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Particle functionalization and encapsulation by initiated chemical vapor deposition (iCVD)

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Abstract

Initiated chemical vapor deposition (iCVD) represents a novel CVD method for functionalization and encapsulation of particle substrates with polymeric materials. Three demonstrations of iCVD coatings on particle substrates are described. In the first, iCVD polytetrafluoroethylene (PTFE) coatings on an array of vertically aligned carbon nanotubes created a superhydrophobic surface. Second, iCVD polyglycidyl methacrylate (PGMA) coatings on microparticles and nanotubes provided reactive surfaces for subsequent binding to produce fluorescent and high refractive index coatings. Finally, iCVD methacrylic acid copolymers on ibuprofen microcrystals delivered enteric drug release properties based on the pH-responsive swelling behavior of the copolymers. Mathematical modeling suggested surface-driven iCVD polymerization kinetics that were analogous to liquid-phase free radical polymerization.

Keywords: Initiated chemical vapor deposition; Polymer coatings; Superhydrophobic surfaces; Reactive coatings; Enteric release; Polymerization kinetics

1. Introduction

Currently, methods for functionalization and encapsulation of 3D substrates, e.g., particles, with polymeric materials are predominantly done in a liquid environment or with the use of liquid solutions. For example, particles can be encapsulated with a polymer by spray coating a solution of the polymer onto a fluidized bed of particles, resulting in a thin wet film of polymer over each particle that then needs to be dried [1]. In another example, an emulsification–solvent evaporation technique can be used to provide once again a wet polymer capsule around core droplets, such that with solvent evaporation, the polymer precipitates around the core particle [2]. Usually, a glidant, surfactant or some form of post-treatment, like a thermal anneal, is required to allow polymer flow or stabilization to form a more coherent coating. Aside from these complexities, liquid-based methods often run into issues with particle agglomeration, especially with coating particles of size below 100 μm [3,4].

Here, we present an all-dry synthesis method that is able to functionalize and encapsulate particles down to the nanoscale. This novel method, initiated chemical vapor deposition (iCVD), combines a solvent-free, precision chemical vapor deposition environment with a liquid-based free radical polymerization chemistry that enables well-defined and controlled chemical synthesis pathways. Fig. 1 summarizes the essential steps believed to occur in iCVD. It involves (1) delivery of initiator and monomer vapors into a reaction chamber maintained at a pressure typically between 0.1 and 1 Torr; (2) activation of an initiator using an array of resistively heated filament wires to a temperature typically between 200 and 400 °C; (3) diffusion and adsorption of primary radicals, generated by initiator decomposition, and monomer from the vapor phase onto a surface; and (4) polymerization of monomer via free radical initiation, propagation and termination events to form a continuous polymer coating on a surface that is typically kept at room temperature.

By bypassing the solvent phase completely, we will show iCVD is able to produce polymer coatings on 3D particles down to the nanoscale conveniently in a single polymerization–polymer coating synthesis step that does not require additional excipients to aid coating formation. Specifically, we will demonstrate the use of iCVD in creating superhydrophobic surfaces on an array of

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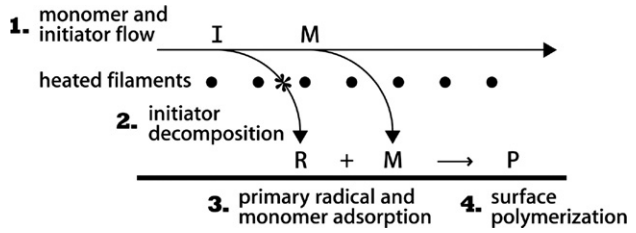

Fig. 1. iCVD reaction mechanism. It involves (1) the delivery of monomer and initiator vapors into the reactor; (2) thermal decomposition of initiator to form primary radicals; (3) adsorption of primary radicals and monomer onto a surface; and (4) surface polymerization via initiation, propagation and termination reactions.

aligned carbon nanotubes, in forming reactive coatings that can subsequently be conjugated with fluorescent and high index molecules, and in encapsulating active core particles with pH-responsive enteric release layers. These examples are expected to prove the versatility and utility of iCVD as a surface coating methodology that can be applied in a broad range of use. Finally, we will summarize our effort to date in understanding iCVD reaction kinetics.

