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Atomic layer deposition of TiO_2 films on particles in a fluidized bed reactor

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Abstract

Atomic layer deposition (ALD) of controlled-thickness TiO_2 films was carried out on particle substrates in a fluidized bed reactor for the first time. Films were deposited on 550 nm SiO_2 spheres and 65 nm ZnO nanoparticles for enhanced optical properties. Nanoparticles were fluidized with the assistance of a magnetically-coupled stirring unit. The metalorganic precursor titanium tetraisopropoxide was used here followed by either H_2O or H_2O_2 to deposit TiO_2 at various substrate temperatures. Growth rates of 0.01 nm/cycle and 0.04 nm/cycle were achieved when using H_2O and H_2O_2 as the oxidizer, respectively. These conformal TiO_2 films were verified using HRTEM, ICP–AES, XPS and UV absorbance measurements. The specific surface area changed appropriately after the particle size increased by the deposition of films with a given density, which showed that primary particles were not agglomerated together due to the coating process. *In situ* mass spectrometry was used to monitor reaction progress throughout each ALD reaction cycle. Bulk quantities of powder were successfully functionalized by TiO_2 nanofilms without wasting excess precursor.

Keywords: Fluidized bed reactor; Atomic layer deposition; Titanium dioxide; Mass spectrometry; Surface coatings

1. Introduction

Titanium dioxide is a versatile material that is found in many high-tech sectors, such as microelectronics and optoelectronics, as well as in commodity markets such as pigments, sunscreens, cosmetics and even in the food industry. TiO_2 is a semiconductor that has a medium bandgap of ~3.1 eV, or 400 nm [1]. TiO_2 has a very high refractive index (RI) and is an efficient broadband scatterer, which gives it a brilliant white appearance ideal for pigments in paints, plastics, cosmetics and food products [2]. Reported RI values range from 2.3 for amorphous atomic layer deposited TiO_2 to 2.9 for that of the rutile phase [3]. These attributes may be added to innumerable materials by using a thin film deposition technique that can provide optically-smooth coatings.

Nanoparticle materials are specifically of interest as these high surface area (SA) substrates can be functionalized by TiO_2 films for a variety of purposes. The onset of absorbance at the UV spectrum makes this material very appealing for use in UV-based photocatalysis applications. Magnetic photoactive composite particles can be fabricated by coating iron nanoparticles with TiO_2 for increased degradation efficiency of aqueous contaminants, while retaining their magnetic moment to remain recoverable. Polymeric particles can be coated with biocompatible TiO_2 films for various polymer-based nanocomposite biomaterials. Advanced gas sensors and battery materials can be developed by using the advantageous properties of a TiO_2 thin film while protecting a high SA core particle to increase product lifetime.

Novel sunscreen materials can be fabricated by coating high RI TiO_2 films on ZnO nanoparticles. UVB rays (λ=290–320 nm) are absorbed by the outer epidermal layers of human skin and are the cause of sunburn; UVA light (λ=320–400 nm) has longer wavelengths and penetrates deeper into the skin and has recently been attributed to the predominant cause of skin cancer [4–6]. The sun protection factor (SPF) is a weighted-average calculation that predicts UV protection, but is skewed far into the UVB spectrum [7]. SPF is a good indicator of how well a sunscreen material will prevent sunburn but does not

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directly predict skin cancer prevention. ZnO nanoparticles are efficient UVA absorbers, but they do not produce high SPF sunscreen materials at typical loadings (2–5 wt.%). TiO_2 films on ZnO nanoparticles can enhance the UVA absorbing core by increasing the propensity to scatter UVB light from a higher RI composite particle surface. These broadband UV blockers are photostable inorganic materials that can immediately be integrated into commercial sunscreen products. The development of a method to deposit TiO_2 films on particle substrates is desirable to be able to functionalize core particles with this versatile semiconductor material.

Atomic layer deposition (ALD) is a thin film growth technique that can be implemented in a scalable fluidized bed reactor to functionalize a variety of particle surfaces [8]. ALD methods utilize self-limiting surface chemistry to achieve growth rates typically on the order of 1 Å/cycle, varying with chemistry and deposition conditions [9]. Under the appropriate conditions, deposition can be limited to the number of functional groups on the surface [10]. Underexposure of either precursor can lead to nodule growth, or islanding, a stochastic process that underutilizes available surface nucleation sites. With an increasing number of cycles, nodules tend to grow together such that an effective growth rate can be defined, which will necessarily be lower than accepted values for any given ALD chemistry. Overexposure, however, does not increase precursor adsorption beyond the surface-saturated threshold value [11], but simply increases manufacturing costs and process time. *In situ* analysis techniques are beneficial to monitor reaction progress and prevent process overruns. Since all reactants and byproducts are gaseous at operating conditions, residual gas analysis using a mass spectrometer is an ideal solution that can be integrated at any scale.

