVD cycles. We found that the morphology of the coating layers, *i.e.*, granular or continuous films, is strongly influenced by initial surface states of the TiO₂ nanopowders, which can be altered by applying a simple heat treatment at a relatively low temperature (*i.e.*, 170 °C). Photocatalytic tests are performed on the as-synthesized SiO₂/TiO₂ nanoparticles to evaluate the catalytic suppression ability of the room-temperature CVD-grown SiO₂, and to study the influence of coating thickness on the suppression ability. The results obtained from our work demonstrate a simple, fast and feasible method for coating SiO₂ on TiO₂ pigment, which is applicable for other powders and can be further developed for large-scale production.

2 Experimental

2.1. Materials

Anatase TiO₂ powders with diameter in the range of 200–300 nm and specific surface area of about 10.7 m² g^{−1} (determined by BET technique) were provided by Taihai TiO₂ pigment Co. (Panzhihua, China). Rhodamine B (RhB) and silicon tetrachloride (SiCl₄) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The TiO₂ powders and the chemicals were used as received without any additional treatment or purification.

2.2. Preparation of SiO₂-coated TiO₂ nanoparticles

The coating apparatus and deposition steps are schematically shown in Fig. 1. TiO₂ powders, without or with heat pretreatment at 170 °C for 1 h (*i.e.*, performed *ex situ* in an oven prior to the CVD), were supported on a porous distributor plate, and were immobilized inside a glass reactor with volume of 1 L (Fig. 1a). The thickness of the TiO₂ layer on the distributor plate is about 2 mm. At this thickness and with a long dosing time (*i.e.*, up to 60 min), the diffusion limitation of the gas molecules to the bottom of the layer can be eliminated.²⁸ Before introducing SiCl₄, the reactor was slowly evacuated to a pressure of 70 mbar using a mechanical pump. This was to create a pressure difference between the chamber and the SiCl₄ vapor precursor (*ca.* 260 mbar at room temperature). SiCl₄ was then fed into the reactor (V1 opened, V2 and V3 closed) with dosing times varying from 3 to 60 min to react with the hydroxyl groups (−OH) on the surface of TiO₂ nanoparticles (Fig. 1b–d). Hereafter, the excess precursor, if any, and the reaction byproducts (*i.e.*, HCl) were removed (V1 and V2 closed, V3 opened). Air containing H₂O vapor (*i.e.*, 44% RH) was then introduced into the chamber and maintained at atmospheric pressure to react with the Si–Cl terminated surface, forming an SiO₂ layer and creating an −OH terminated surface (Fig. 1e), which is necessary for the chemisorption of SiCl₄ in the next cycle. The use of air containing H₂O vapor instead of pure H₂O is due to the fact that SiCl₄ can react robustly with H₂O, which could lead to the uncontrollable deposition.

2.3. Material characterization

The thickness of the SiO₂ layers on the TiO₂ particles was measured by transmission electron microscopy (TEM) using



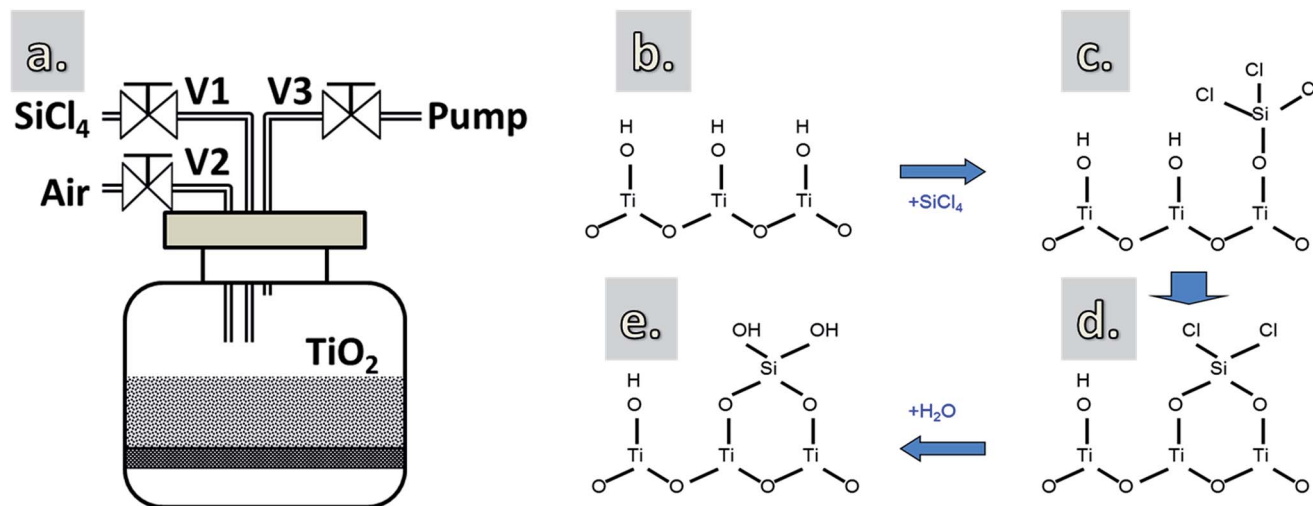


Fig. 1 A schematic drawing of the reactor (a) and the proposed growth mechanism of SiO₂ using SiCl₄ and H₂O vapor (b–e).

a JEOL JEM1400 operating at a voltage of 120 kV and a current density of 50 pA cm⁻². The composition of the SiO₂ layers was characterized by X-ray photoelectron spectroscopy (XPS) (XSAM800, Kratos, UK) with monochromatized Al K α radiation at constant dwell time of 100 ms and pass energy of 55 eV. The peaks positions were calibrated according to the C 1s peak at 284.8 eV. The infrared spectra were acquired using FTIR spectroscopy (Spectrum II L1600300 spectrometer, PerkinElmer) in transmission mode.

