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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

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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 ~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 ~12 nm to ~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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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.

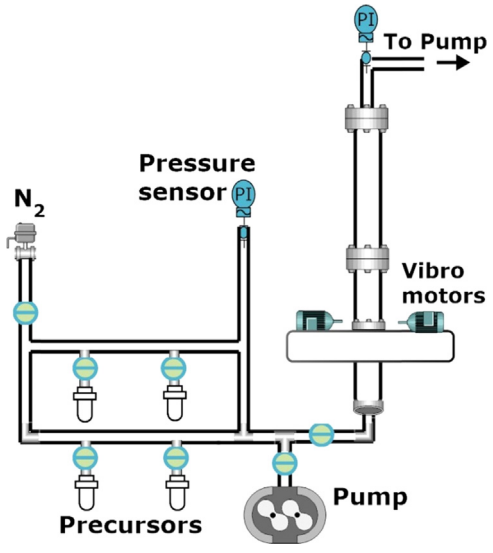

Fig. 1. Schematic of MLD fluidized bed reactor.

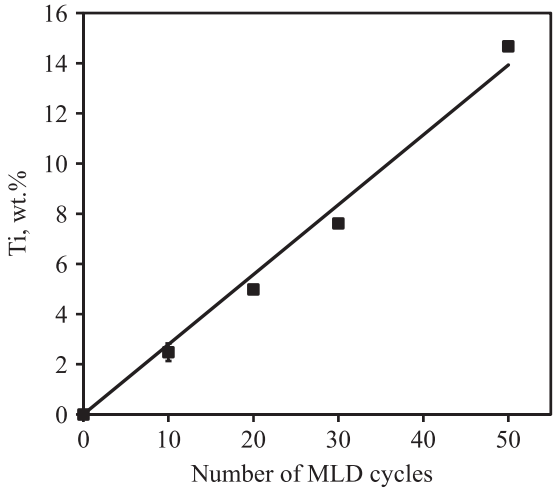

Fig. 2. Titanium content on 500 nm silica particles versus the number of MLD-coating cycles.