2. Experimental

2.1. Superhydrophobic surfaces

Polytetrafluoroethylene (PTFE) coatings were applied to arrays of vertically aligned carbon nanotube forests (Cambridge University, U.K.) through an iCVD process, using hexafluoropropylene oxide (HFPO) as the precursor to generate CF_2 and perfluorobutane-1-sulfonyl fluoride (PFBSF) as the initiator. Details of the iCVD reactor configuration have been described elsewhere [5]. Contact angles were measured using the sessile drop method. Fourier transform infrared spectroscopy (FTIR) was carried with a Thermo Nicolet NEXUS 870 equipped with a DTGS detector. Scanning electron microscopy (SEM) was performed on an FEI/Philips XL30 FEG ESEM at 30 kV. To induce condensation, water was introduced into the ESEM chamber such that at a sample stage of 3.4 °C, a water vapor pressure of 5.5 Torr resulted in the formation of water droplets.

2.2. Reactive coatings

Polyglycidyl methacrylate (PGMA) coatings were applied to 28.5 μm diameter glass microspheres (Whitehouse Scientific) and 20–50 nm diameter, 5–20 μm length multiwalled carbon nanotubes (NanoLab) using iCVD reactor setups described elsewhere [5,6]. Glycidyl methacrylate and *tert*-amyl peroxide were the monomer and initiator, respectively. FTIR relied on a Thermo Nicolet NEXUS 870 equipped with a DTGS detector. X-ray photoelectron spectroscopy (XPS) utilized a Kratos AXIS Ultra using a monochromatic source from an Al anode at 150 W with charge neutralization. SEM was done using an FEI/Philips XL30 FEG ESEM at 12 kV. Transmission electron microscopy (TEM) was carried out on a JEOL 200 CX at 200 kV. Confocal laser scanning microscopy (CLSM) required the use of a Zeiss LSM 510 with a Zeiss Axiovert 100 M microscope, with argon laser excitation and fluorescence detection between 505 and 530 nm. Index of refraction was determined on blanket films over silicon substrates with variable angle spectroscopic ellipsometry (VASE) on a J. A. Woollam M-2000S over wavelengths between 315 and 718 nm.

2.3. Controlled release formulations

Polymethacrylic acid-co-ethylene dimethacrylate coatings were applied to 25 μm ibuprofen microcrystals (DuPont) using an iCVD reactor described previously [6]. Methacrylic acid and ethylene dimethacrylate were the comonomers, the latter also acting as a crosslinking agent, and *tert*-amyl peroxide was the initiator. Swelling measurements were made on blanket films over silicon substrates using a liquid soak cell attached to a J. A. Woollam M-2000S VASE system. Drug release profiles were derived by tracing drug dissolution through light absorption using a Varian Cary 6000i UV–vis spectrophotometer on ibuprofen microcrystals compressed using a manual press into pellets.

2.4. iCVD reaction kinetics

Polymerization of butyl acrylate was done with iCVD protocols and reactor setups described previously [5]. Film thickness and deposition rate was determined through a J. A. Woollam M-2000S VASE. Polymer molecular weight was determined using a Waters gel permeation chromatography (GPC) system equipped with an isocratic HPLC pump, an in-line degasser, an autosampler, a Styragel HR column and a refractive index detector.

3. Results and discussion

3.1. Superhydrophobic surfaces

Superhydrophobic surfaces are defined as surfaces displaying an equilibrium water contact angle in excess of 150°. In nature, superhydrophobicity is commonly observed in a variety of plant leaves, including the lotus leaf (*Nelumbo nucifera*). When rain droplets fall on the leaf, the water rolls off, picking up any dust or contaminant particles on its surface. This self-cleaning or Lotus effect is caused by a unique combination of low surface energy from the waxy material covering the leaf surface together with heterogeneous surface roughness created by protrusions and nodules ranging from micrometer to nanometer in size that are present on the leaf surface. This makes it extremely difficult for the water to penetrate down to the bottom of the leaf surface, enabling the water droplet to essentially "float" on air that is trapped in the cavities beneath the droplet. This results in a near-spherical droplet shape and the observed superhydrophobic effect of water roll-off.

We successfully reproduced this phenomenon by creating an artificial superhydrophobic surface using an array of vertically aligned multiwalled carbon nanotubes that were coated with a thin layer of polytetrafluoroethylene (PTFE) using an iCVD polymerization and deposition process [7]. As shown in Fig. 2a, after iCVD treatment, a thin PTFE coating of ca. 40 nm in thickness (deposition rate ca. 1 nm/min) was observed to encase each