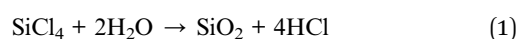
2.4. Photocatalytic activity determination

The photocatalytic activity of the SiO₂-coated TiO₂ powders was evaluated by the photodegradation of RhB solution. For each test, 150 mg powders were added to 30 mL RhB solution (concentration of 9 mg L⁻¹) and continuously stirred in the dark for 30 min to obtain a uniform suspension. Thereafter, the suspension was exposed to UV radiation generated by a mercury lamp with a power of 300 W or 500 W for different exposure times. The set-up allowed to carry out up to 10 samples simultaneously, which ensured that all samples were irradiated under the same conditions, such as light intensity, exposure time, and temperature. The suspension was then centrifuged to separate the powders from the solution. Finally, the solution was analyzed by UV-visible spectrophotometry to determine the residual concentration of the RhB in solution, which was used to evaluate the catalytic activity suppression of the SiO₂ layers.

3 Results and discussion

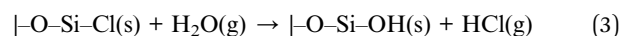
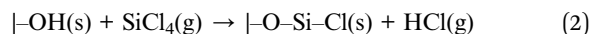
3.1. Reaction mechanism

The chemical reactions in CVD of SiO₂ using SiCl₄ and H₂O are generally described as:²⁴

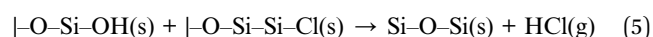
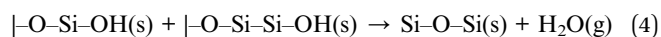


However, it has been reported that the actual growth of SiO₂ CVD consists of a number of reactions, which can be divided into homogeneous and heterogeneous reactions.^{22,23} Homogeneous

reactions occur between SiCl₄ and H₂O molecules in the gas phase, forming oligomers or particles. These reactions have slow kinetics.^{22,23,29} The heterogeneous reactions take place directly on the surface *via* substitution reactions of surface groups (*i.e.*, –Cl and –OH groups). In this case, the reactions are described as:^{22,23}



where |–OH(s) and |–Si–Cl(s) represent the surface hydroxyl and chlorosilicon groups, respectively. In addition to these reactions, condensation reactions simultaneously take place between two –OH groups or –OH and Si–Cl groups on the surface to form siloxane bonds (Si–O–Si), described as:^{22,23}



Therefore, CVD of SiO₂ using SiCl₄ and H₂O might consist of gas-phase reactions, substitution reactions of surface functional groups and condensation reactions.

3.2. Morphology and composition of the coating layers

Tsapatsis *et al.* postulated that the surface morphology of the coating layer is influenced by the reactant species, *i.e.*, H₂O molecules (vapor and physisorbed H₂O) and –OH groups (chemisorbed H₂O). Accordingly, the reactions between SiCl₄ and H₂O molecules may lead to the formation of a granular surface.^{22,23} However, this has not been experimentally demonstrated. Here, we observed that the deposition of SiO₂ on TiO₂ particles without pretreatment resulted in granular and porous surfaces (Fig. 2a). This is attributed to the presence of a thick hydration shell with abundant physisorbed H₂O and –OH groups on the particle surface,³⁰ as detected by FTIR spectra (Fig. 2c). The peak at 3400 cm⁻¹ is attributed to the stretching vibration of –OH groups ($\nu_{\text{O-H}}$) on the surface of TiO₂ particles, whereas the peak at



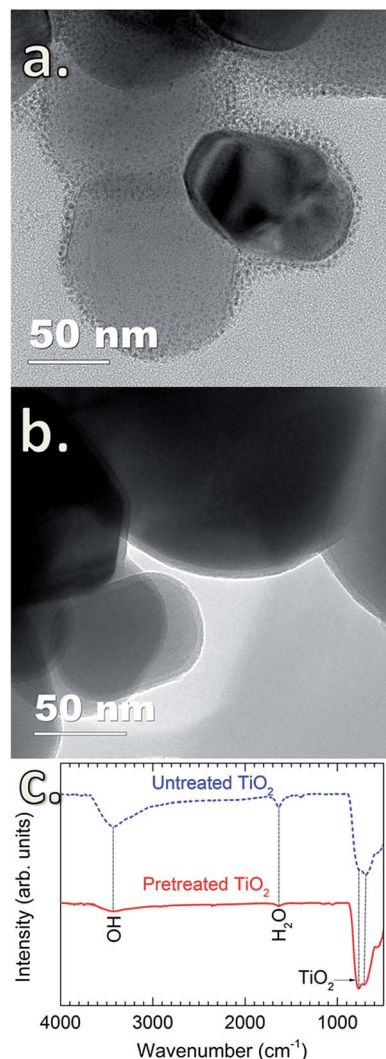


Fig. 2 TEM images of SiO₂-coated anatase TiO₂ particles (a) without heat pretreatment and (b) with heat pretreatment at 170 °C for 1 h, and (c) FTIR spectra of the SiO₂-coated TiO₂ particles without and with heat pretreatment. CVD reaction conditions: SiCl₄ dosing time of 60 min and air exposure time of 60 min. The average thickness of the SiO₂ coating layer is 3.4 ± 0.1 nm.

