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Rajankumar L. Patel

Ying Bing Jiang

Xinhua Liang
Missouri University of Science and Technology, liangxin@mst.edu

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Highly porous titania films coated on sub-micron particles with tunable thickness by molecular layer deposition in a fluidized bed reactor

Rajankumar L. Patel[a], Ying-Bing Jiang[b], Xinhua Liang[a,*]

[a]Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, Missouri 65409, USA
[b]TEM Laboratory, University of New Mexico, Albuquerque, New Mexico 87131, USA

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Abstract

Titanium alkoxide (titanicone) thin films were coated on large quantities of sub-micron sized silica particles at 100 °C using molecular layer deposition (MLD) in a fluidized bed reactor. Titanium tetrachloride and ethylene glycol were used as precursors. The content of titanium on the particles increased linearly as the number of MLD coating cycles increased. The conformity of the films, with a thickness of $\sim$12 nm, was verified using TEM for silica particles coated with 50 cycles of titanicone. The composition of the titanicone films was confirmed using energy dispersive X-ray spectrometry. Porous titanium oxide films were formed for the particles coated with 50 cycles of titanicone MLD by oxidation in air at 400 °C or by decomposition of the organic components of the titanicone films in the presence of water. The thicknesses of the films were reduced from $\sim$12 nm to $\sim$8 nm after oxidation in air at 400 °C for 1 hr. The effect of aging on the titanicone films was studied at different lengths of aging time in the presence of water. A greatly increased surface area of 48.8 $m^2\ g^{-1}$ was obtained for the particles exposed to water for 24 hr, compared to the as-deposited 50 cycles of titanicone coated sample with a surface area of 7.7 $m^2\ g^{-1}$. The decomposition of titanicone films, after exposure to water vapor for various lengths of time, was studied using Fourier transform infrared spectroscopy.

Keywords: Ultra-thin; Porous film; Molecular layer deposition (MLD); Titanium alkoxide (titanicone); Titanium oxide (titania); Fluidized bed reactor

1. Introduction

Titania possesses properties such as chemical inertia [1] and high surface affinity toward ligands [2,3]. Its optical and electronic activities make it an extremely attractive material for a great variety of applications, including pigments [4,5], photocatalysts [6,7], and energy conversion [8,9]. Many applications (e.g., solar cells, sensors) require processing of thin films with high surface areas, high porosity, and high purity to obtain improved device efficiency [8–12]. Fabrication control of porous titania films is significant, as it can impart a profound effect on surface reactions and fine tuning of material properties [6,13,14]. Currently, most of the preparation methods used involve organic templates. Organic–inorganic films are prepared first, and the organic templates must be removed gently by calcination at high temperature in order to create porous structures. Sol–gel [15], self-assembly [16,17], layer-by-layer assembly [18], and Langmuir–Blodgett [19] were each developed for fabricating polymeric thin films. Although these techniques can fabricate organic–inorganic films, often they lack a porous framework with structural integrity, precise composition, and thickness control.

Similar to atomic layer deposition (ALD), the vapor-phase molecular layer deposition (MLD) approach is ideal for the deposition of organic or organic–inorganic hybrid materials [20–24]. This MLD approach utilizes alternating self-limiting heterogeneous surface reactions to build up a solid-state thin film through a sequence of molecular adsorption/reaction steps. This process allows a film to be conformally constructed on surfaces with arbitrary shapes and surface areas. MLD can provide precise control over film thickness, composition, and conformity at the molecular level. It has recently been demonstrated that ultrathin porous aluminum oxide films can be prepared from MLD prepared organic–inorganic hybrid polymer

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*Corresponding author.
E-mail address: liangxin@mst.edu (X. Liang).

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films by removing the organic components [25,26]. The porosity of the resulting inorganic films will depend on the volume occupied by the organic constituting part. It is expected that ultrathin porous titania films can also be prepared by a similar process. The MLD chemistry of hybrid organic–inorganic titanium alkoxide (titanicone) films has been reported using alternating reactions of titanium tetrachloride ($TiCl_4$) and ethylene glycol (EG) [27,28]. The photocatalytic activity of the thermally annealed titanicone film was about a 5-fold increase when compared to that of the TiO_2 film prepared using ALD under optimal processing conditions [28]. Thus far, no study has been conducted for titanicone MLD on a large quantity of particles and their porous film formation.

