



Commentary

Introduction to nanocoatings produced by layer-by-layer (LbL) self-assembly[☆]Melgardt M. de Villiers^{a,*}, Daniel P. Otto^b, Schalk J. Strydom^{a,b}, Yuri M. Lvov^c^a School of Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin 53705-2222, USA^b Unit for Drug Research and Development, Faculty of Health Sciences, North-West University, Potchefstroom, 2520, South Africa^c Institute for Micromanufacturing and Biomedical Engineering Program, Louisiana Tech University, Ruston, LA 71272, USA

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ABSTRACT

Studies on the adsorption of oppositely charged colloidal particles ultimately resulted in multilayered polyelectrolyte self-assembly. The inception of layer-by-layer constructed particles facilitated the production of multifunctional, stimuli-responsive carrier systems. An array of synthetic and natural polyelectrolytes, metal oxides and clay nanoparticles is available for the construction of multilayered nanocoats on a multitude of substrates or removable cores. Numerous substrates can be encapsulated utilizing this technique including dyes, enzymes, drugs and cells. Furthermore, the outer surface of the particles presents an ideal platform that can be functionalized with targeting molecules or catalysts. Some processing parameters determining the properties of these successive self-assembly constructs are the surface charge density, coating material concentration, rinsing and drying steps, temperature and ionic strength of the medium. Additionally, the simplicity of the layer-by-layer assembly technique and the availability of established characterization methods, render these constructs extremely versatile in applications of sensing, encapsulation and target- and trigger-responsive drug delivery.

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1. Historical perspective on layer-by-layer self-assembly

Novel materials have always been sought and the employment of surface modification at the molecular level realized this goal. Surface modification resulted in a multitude of new properties that were previously not associated with the native material. These changes include modifications of the electrical, optical, magnetic, physico-chemical and biological properties of the material in question. As a consequence, several disciplines of natural science have experienced the impact of surface modifications, changing the fundamental properties of materials at the building-block-level. The historical evolution of self-assembly will, therefore, be discussed.

The development of surface science resulted from the ancient superstitious belief that pouring oil on water can calm the ripples caused by wind. This ancient belief was scientifically addressed by Franklin [1] and Rayleigh and his peers [2–4] followed by seminal work by Langmuir to finally realize monomolecular surface coating of solid substrates [5–7]. Blodgett expanded the Langmuir film technique to produce multilayer coatings known as the Langmuir–Blodgett (LB) technique [8–11].

The group of Kuhn [12,13] then explored the possibility to adsorb different oppositely charged dyes with the LB technique, discovering the potential of layer thickness and energy transfer. The LB-technique was however difficult and limited to only certain colloids. Iler [14] however observed that oppositely charged colloids could be alternately assembled onto glass substrates and work by Nicolau and colleagues illustrated successive layering of substrates with oppositely charged metal ions to produce polycrystalline coatings [15,16] and successive polymerizations steps *in situ* to produce alternating polymer coats onto a substrate [17,18].

The work of Iler and Nicolau probably inspired the seminal breakthrough made by the group of Decher, who used synthetic polyelectrolytes i.e. polymers with ionizable surface groups to form polyions that were successively layered onto a substrate by electrostatic interaction [19]. This method is robust, simple, does not require sophisticated equipment and precise stoichiometry, nor does it rely on complicated chemical reactions to deposit successive layers. Layer-by-layer self-assembly (LbL) is still seen as the true alternative to the LB technique.

Several characterization studies were undertaken on polyelectrolyte multilayers (PEM) in early to mid 1990s. The classic PEM characterization techniques were established using X-ray diffraction, UV-analysis [20,21] and gravimetric analysis by quartz crystal microbalance (QCM) dissipation [22]. Novel coating colloids including proteins [22] and DNA [23] were also introduced.

Since the late 1990s, work has focused on development of multilayer composites based on interactions other than electrostatic

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interactions such as hydrogen bonding [24–27]. Controllable polymerization reactions also resulted in novel approaches to assemble layer-by-layer constructs through successive polymerization [28,29]. This development enabled LbL construction and applications in which organic, instead of aqueous working media could be employed.

Highly efficient covalent “click” chemistry was introduced modularly build or modify materials, providing an alluring alternative to a dispersion force assembly [30]. Fig. 1 provides a timeline of the evolution of LbL modification techniques.

The layer-by-layer (LbL) self-assembly of multiple polyelectrolytes and other particles resulted in the production of multifunctional hybrid carrier systems [31–34] for dyes [35,36], sensors [37–39], enzymes [40,41], drugs [42–44], multiple components [45] and cells [46,47]. Additionally, nanocoated substrates provide a surface platform for the attachment of targeting molecules, i.e. folic acid [48–50], antibodies [51] or a variety of surface functional groups such as hydroxyl, carboxyl and thiol groups [52].

Moreover stimuli-responsive properties could be introduced by the inclusion of responsive materials in LbL constructs [34]. The following sections describe the robust nature of LbL self-assembly for the production of versatile carrier systems that comprise oppositely charged substances onto a substrate, resulting in a PEM-coated system [53,54]. In Section 7, the LbL drug delivery technology will be featured.