1625 cm⁻¹ corresponds to the bending vibration of physisorbed H₂O molecules ($\delta_{\text{H}_2\text{O}}$).^{31,32} In the fingerprint region (*i.e.*, wavenumber below 1000 cm⁻¹), the peaks located in the wavenumber range of 500–700 cm⁻¹ are ascribed to the bending vibration of Ti–O–Ti ($\delta_{\text{Ti–O–Ti}}$) of the TiO₂ particles.³¹ Upon the heat pretreatment of TiO₂ particles at 170 °C for 1 h, the intensity of the characteristic peaks of $\nu_{\text{O–H}}$ and $\delta_{\text{H}_2\text{O}}$ significantly decreases (Fig. 2c), indicating that a large amount of the physisorbed H₂O molecules and –OH groups has desorbed from the TiO₂ surface.^{33–37} Therefore, for the untreated TiO₂ particles, the physisorbed H₂O can react with SiCl₄ to form SiO₂ following reaction (1), and in accordance with the previous assumption by Tsapatsis *et al.*, a granular film is formed.²² In comparison with the previous findings that the reaction between SiCl₄ and H₂O either required high temperatures²² or the presence of catalysts to enable the deposition at room temperature,²⁴ our work has

demonstrated the deposition of SiO₂ at room temperature without the use of catalyst. This is probably due to the higher pressure range in the reactor, as well as the catalytic TiO₂ surface. Klaus and George also observed that increasing H₂O partial pressure resulted in the enhanced deposition of SiO₂ in SiCl₄/H₂O CVD.²⁴ Nevertheless, this requires further studies to verify, which is out of the scope of this work. On the pretreated TiO₂ particles, highly uniform, continuous and dense SiO₂ films are formed (Fig. 2b), which is substantially different from the porous and granular SiO₂ films on the untreated TiO₂ particles. This is ascribed to the different reaction mechanism. CVD of SiO₂ on the pretreated TiO₂ particles proceeds following the reactions (2)–(5) (*i.e.*, *via* surface reactions with |–OH and |–Cl groups), thus resulting in the formation of continuous and dense layers.

Fig. 3 shows the O 1s and Ti 2p core-level XPS spectra of uncoated and SiO₂-coated TiO₂ powders. For the uncoated TiO₂, the O 1s spectrum is fitted to two peaks with binding energies (BE) at 529.5 and 530.8 eV (Fig. 3a) corresponding to the O–Ti and O–H chemical states, respectively.³⁸ This is consistent with the results obtained from FTIR shown in Fig. 2c. The O 1s spectrum of the SiO₂-coated TiO₂ shows a noticeable difference with an intense peak at 532.69 eV, representing the Si–O chemical state in SiO₂.³⁹ The fitted spectrum also reveals the presence of additional components located at 534.5 eV (Si–O_x) and 531.64 eV (Si–O–Ti).³⁹ No significant change was observed for the Ti 2p spectra of uncoated and SiO₂-coated TiO₂ particles. In addition, no considerable amount of Cl contamination was detected by XPS, suggesting the complete consumption of –Cl by the chemical reactions with H₂O.

The presence of SiO₂ is additionally confirmed by the FTIR spectra obtained for TiO₂ powders coated with SiO₂ layers with different SiCl₄ dosing times (Fig. 4). The characteristics of SiO₂ are represented by the two sharp peaks at 1227 and 1080 cm⁻¹.⁵ The results show that the absorption increases drastically with the increase of SiCl₄ dosing time from 3 to 30 min, which is indicative of the increase of the coating thickness consistent with the results obtained from TEM (Fig. 5). The images indicate that highly uniform and conformal SiO₂ layers with a thickness as thin as 1 nm can be achieved, which is commonly difficult to obtain by conventional CVD. With increasing dosing time from 7 to 30 min, the coating thickness rises rapidly from 1.4 to 3.0 nm, and gradually reaches saturation with the further increase of dosing time. This saturation may be caused by the complete consumption of the –OH functional groups and adsorbed H₂O on the surface by SiCl₄, which consequently terminates the chemical reactions. A small increase in thickness with increasing dosing time from 30 to 60 min is attributed to the contribution of the residual H₂O vapor inside the chamber and the condensation reactions described above (*i.e.*, reactions (4) and (5)).