In this study, ultrathin titanicone films were coated on primary sub-micron SiO_2 particles. The reason for using particles with such a low surface area is because it was easier to verify the particle surface area increment due to the formation of porous structures from MLD films. This type of porous coating can be used for fine tuning some porous materials, such as zeolite for gas separation [29], and catalysts with enhanced performance (i.e., increased thermal stability [30] and reaction selectivity [31]). The organic constituents in the films were removed by either calcination in air at elevated temperatures or decomposition in the presence of water at room temperature, which could be very important for coating temperature-sensitive substrates. The resulting porous structures had both micropores and mesopores.

2. Experimental details

2.1. MLD of titanicone films

Titanicone MLD was performed in a fluidized bed reactor, as shown in Fig. 1. This reactor system consisted of a reactor column, a vibration generation system, a gas flow control system, and a data acquisition and control system with LabView®, which has been described in detail previously [24]. Silica powder (500 nm, 99.9%, from Alfa Aesar) was used as the substrate. Titanium tetrachloride (99.9%, from Sigma Aldrich) and EG (anhydrous, 99.8%, from Sigma Aldrich) were used as precursors. All of the chemicals were used as received without any treatment. For a typical run, 10 g of particles were loaded into the reactor. The reaction temperature was 100 °C. The minimum fluidization superficial gas velocity was determined by measuring the pressure drop across the particle bed versus the superficial gas velocity of purge gas. The base pressure was ~3.5 Torr at the minimum fluidization velocity. During the MLD reaction, $TiCl_4$ was fed through the distributor of the reactor, based on the driving force of its room-temperature vapor pressure. A needle valve was used to adjust the $TiCl_4$ flow rate and ensure that the $TiCl_4$ pressure was high enough to promote particle fluidization. The reactor was also subjected to vibration via vibrators to improve the quality of particle fluidization during the MLD process. The vapor of EG was delivered into the reactor using a bubbler, which was heated at 65 °C. The feed lines were kept at ~100 °C to avoid excessive adsorption of EG in the internal walls of the system that could promote side-reactions of chemical vapor deposition (CVD).

The entire coating-sequence process was controlled and monitored using a LabView® program. Each MLD coating cycle consisted of six steps: $TiCl_4$ dose (90 s), N_2 flush (600 s), vacuum (30 s), EG dose (720 s), N_2 flush (600 s), and vacuum (30 s). These steps helped ensure that direct contact between the two precursors was avoided and CVD side-reactions were prevented. N_2 gas flow rate was controlled by an MKS mass flow controller during the process. Before the reaction, the particles were outgassed at 100 °C with a continuous N_2 flow for at least 5 hr. The MLD reaction was carried out for 10, 20, 30, 40, and 50 cycles.

To form porous MLD films, two post-treatment procedures were applied: thermal annealing and water soaking. The 50 cycles of titanicone MLD-coated silica particles were oxidized in air at 400 °C for 1 hr at a heating and cooling rate of 1 °C/min.

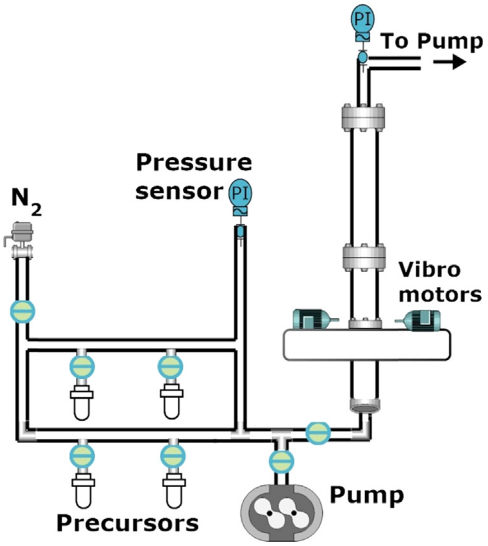

Fig. 1. Schematic of MLD fluidized bed reactor.