2. Basic principles of the layer-by-layer technique

The formation of nanocoatings using LbL self-assembly technique distinguishes itself in its simplicity from other surface modification methods such as spin-coating, solution casting, thermal deposition, chemical self-assembly and the LB technique and will be discussed next.

2.1. Mechanism of self-assembly

The buildup of LbL multilayers is driven by the electrostatic attraction between the oppositely charged constituents [14]. However, hydrogen bonding [55–57], hydrophobic interactions [58] and van der Waals forces [59,60] may be exploited to assemble LbL systems or influence the stability, morphology and thickness of the films, particle/molecule depositions and permeation properties of the film [19,61,62].

Generally, LbL self-assembly proceeds as follows: (1) A charged substrate is immersed in a solution of an oppositely-charged colloid to adsorb the first monolayer, (2) a washing cycle follows to remove unbound material and preclude contamination of the subsequent oppositely-charged colloid, (3) in which the coated substrate is submerged to deposit a second layer and the multilayered structure is formed [62] (Fig. 2). Some LbL processes require no washing cycles thus shortens the duration of the assembly process [63].

The polyelectrolytes or colloids, which exhibit a high linear surface charge density, are utilized in excess to prime the substrate. Therefore, a non-stoichiometric excess of charge is absorbed after each step relative to the preceding layer [53,64]. This surplus of charge provides the step-wise mechanism for the reversal of the surface charge polarity, facilitating a favorable surface for the adsorption of the subsequent layer.

Techniques, not reliant on intermolecular forces, i.e. covalent or click chemistry were developed to produce stable [65,66] or biodegradable [67,68] multilayered structures. However, the principle of successive layering still applies.

The LbL self-assembly methods have advantages compared to the more conventional coating methods, including (1) the simplicity of the LbL process and equipment, (2) its suitability to coating most surfaces, (3) the availability of an abundance of natural and synthetic colloids, (4) the flexible application to objects with irregular shapes

and sizes, (5) the formation of stabilizing coats and (6) control over the required multilayer thickness [69–71].

3. Coating materials and substrates

Several polyelectrolytes and nanoparticles can be utilized to form the ultrathin multilayer structures using the LbL self-assembly technique. Furthermore, several substrates can be coated with nanothin multilayers.

3.1. Polyelectrolytes

Polyelectrolytes are classified according to their origin. Standard synthetic polyelectrolytes include poly(styrene sulfonate) (PSS), poly(dimethyldiallylammonium chloride) (PDDA), poly(ethylenimine) (PEI), poly(*N*-isopropyl acrylamide) (PNIPAM), poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), poly(vinyl sulfate) (PVS) and poly(allylamine) (PAH) [69].

Natural polyelectrolytes include nucleic acids [70], proteins [71] and polysaccharides [72] of which alginic acid, chondroitin sulfate [73], DNA [74] heparin, chitosan, cellulose sulfate, dextrans sulfate and carboxymethylcellulose are most common [73–75].

3.2. Nanoparticles and nanoobjects

Nanoparticles utilized for LbL constructs are derived from stabilized colloidal dispersions of charged silica, charged poly(styrene) spheres, metal oxides [14], polyoxometalates [76,77] and conducting liquid crystalline polymers [78].

Positively and negatively charged platelets utilized for multilayer construction are derived from naturally-occurring clays such as hectorite, montmorillonite and saponite [79]. Charged liquid crystalline polymers i.e. hydrotalcite were successfully assembled with these clay nanoobjects [78,79].

Dendrimers have also been successfully used to form PEMs, with poly(amidoamine) (PAMAM) dendrimers most commonly used [80,81].

Carrier systems can be functionalized with stimuli-responsive components that respond to temperature, pH and ionic strength [82,83]. The polymers/colloids used in the LbL technique can also be functionalized to alter its properties preceding LbL assembly.

3.3. Substrates

The prerequisite for successful LbL coating is the presence of a minimal surface charge, which is one of the few disadvantages of the technique. However, charge can be induced to still facilitate LbL [84]. Most commonly glass, quartz, silicon wafers, mica, gold-coated substrates are coated. The type of substrate that is encapsulated depends primarily on the colloids assembled into PEMs and analytical monitoring techniques for the coating steps [69].

Surface charge is not the only factor that may affect the multilayer adhesion. The surface texture could also affect the adhesion properties. Pretreatment of a substrate by annealing with sodium chloride smoothed the surface of the substrate, resulting in more intimate contact between the substrate and colloid to produce higher quality coats [85,86].

Furthermore, the coating elasticity, could also affect the surface adhesion of the coating layers to the substrate. The effect of the coating modulus is, however, ambiguous since some studies indicated an improvement in surface adhesion for elastic PAH-based coats [87,88] based on the morphology of the films and the polarity of the surface charge. However, a detrimental effect on coating interactions for highly elastic layers i.e. aminosilane-based PEMs adsorbed to glass was found [85]. The substrate might therefore

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