3.3. Catalytic suppression of SiO₂ coating layers

Fig. 6a shows the photocatalytic activity toward the degradation of RhB of the uncoated TiO₂ and the TiO₂ coated with SiO₂ layers obtained for different SiCl₄ dosing times. Prior to the UV irradiation, the solution was constantly stirred in the dark (light-off stage) for 30 min to obtain uniform particle dispersion. The



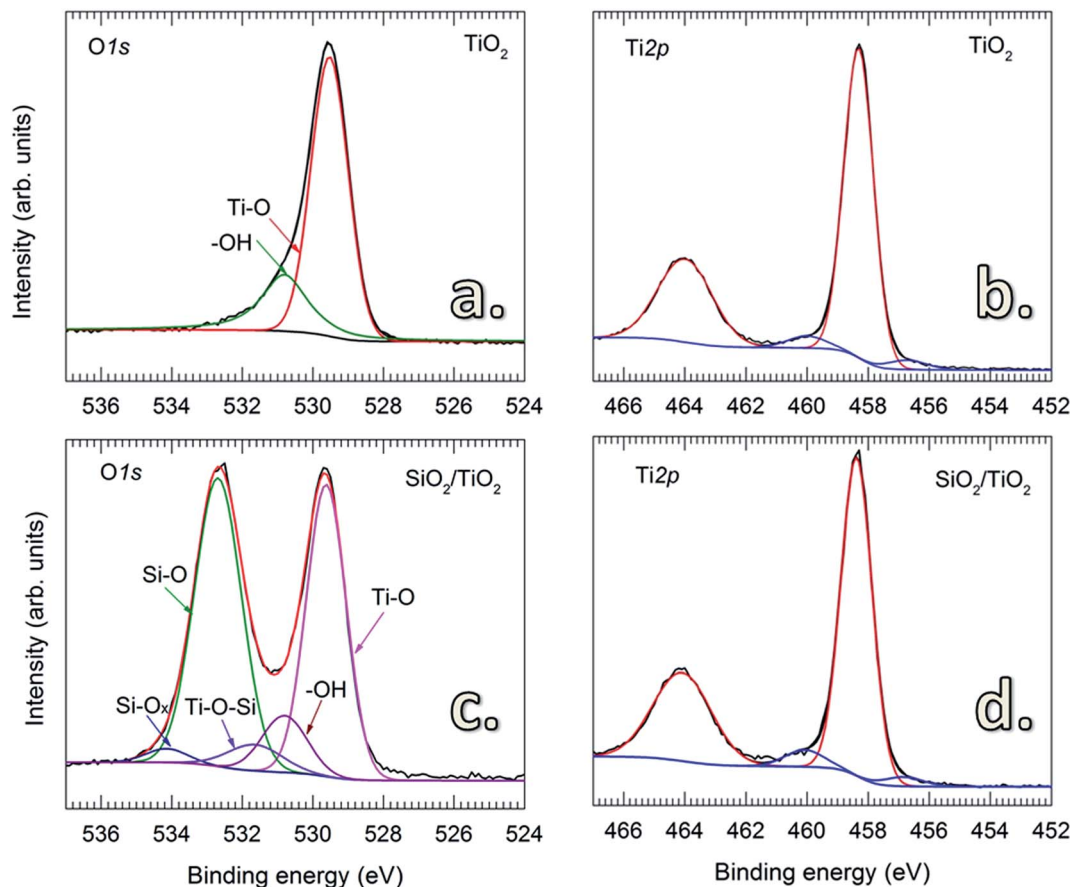


Fig. 3 XPS spectra of O 1s and Ti 2p of uncoated (a and b) and SiO_2 -coated TiO_2 (c and d) powders. CVD was performed on pretreated TiO_2 particles with SiCl_4 dosing time of 15 min and air exposure time of 60 min.

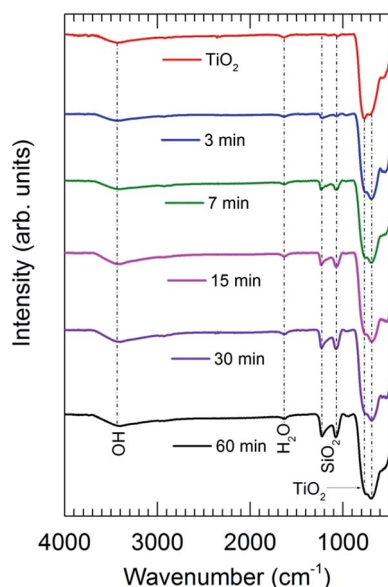


Fig. 4 FTIR spectra of the uncoated TiO_2 and SiO_2 -coated TiO_2 with different SiCl_4 dosing times. CVD was performed on pretreated TiO_2 particles with an air exposure time of 60 min.