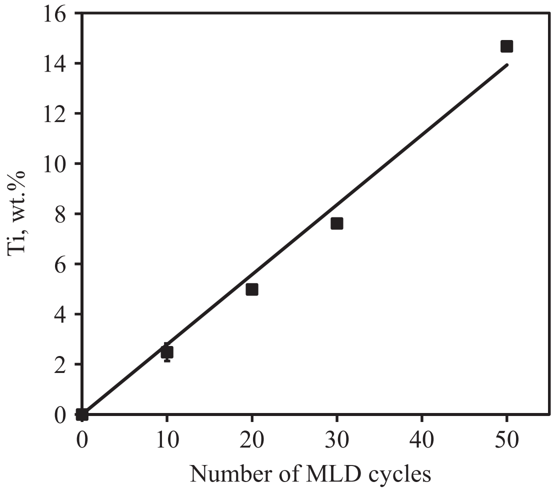

Fig. 2. Titanium content on 500 nm silica particles versus the number of MLD-coating cycles.

A different set of the same particles was soaked in deionized water for different lengths of time and then dried under vacuum at room temperature.

2.2. Characterization

The coated particles were visualized with an FEI Tecnai F20 field emission gun high-resolution TEM/STEM equipped with an energy dispersive X-ray spectrometer (EDS) system. TEM samples were prepared by placing the particles on holey-carbon films supported on Cu grids. To quantify the amount of Ti on the surface of the particles, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used. A Perkin-Elmer Optima 7300DV instrument was used to perform ICP-AES. A Quantachrome Autosorb-1 was used to obtain nitrogen adsorption and desorption isotherms at −196 °C, for the uncoated, and the MLD-coated particles before and after the removal of the organic components. Before starting the adsorption measurements, the as-deposited samples were outgassed at 50 °C under vacuum for 24 hr, and the samples that were water treated and oxidized were outgassed at 120 °C under vacuum for 24 hr. The specific surface areas of the samples were calculated using the Brunauer–Emmett–Teller (BET) method in a relative pressure range of 0.05–0.25. The pore size distribution curves were derived from the adsorption and desorption isotherms using the Horvath–Kawazoe (HK) and the Barrett–Joyner–Halenda (BJH)