Using self-limiting ALD growth techniques, a wide variety of materials have been deposited with atomic layer control [12,13]. The binary reaction for TiO_2 chemical vapor deposition (CVD), using the metalorganic precursor titanium tetraisopropoxide (TTIP) with water is:

$$Ti(OCH(CH_3)_2)_4 + 2H_2O \rightarrow TiO_2 + 4CH(CH_3)_2)OH$$

This binary CVD reaction can be divided into two half-reactions that occur solely on a surface to define TiO_2 ALD:

$$A)[S] : (OH)^*_x + Ti(OCH(CH_3)_2)_4 \rightarrow$$
$$[S] : (O)_x Ti(OCH(CH_3)_2)^*_{4-x} + x \cdot CH(CH_3)_2OH,$$
$$B)[S] : (O)_x Ti(OCH(CH_3)_2)^*_{4-x} + 2H_2O \rightarrow$$
$$[S] : TiO_2 : (OH)^*_x + (4-x) \cdot CH(CH_3)_2OH.$$

The asterisks indicate the surface species, and [*S*] denotes the particle substrate. The sequential application of AB reactions can produce atomic layer controlled TiO_2 deposition. These types of sequential surface reactions have been studied extensively using Fourier transform infrared (FTIR) vibrational spectroscopy and other *in situ* techniques and had shown to be self-limiting [14,15]. The number of ligands removed during each half-reaction depends on operating conditions [16]. The desorbed products were not solely in the form of isopropanol; observed products have also included acetone, propene and others [17,18]. Isopropanol is shown in the equation to effectively balance the reaction. Similar sets of half-reactions can be generated with H_2O_2 as the oxidizing agent, in place of H_2O, with oxygen as an additional product. Likewise, other titanium alkoxide precursors (e.g. methoxide, ethoxide and more extravagant) are available [19,20]; TTIP was selected as it has received significant attention in other work [16,17]. TTIP is favorable because it is a liquid at room temperature and is fairly inexpensive. Titanium halides have been well-studied for TiO_2 ALD [21–24] but were undesirable due to the non-negligible amount of acid byproducts released when coating high surface area (SA) powders in a fluidized bed reactor (FBR). The total bed SA at the lab scale is often four or five orders of magnitude higher than ALD processes currently found in the semiconductor industry on flat surfaces.

ALD of nanothick TiO_2 films on two particle types is presented here to enhance the optical properties of each substrate material. Spherical SiO_2 particles are used in the cosmetics industry to effuse visible light and decrease the visibility of underlying features. TiO_2 coatings on these particles can enhance the visible light scattering power while simultaneously providing UV protection to the user. ZnO nanoparticles are currently used in some commercial sunscreens. TiO_2 ALD is beneficial here to fabricate superior sunscreen composite particles by combining the optical properties of the core and shell materials. These two case studies are used to demonstrate TiO_2 ALD on particles in a fluidized bed reactor.

2. Experimental

An FBR was used to deliver reactive ALD precursors to the surfaces of primary powders. The reactor setup can be seen in Fig. 1. The details of this configuration have been described previously [8]. The pressure drop across the empty bed ($P_2 - P_1$) was recorded at the desired operating temperatures. A batch of either 550 nm SiO_2 spheres (Cosmo-55™, Presperse, Inc., Somerset, NJ) or 65 nm ZnO particles (Z-Cote™, BASF Corp., Florham Park, NJ) was put into the FBR. The BET SA was 5.6 ± 0.3 m^2/g for SiO_2 and 13.5 ± 0.3 m^2/g for ZnO. These powders have been successfully fluidized using bed masses of approximately 10 to 50 g, corresponding to total bed surface areas ranging from 50–675 m^2. The tap density of the spherical SiO_2 powder was 0.35 g/cm^3 and that of the ZnO nanopowder was 0.26 g/cm^3. Therefore, bed heights were not contrastingly different.

The fluidization behavior of each powder is shown in Fig. 2a. N_2 was used as the inert fluidizing gas and a magnetically-coupled stirring unit was employed to assist in the low-pressure fluidization of the nanoparticle bed. Qualitatively, the efficiency of vibrofluidization, which pulsates in the axial direction, relative to stirring has been shown to decrease with an increase in the bed height for a given reactor size. In addition, bed segregation may become an issue during the vibrofluidization of powders with wide particle size distributions. The stirring-induced radial blending of the entire bed serves to