samples were collected after certain time-intervals to determine the concentration of the remaining RhB. In the absence of TiO_2 powders, the results show that during this stage, the concentration of RhB remained unchanged. However, a small drop of RhB concentration was observed for the solutions with TiO_2 powders (both uncoated and coated with SiO_2). This drop is caused by the adsorption of a fraction of RhB molecules on the surface of the particles. Thereafter, upon the exposure to UV radiation (light-on stage), the concentration of RhB decayed rapidly for the uncoated powders, indicating the high photocatalytic activity of TiO_2 . Similar effects were observed for the TiO_2 coated with SiO_2 deposited with short SiCl_4 dosing times (up to 15 min). This could be due to the insufficient thickness of the coating and/or the devoid pin-hole free films. As shown in Fig. 5a and b, the thickness of the SiO_2 layers for short dosing times is 2 nm or less (*i.e.*, 1.4 and 2.0 nm for 7 and 15 min of dosing time, respectively). SiO_2 films with a thickness of 3 nm and thicker obtained for longer SiCl_4 dosing times showed significant improvement in the suppression of TiO_2 photocatalytic activity. The small decrease in RhB concentration observed for these two powders (*i.e.*, with SiO_2 layers obtained for 30 and 60 min SiCl_4 exposures) is nearly identical to the decrease observed for RhB without powders, which is attributed to the self-degradation of RhB under the UV irradiation. This is better indicated by the reaction kinetic



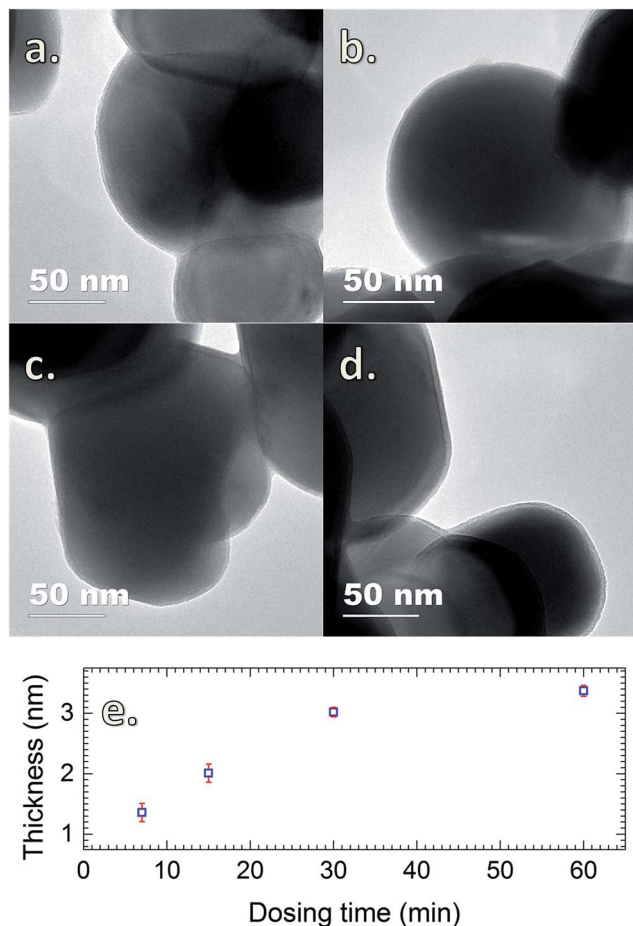


Fig. 5 TEM images of SiO₂-coated TiO₂ particles with different SiCl₄ dosing times: 7 min (a), 15 min (b), 30 min (c) and 60 min (d). (e) shows the increasing trend of the coating thickness with dosing time. CVD was performed on pretreated TiO₂ particles.

plots shown in Fig. 6b obtained from the kinetic equation described as:⁴⁰

$$\ln(C_0/C) = k_{app}t, \text{ or } C = C_0 \exp(-k_{app}t) \quad (6)$$

where k_{app} is the apparent first-order kinetic constant, which represents the reaction rate. From eqn (6), k_{app} value for each reaction can be extracted from the slope of the linear fitting (Table 1). The results show that the k_{app} values obtained for the powders coated with SiO₂ with long SiCl₄ dosing times are only slightly higher than that of the RhB self-degradation (0.043 and 0.046 compared to 0.032 of RhB), suggesting good catalytic activity suppression by these coatings. In other words, a film thickness of above 3 nm ensures sufficient photocatalytic suppression. The enhancement of the catalytic suppression for the longer dosing time may be ascribed partially to the reconstruction of the layers during the exposure. As discussed above, the small increase in SiO₂ thickness with increasing dosing time might be attributed to the condensation reactions of the precursor molecules (*i.e.*, reactions (4) and (5) in Section 3.1), which create siloxane bonds (Si–O–Si), resulting in fewer pin-holes and denser films. This consequently increases the