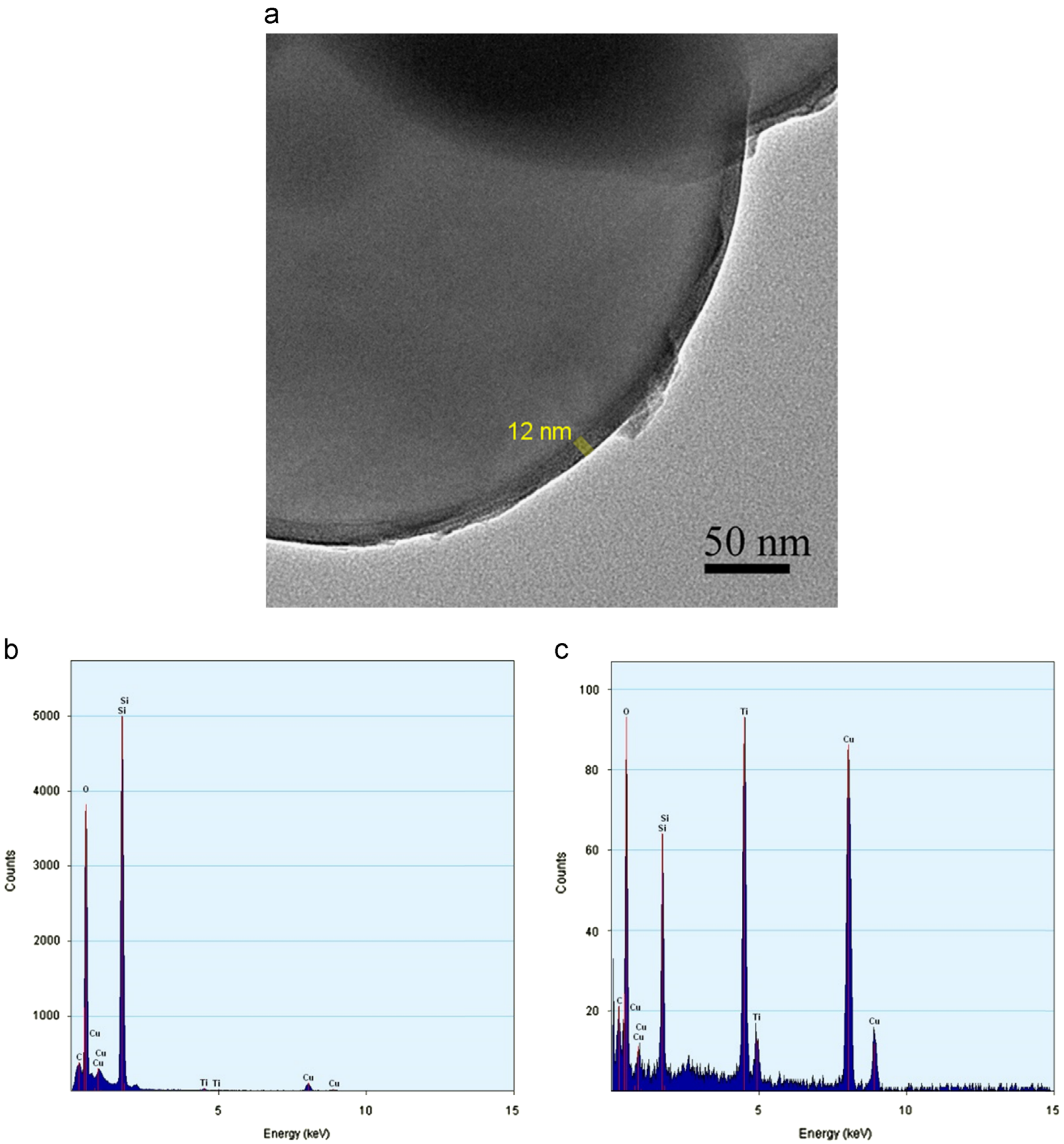

Fig. 3. (a) TEM image of one 500 nm silica particle coated with 50 cycles of titanicone MLD film and EDS spectra of (b) the silica substrate and (c) the titanicone MLD film.

methods. The infrared spectroscopy (IR) spectra of the samples were obtained from Nicolet Nexus 470 FT-IR Spectrometer (Thermo Nicolet) in the transmission mode, and continuously purged with purified dry air. Samples were measured with 100 scans at a 4 cm^{-1} resolution.

3. Results and discussion

3.1. Growth of titanicone MLD films on SiO_2

Titanicone films of different thicknesses were coated on SiO_2 particles by controlling the number of MLD cycles. The Ti content on the silica particles of each sample was measured using ICP-AES. As shown in Fig. 2, titanium content followed a linear path with increase in the number of MLD cycles. The titanicone film thickness was much smaller than the sub-micron sized silica particles. This resulted in a linear proportionality between the titanium content and the number of coating cycles. The thicknesses of titanicone films were reflected by the content of Ti on the particles. The linearity of the plot also clearly indicated the layer-by-layer growth of the titanicone MLD films on the substrate particles. Therefore, the thickness of each film can be precisely controlled by the number of MLD-coating cycles. No nucleation period was required to deposit MLD coating on the silica particles, because native hydroxyl groups were present on the surfaces of the silica particles. The uniformly deposited titanicone films were directly observed using TEM imaging. As shown in Fig. 3a, the thickness of the film was ~12 nm for particles coated with 50 cycles of MLD coating. This thickness indicated that the growth rate of the titanicone films was ~0.24 nm per $TiCl_4$/EG cycle. This observed growth rate was a bit slower than the reported growth rate of titanicone MLD, which was 0.44 nm/cycle at 100 °C [27]. The composition of the films was directly confirmed using EDS, as shown in Figs. 3b and c. The former spectrum is for the silica substrate and the latter spectrum is for the titanicone MLD film.

