



Review

Functionalization of fine particles using atomic and molecular layer deposition

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ABSTRACT

The functionalization of fine primary particles, including nanoparticles and nanotubes, is easily carried out using atomic or molecular layer deposition (ALD or MLD, respectively) techniques. Particle ALD/MLD can be used to deposit conformal and pinhole-free films of refractory oxides, non-oxides, metals, and hybrid polymer-based materials, amongst others. Fluidized bed reactors are well-suited for large scale operations and can be operated at reduced pressures while using inert gases necessary for standard self-limiting, flow-based ALD/MLD processes. The continuous-flow processing allows for process control using an in-line mass spectrometer downstream from the reactor chamber. Many insulating, semiconducting, metallic, polymeric and hybrid inorganic/organic films have been successfully deposited on primary particle surfaces in fluidized bed reactors using a variety of precursor types. This paper reviews some of the Particle ALD/MLD work carried out by the authors, including techniques and measurements used in Particle ALD/MLD. Some current and future applications of functionalized or passivated nanomaterials are also highlighted here.

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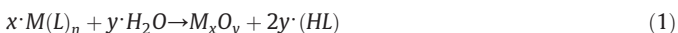
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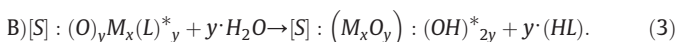
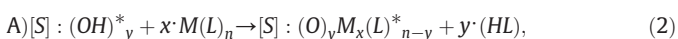
1. Introduction

There are many industrial and scientific applications where there is a strong desire to functionalize the surfaces of ultrafine powders to achieve a variety of purposes. Surface functionality can be broken up into two categories, inactive and active. Inactive coatings include inert films that are applied to eliminate the spontaneous interaction between the core powder and its surroundings. One example of an inactive coating is the deposition of insulating Al_2O_3 films on metal nanopowders in order to prevent detrimental combustion reactions that render the metal useless. Another is the deposition of SiO_2 films on TiO_2 nanopowders used in sunscreens and pigments, and are pore-free and thick enough to eliminate the photoactivity of the core powder that prevents the powder from adversely affecting the surrounding organic molecules in the liquid vehicle. Many other industrially-relevant functionalization needs exist, including the incorporation of ceramic films on polymeric particles that can then be fabricated into hybrid organic-inorganic composite materials.

Using self-limiting atomic layer deposition (ALD) growth methods, a wide variety of materials have been deposited with atomic layer control [1–7]. ALD involves the sequential dosing of two or more precursors, oftentimes ones used for chemical vapor deposition (CVD), with essential purge steps that prevent unwanted gas-phase reactions between precursors. The generic formula for CVD of a metal oxide can be described as



where M represents the metal species, n is the number of ligands, L ; and $x:y$ is the metal:oxide ratio. The two main classes of precursors are metal halides and metalorganics. Metal halides emit strong acid vapors as products, whereas metalorganics tend to emit alkanes, alcohols or alkylamines for alkyl-, alkoxide- and amine-based precursors, respectively. Any binary metal oxide CVD reaction can be divided into two half-reactions that occur solely on a particle surface to define ALD:



$[S]$ represents the particle surface and an asterisk represents the active surface species. If each half-reaction is self-limiting and self-terminating, the repetitive application of these reactions in an ABAB... sequence can produce atomic layer controlled metal oxide deposition [2]. These types of sequential surface reactions have been studied extensively with Fourier transform infrared (FTIR) vibrational spectroscopy and other in-situ techniques and have been shown to be self-limiting. In addition to ceramic films, ALD methods for metal and polymer films, which have been extensively demonstrated on flat surfaces, have also been transferred to particle-based substrates.

Ferguson et al. were the first to demonstrate that ALD techniques could be used to coat ALD films on the surfaces of primary particles [8–11]. The particles were pressed into a stainless steel

grid as a support for deposition in a viscous flow reactor. Though the particles were sometimes not usable for application-specific testing, this proof of concept work was critical to begin exploring more traditional particle coating unit operations. Shortly thereafter, Wank et al. demonstrated that a fluidized bed reactor operating under vacuum could be used to deposit Al_2O_3 films on bulk quantities of micron-sized iron particles using ALD techniques [12–14]. Hakim et al. studied the fluidization behavior of nanoparticles and was the first to demonstrate that ALD techniques can be used to apply conformal, pinhole-free films to the surfaces of high surface area nanoparticles [15–21]. Wilson et al. were the first to deposit metal films (tungsten) on metal or polymeric particles using a rotary reactor [22,23], and Liang et al. were the first to deposit ceramic films on polymers using a fluidized bed reactor [24–26]. King et al. were the first to demonstrate ZnO, TiO_2 and SiO_2 ALD in a fluidized bed reactor [27–33]. Even though the initial groundwork for particle ALD research was performed at the University of Colorado, many other institutions have since begun independent explorations of the benefits of applying particle ALD techniques to deposit ceramic films and metal nanoclusters on the surfaces of particles for a variety of applications [34,35]. Several particle ALD advances have been made in the deposition of Pt and other metal nanoclusters, as well as ALD on carbonaceous substrates (e.g. nanotubes, aerogels, graphite, graphene) for improved catalysis processes and next generation electrode materials for fuel cells and batteries [36–41].

Molecular layer deposition (MLD), also known as alternating vapor deposition polymerization (AVDP) and layer-by-layer growth, was first introduced by several groups from Japan in the 1990s. The MLD method was developed from the earlier gas phase polymer growth technique known as vapor deposition polymerization (VDP). VDP utilizes the co-evaporation of two types of bifunctional monomers under vacuum with each evaporator controlled thermostatically. MLD is an analog of a one-step VDP reaction, and it is based on bifunctional monomer precursors such as A–L–A and B–M–B. In these precursors, “A” and “B” are chemical functional groups and “L” and “M” are organic fragments. In the MLD process, the chemical functionality of the surface species switches in a digital manner and molecules are stacked on substrates one by one in order of preference under vacuum. MLD can deposit conformal and precise ultra-thin polymer films with molecular layer control. The thickness and “molecular weight” of polymeric thin films can be effectively controlled by the number of reaction cycles. This process is similar to the ALD method except for the anisotropic linear chain molecules. The linear chain molecules play an important role in molecular orientation perpendicular to the substrate. This dry vapor-phase method, which operates under vacuum and does not require solvents or catalysts, is a useful and promising technique for the fabrication of functional ultra-thin polymeric layers [52–54].

A number of studies have been performed on the growth of different polymer MLD films, such as polyamide, polyurea, polyimide, polyimide-polyamide, and poly(p-phenylene terephthalamide). MLD can also be used to deposit hybrid inorganic/organic thin films using suitable precursors, such as TMA and ethylene glycol (EG) for aluminum alkoxide (alucone) hybrid polymer films. The properties of the composite film can be tuned by the assembly of different organic/

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