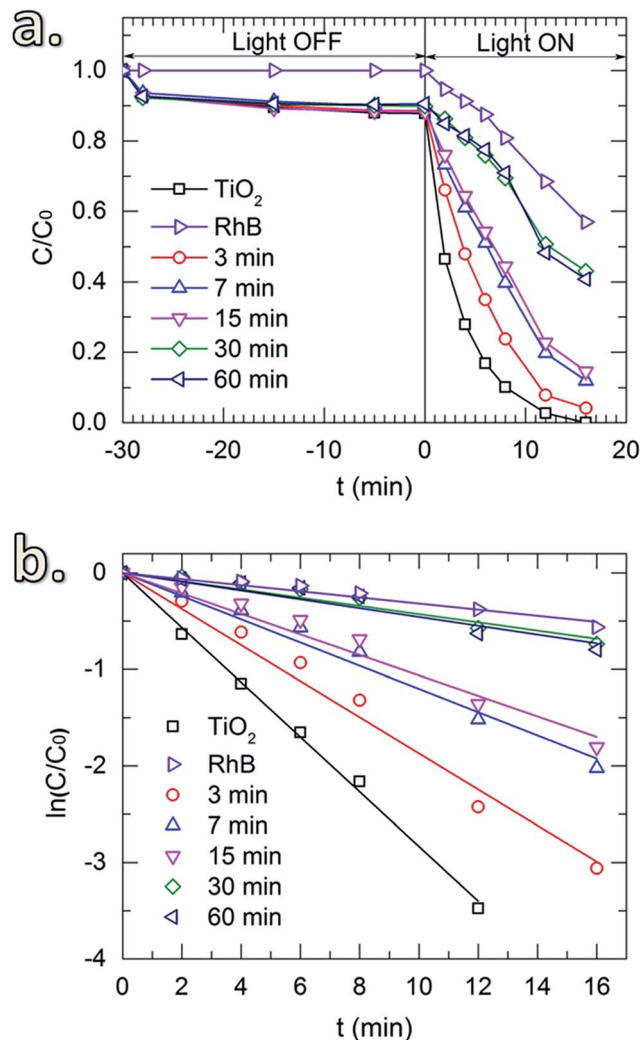


Fig. 6 The photocatalytic degradation of RhB under 500 W UV light using SiO₂-coated TiO₂ powders with different SiCl₄ dosing times (a) and the corresponding reaction kinetic plots (b). The k_{app} values are extracted from the slopes of the linear fitting of the measured data.

Table 1 Apparent first-order rate constant, k_{app} , of TiO₂ powders coated with SiO₂ with different SiCl₄ dosing times

Dosing time/min	k_{app}/min^{-1}	R^2 of fitting
0 (uncoated TiO ₂)	0.283 ± 0.004	0.99
3	0.187 ± 0.006	0.99
7	0.120 ± 0.005	0.99
15	0.106 ± 0.005	0.98
30	0.043 ± 0.003	0.97
60	0.046 ± 0.004	0.95
RhB (without powders)	0.032 ± 0.002	0.98

suppression ability of the coating layers. The results from TEM imaging show that the surface morphology of the coating layer was unaffected by the photocatalytic reactions (not shown), indicating the stability of the coating layer.



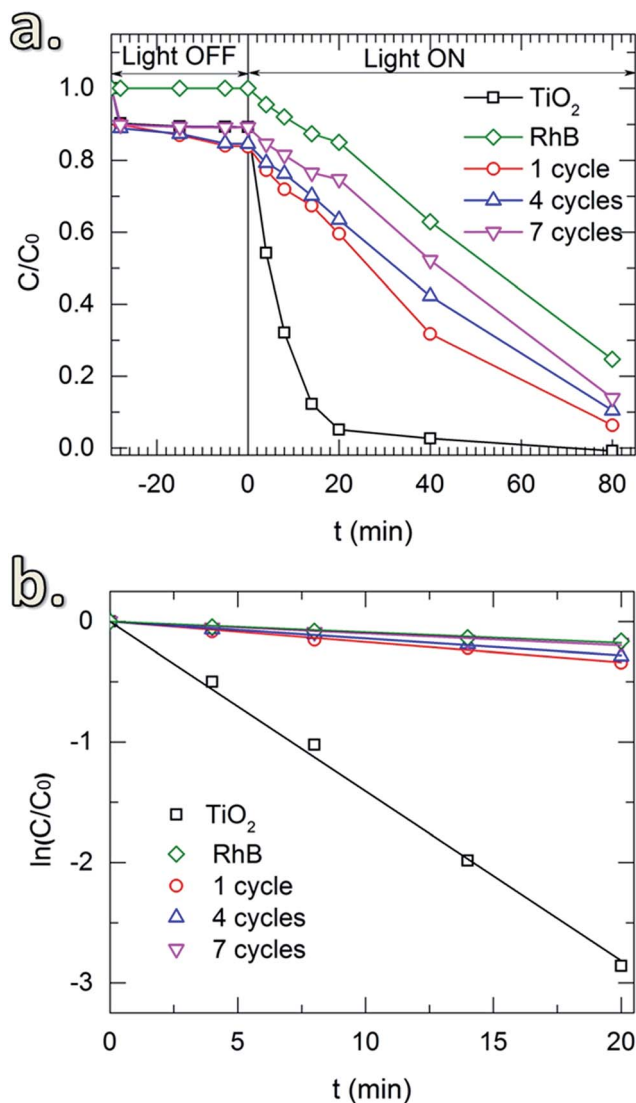


Fig. 7 Photocatalytic degradation of RhB under 300 W UV light using SiO₂-coated TiO₂ powders with different number of SiO₂ CVD cycles (1, 4 and 7). CVD reaction conditions: SiCl₄ dosing time of 30 min and air exposure time of 60 min.