Most of the primary particles were coated with titanicone films during the coating process, which was indirectly supported by the BET surface area analysis as shown in Fig. 4. The gradual decrease in the surface area of the particles was analogous to the proven results that MLD coating occurred on the primary particles despite small-sized aggregates [24]. There was no dramatic decrement in surface area with an increase in the number of MLD-coating cycles. The surface area of uncoated silica particles gradually decreased from 10.0 m^2 g^{-1} to 7.4 m^2 g^{-1} for the particles coated with 40 cycles of titanicone film. The surface area did not decrease further beyond 40 cycles of MLD coating. The reduction in surface area before 40 cycles could be explained by the larger particles, the density changes, and the slight aggregation of particles after MLD coating. The increase in surface area after 40 cycles could be explained by the partial formation of porous films, which would contribute to higher surface areas of the particles. This similar behavior has also been documented for alucone and zincone films in previous studies [26,32], where it was found that porous metal oxide films could form during the deposition process.

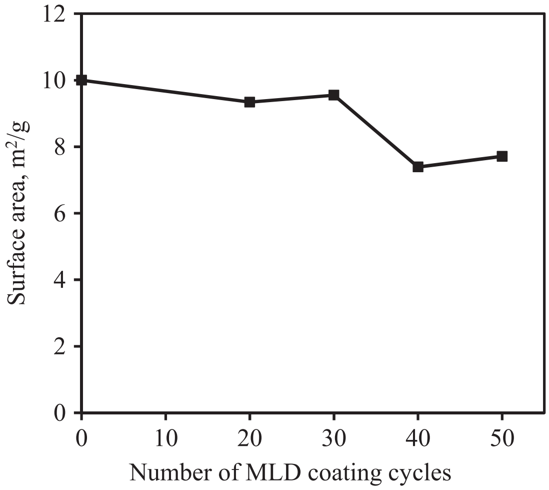

Fig. 4. Surface area of silica particles versus the number of MLD-coating cycles.

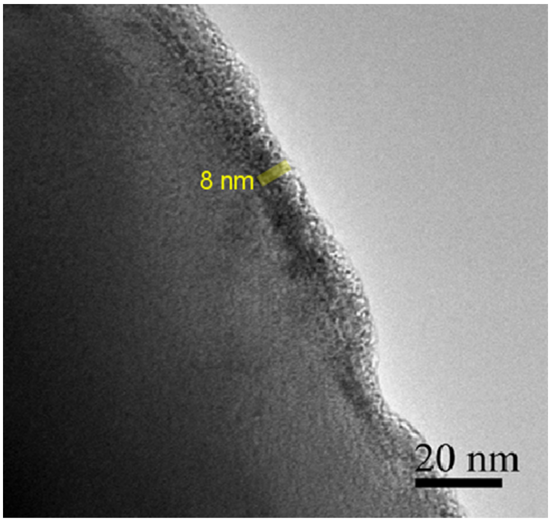

Fig. 5. TEM image of one 500 nm silica particle coated with 50 cycles of titanicone MLD film after oxidation in air at 400 °C for 1 hr.

3.2. Porous MLD films

Silica particles coated with 50 cycles of titanicone films were oxidized in air at 400 °C for 1 hr to create porous structures within the films. The TEM image, in Fig. 5, of one such particle confirms the resultant conformal film after oxidation. The surface area of the oxidized particles was 22.0 m^2 g^{-1}, and this increment can be attributed to the formation of porous structures of TiO_2. During oxidation in air, the organic components should be degraded to create a porous structure of a conformal titania film. As clearly shown in Figs. 3a and 5, the film thickness decreased from ~12 nm to ~8 nm for the oxidized particles. At the oxidation temperature of 400 °C, amorphous titania could be crystallized to form anatase phase titania. Such phase transformation may affect the stability of the porous structure and result in a lower surface area of porous titania. This set of experiments indicates the potential of the MLD method for the uniform coating of high geometric aspect ratio nanoscale structures. As thermal annealing of titania results phase change from amorphous to anatase, the MLD technique can also be crucial for the thermal annealing compatibility process [28,33]. However, the XRD results of the oxidized samples showed no confirmed sign that the anatase phase was present. It seems that the amount of crystalline titania was not substantial enough to be detected by XRD. This could be due to low crystallinity of titania present in the samples, as the samples were heated at 400 °C for only 1 hr and the presence of carbon could have suppressed the phase transition [28].