Fig. 7 shows the RhB degradation of the SiO₂-coated TiO₂ with different numbers of coating cycles. In this case, an SiCl₄ dosing time of 30 min was applied for all of the depositions. Samples for 1, 4 and 7 cycles were tested. In addition, the UV irradiation power was reduced to 300 W to enable the study of the degradation up to 80 min. The same drop of RhB concentration caused by the surface adsorption was observed in the light-off stage (Fig. 7a). In the light-on stage, the reaction kinetic plots (Fig. 7b) show negligible effect of thickness on the photocatalytic degradation, demonstrating the sufficient suppression of the SiO₂ layers deposited with a small number of CVD cycles. In comparison with the materials and coating methods that have been used to mitigate the photocatalytic activity of TiO₂ pigmentary materials (Table 2), our approach showed several advantages in providing a fast, simple and efficient process. Especially, for the first time in literature a room-temperature gas-phase deposition technique for pigmentary coating applications is introduced.

4 Conclusions

We have demonstrated the room-temperature pulsed-CVD of SiO₂ thin films on TiO₂ nanoparticles using SiCl₄ as the Si precursor and air containing water vapor as the oxidizing agent without the use of catalysts. The formation of SiO₂ was confirmed by XPS and FTIR spectroscopy. The deposition on the TiO₂ powders without preheating resulted in a granular surface, whereas on pretreated TiO₂ (at 170 °C for 1 h) highly uniform, conformal and continuous SiO₂ films were obtained. The thickness of the SiO₂ layer increased with SiCl₄ dosing time and reached saturation most likely upon the consumption of the surface hydroxyl groups and water vapor. This enabled the control of coating thickness at nanometer level precision, and consequently, the study of the influence of film thickness on photocatalytic suppression ability of SiO₂ films. Accordingly, we found that a minimum thickness of about 3 nm is needed to sufficiently suppress the photocatalytic properties of TiO₂

Table 2 Thin film coating methods and materials for suppressing photocatalytic activity of TiO₂ pigmentary materials

TiO ₂ material	Coating method	Coating material	Coating thickness (nm)	Deposition temperature (°C)	Photocatalytic reaction	Ref.
P25	ALD	Al ₂ O ₃	6	177	Methylene blue	41
Anatase	ALD	SiO ₂	2	500 for SiO ₂	IPA to acetone	12
		SiO ₂ /Al ₂ O ₃	1/1	177 for Al ₂ O ₃		
		SiO ₂ /Al ₂ O ₃ /SiO ₂ /Al ₂ O ₃	0.5/0.5/0.5/0.5			
P25	ALD	Al ₂ O ₃	3.8	150	RhB	42
Anatase	ALD	SiO ₂	6	175	Methylene blue	13
P25			9			
Anatase	MLD	Alucone	7–10	100–160	Methylene blue	14
Rutile	CVD	SiO ₂	1–2	900–1000	Methylene blue	10
Rutile	Wet-chemistry	ZrO ₂	5	40	RhB	15
		CeO ₂	1–2	60		
Rutile	Wet-chemistry	CeO ₂	1–2	60	RhB	43
ST-21	Wet-chemistry	SiO ₂	4	40	Methylene blue	4
P25	Wet-chemistry	Porous SiO ₂	20	Room temperature	RhB	6
Anatase	Pulsed-CVD	SiO ₂	3	Room temperature	RhB	This work



toward the degradation of RhB. A further increase in film thickness resulted in only insignificant improvement in the suppression performance. Our work has demonstrated a simple, fast and feasible method for depositing SiO₂ on TiO₂ pigment at room temperature, which is applicable also for other powders, especially for heat-sensitive materials, and can be further developed for large-scale production.

Acknowledgements

The authors would like to acknowledge the financial support of key project of National Natural Science Foundation of China (No. 21236004), and China Scholarship Council.

References

- H. Shi, R. Magaye, V. Castranova and J. Zhao, *Part. Fibre Toxicol.*, 2013, **10**, 15–47.
- C. L. Bianchi, C. Pirola, F. Galli, G. Cerrato, S. Morandi and V. Capucci, *Chem. Eng. J.*, 2015, **261**, 76–82.
- X. Feng, S. Zhang and X. Lou, *Colloids Surf., B*, 2013, **107**, 220–226.
- H. Lee, S. Koo and J. Yoo, *J. Ceram. Process. Res.*, 2012, **13**, S300–S303.
- O. K. Park and Y. S. Kang, *Colloids Surf., A*, 2005, **257**, 261–265.
- Y. Ren, M. Chen, Y. Zhang and L. Wu, *Langmuir*, 2010, **26**, 11391–11396.
- Y. Liu, C. Ge, M. Ren, H. Yin, A. Wang, D. Zhang, C. Liu, J. Chen, H. Feng and H. Yao, *Appl. Surf. Sci.*, 2008, **254**, 2809–2819.
- Y. Zhang, H. Yin, A. Wang, M. Ren, Z. Gu, Y. Liu, Y. Shen, L. Yu and T. Jiang, *Appl. Surf. Sci.*, 2010, **257**, 1351–1360.
- H.-X. Wu, T.-J. Wang and Y. Jin, *Ind. Eng. Chem. Res.*, 2006, **45**, 5274–5278.
- D. J. Simpson, A. Thilagam, G. P. Cavallaro, K. Kaplun and A. R. Gerson, *Phys. Chem. Chem. Phys.*, 2011, **13**, 21132–21138.
- Q. H. Powell, T. T. Kodas and B. M. Anderson, *Chem. Vap. Deposition*, 1996, **2**, 179–181.
- D. M. King, X. Liang, B. B. Burton, M. K. Akhtar and A. W. Weimer, *Nanotechnology*, 2008, **19**, 255604–255611.
- X. Liang, K. S. Barrett, Y.-B. Jiang and A. W. Weimer, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2248–2253.
- X. Liang and A. W. Weimer, *J. Nanopart. Res.*, 2010, **12**, 135–142.
- B.-X. Wei, L. Zhao, T.-J. Wang, H. Gao, H.-X. Wu and Y. Jin, *Adv. Powder Technol.*, 2013, **24**, 708–713.
- B.-X. Wei, L. Zhao, T.-J. Wang and Y. Jin, *Ind. Eng. Chem. Res.*, 2011, **50**, 13799–13804.
- S. M. George, *Chem. Rev.*, 2010, **110**, 111–131.
- H. Van Bui, F. Grillo and J. R. van Ommen, *Chem. Commun.*, 2017, **53**, 45–71.
- F. S. Becker, D. Pawlik, H. Anzinger and A. Spitzer, *J. Vac. Sci. Technol., B*, 1987, **5**, 1555–1563.
- A. Adams and C. Capio, *J. Electrochem. Soc.*, 1979, **126**, 1042–1046.
- K. Watanabe, T. Tanigaki and S. Wakayama, *J. Electrochem. Soc.*, 1981, **128**, 2630–2635.
- M. Tsapatsis, S. Kim, S. W. Nam and G. R. Gavalas, *Ind. Eng. Chem. Res.*, 1991, **30**, 2152–2159.
- M. Tsapatsis and G. R. Gavalas, *AIChE J.*, 1992, **38**, 847–856.
- J. W. Klaus and S. M. George, *J. Electrochem. Soc.*, 2000, **147**, 2658–2664.
- S. Chaudhary, A. R. Head, R. Sánchez-de-Argas, H. Tissot, G. Olivieri, F. Bournel, L. Montelius, L. Ye, F. Rochet, J.-J. Gallet, B. Brena and J. Schnadt, *J. Phys. Chem. C*, 2015, **119**, 19149–19161.
- Q. H. Powell, G. P. Fotou, T. T. Kodas and B. M. Anderson, *Chem. Mater.*, 1997, **9**, 685–693.
- Q. H. Powell, G. P. Fotou, T. T. Kodas, B. M. Anderson and Y. Guo, *J. Mater. Res.*, 1997, **12**, 552–559.
- D. Longrie, D. Deduytsche and C. Detavernier, *J. Vac. Sci. Technol., A*, 2014, **32**, 010802.
- M. L. Hair and W. Hertl, *J. Phys. Chem. C*, 1969, **73**, 2372–2378.
- V. N. Koparde and P. T. Cummings, *J. Phys. Chem. C*, 2007, **111**, 6920–6926.
- S. Musić, M. Gotić, M. Ivanda, S. Popović, A. Turković, R. Trojko, A. Sekulić and K. Furić, *Mater. Sci. Eng., B*, 1997, **47**, 33–40.
- S. Sivakumar, P. K. Pillai, P. Mukundan and K. G. K. Warriar, *Mater. Lett.*, 2002, **57**, 330–335.
- S. Benkoula, O. Sublemontier, M. Patanen, C. Nicolas, F. Sirotti, A. Naitabdi, F. Gaie-Levrel, E. Antonsson, D. Aureau, F.-X. Ouf, S.-I. Wada, A. Etcheberry, K. Ueda and C. Miron, *Sci. Rep.*, 2015, **5**, 15088.
- M. A. Henderson, *Langmuir*, 1996, **12**, 5093–5098.
- L. Walle, A. Borg, P. Uvdal and A. Sandell, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **80**, 235436.
- S. Wendt, R. Schaub, J. Matthiesen, E. K. Vestergaard, E. Wahlström, M. D. Rasmussen, P. Thøstrup, L. M. Molina, E. Lægsgaard, I. Stensgaard, B. Hammer and F. Besenbacher, *Surf. Sci.*, 2005, **598**, 226–245.
- U. Aschauer, Y. He, H. Cheng, S.-C. Li, U. Diebold and A. Selloni, *J. Phys. Chem. C*, 2009, **114**, 1278–1284.
- B. Erdem, R. A. Hunsicker, G. W. Simmons, E. D. Sudol, V. L. Dimonie and M. S. El-Aasser, *Langmuir*, 2001, **17**, 2664–2669.
- G. Kovács, Z. Pap, C. Coteț, V. Coșoveanu, L. Baia and V. Danciu, *Materials*, 2015, **8**, 1059–1073.
- S. Wang, F. Teng and Y. Zhao, *RSC Adv.*, 2015, **5**, 76588–76598.
- L. F. Hakim, D. M. King, Y. Zhou, C. J. Gump, S. M. George and A. W. Weimer, *Adv. Funct. Mater.*, 2007, **17**, 3175–3181.
- E. Jang, K. Sridharan, Y. M. Park and T. J. Park, *Chem.-Eur. J.*, 2016, **22**, 12022–12026.
- H. Gao, B. Qiao, T.-J. Wang, D. Wang and Y. Jin, *Ind. Eng. Chem. Res.*, 2014, **53**, 189–197.