The particles from the same batch, 50 cycles of titanicone coated silica, were soaked in deionized water for different lengths of time, and then dried. The porous structures of titania particles were studied by nitrogen adsorption and desorption analysis. Fig. 6 shows nitrogen adsorption and desorption isotherms, surface area, pore volume, and pore size distributions of 50 cycles of titanicone MLD-coated silica particles after being soaked in water for different lengths of time. The adsorption–desorption isotherm is a type II isotherm, according to the IUPAC recommendations. The pore diameter of the micropores was estimated to be ~0.6 nm by using the HK method. Mesopores, with an estimated diameter of ~1.1 nm by using the BJH method, were also observed. The high surface areas of the water-soaked particles were due to the formation of these micropores and mesopores in the films. After being soaked in water for 24 hr, most of the organic components were removed, and the surface area of the porous titania films greatly increased to 48.8 m^2/g, as compared to the surface area of 7.7 m^2/g for the as-deposited silica particles. However, the surfaces of the particles decreased with soaking times longer than 24 hr, which was due to the collapse of

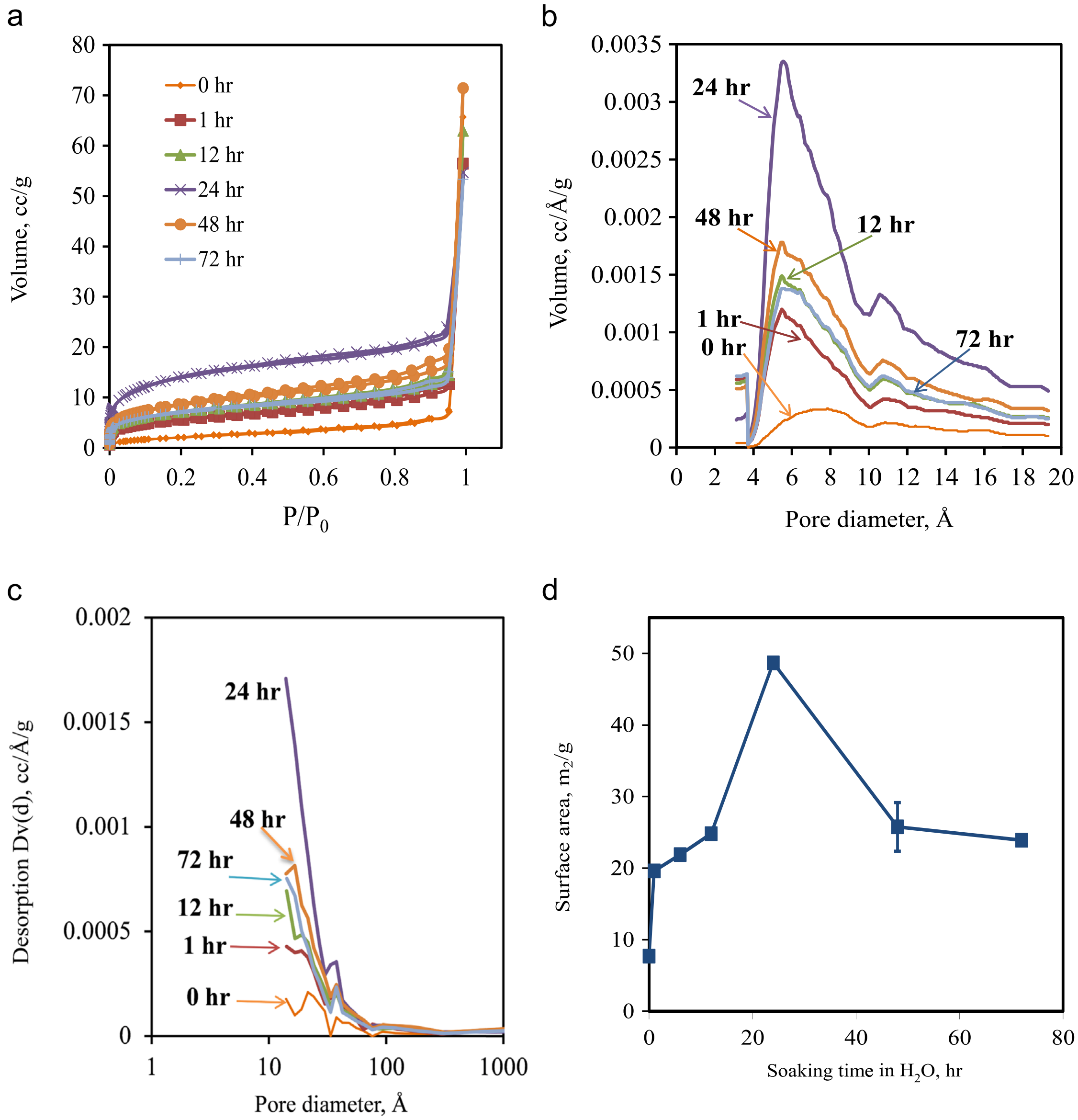

Fig. 6. (a) Nitrogen adsorption and desorption isotherms, pore size distributions of (b) micropores and (c) mesopores, and (d) surface area of silica particles coated with 50 cycles of titanicone MLD film after being soaked in water for different lengths of time.

micropores and mesopores that formed larger pores and promoted instability of the titania films. It is worthy to mention that the surface area of the titania film itself was much higher, as this was the surface area of 500 nm SiO_2 particles coated with one layer of porous titania film. The TEM image, as shown in Fig. 7, of the silica particle coated with 50 cycles of titanicone MLD film after being soaked in water for 24 hr, revealed that the continuous layer of film had collapsed due to drastic decomposition of the organic components by directly soaking the particles in water. The porous structure was damaged, and the porous film was not conformal.

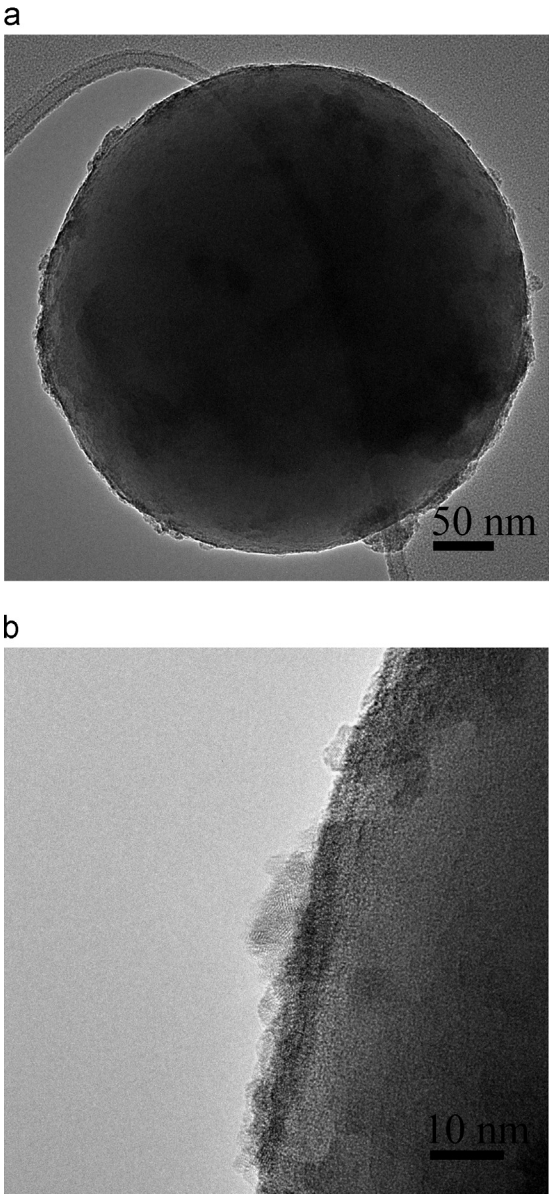

Fig. 7. (a, b) TEM images of one 500 nm silica particle coated with 50 cycles of titanicone MLD film after being soaked in water for 24 hr.

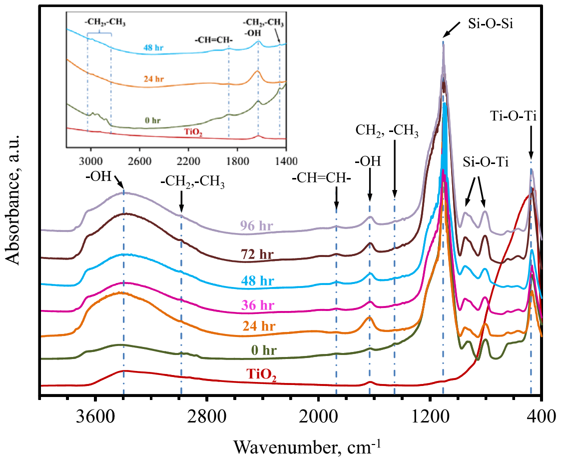

Fig. 8. FTIR spectra of silica particles coated with 50 cycles of titanicone MLD film after being exposed to water vapor for different lengths of time. The inset spectra clearly show the presence of $–CH_2$, $–CH_3$ groups on the as-deposited silica particles.

To unfold the decomposition of the titanicone films in the presence of water, 50 cycles of titanicone-coated silica particles were exposed to water vapor for different lengths of time and the composition changes of the films were analyzed using FTIR. As shown in Fig. 8, a broad absorption peak was seen at 3100–3800 cm^{-1}, which was assigned to the stretching modes of O–H bands and related to free water (capillary pore water and surface absorbed water) [34]. The peak at ~1620 cm^{-1} was due to the bending vibration of the H–O–H band, which was assigned to the –OH present in the sample. In all samples, a band at 1000–1250 cm^{-1} was clearly visible, and was assigned to the asymmetric stretching vibrations of the Si–O–Si band [34]. The two absorption peaks between 760 and 950 cm^{-1} were ascribed to the symmetric vibrations of the stretching Si–O–Ti band. In the low-frequency region, the appearance of low intensity at 500 cm^{-1} indicated the Ti–O–Ti modes. The peaks related to the $–CH_3$ and $–CH_2$ groups were observed at 1367, 1532, and 2950 cm^{-1}. An indicative peak at ~1880 cm^{-1} showed a possible alkene (–CH═CH–) group stretching. Over a period of more than 24 hr, these components were decomposed in the presence of water, as evident from the FTIR. The series of FTIR spectra, for the samples exposed to water vapor for different lengths of time, elucidated the presence of organic components in the titanicone films and their decomposition after their exposure to water vapor. This finding also confirms that the titanicone films became titania films after removal of that organic components. It also explains the increase in the surface areas of the titania films after 24 hr water vapor exposure, which was the result of space left after decomposition of the organic components.

4. Conclusions

Sub-micron silica particles were coated with ultrathin titanicone films using MLD at 100 °C in a fluidized bed reactor. TEM and EDS studies confirmed the conformality and the composition of the titanicone MLD films, respectively. Porous titania films were created by oxidizing the MLD-coated particles in air at 400 °C or by decomposition in the presence of water. The surface area was increased from 7.7 $m^2\ g^{-1}$ for the as-deposited 50 cycles titanicone MLD-coated silica particles to 22.0 $m^2\ g^{-1}$ for the particles oxidized at 400 °C, and to 48.8 $m^2\ g^{-1}$ for the sample after being soaked in water for 24 hr. The lower surface areas of the oxidized particles were due to the phase transformation of amorphous titania to anatase titania at the oxidation temperature of 400 °C. The decomposition of organic components was studied using FTIR for titanicone films exposed to water vapor for different lengths of time. This study demonstrated a process for preparing porous titania films with a tunable thickness, which could have many potential applications, such as catalysis, separation, sensing, and energy conversion and storage.

Acknowledgments

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