POLYMER FILMS

Just spray it

Spray-coating of multilayer films on fibre mats yields conformal coatings, opening up new possibilities for the fabrication of protective clothing and reactive membranes.

Merlin Bruening and David Dotzauer

Thin polymer films have important practical applications in areas ranging from corrosion protection to reverse osmosis. The films are traditionally fabricated by depositing them on a substrate using methods that include spin- and dip-coating, interfacial polymerization, painting, spraying and electrophoretic deposition. During the past 15 years, many researchers have developed methods for depositing functional thin films in a layer-by-layer (LbL) fashion[1] (Fig. 1). These methods involve alternating adsorption of complementary materials, such as polycations and polyanions, and such techniques are attractive because they afford nanometre-scale control over film thickness through variation of the number of deposited layers. More importantly, the materials capable of forming these coatings range from simple polymeric electrolytes to viruses and nanoparticles[2]. Thus, LbL films can perform a variety of functions, and different functionalities can reside in specific sections of a film.

Unfortunately, by its nature the LbL process involves numerous deposition and rinsing steps, and this complexity greatly limits the potential applications of multilayer coatings, in spite of exquisite control over thickness and functionality. To overcome this challenge, several studies have examined the possibility of spray-coating multilayer films to increase the rate and convenience of deposition, and in some cases to avoid rinsing steps[3–5]. Under appropriate conditions, convective transport of the adsorbing materials to the surface can decrease the deposition time by more than an order of magnitude. But compared with the traditional 'dip and rinse' LbL method, the spraying process may decrease control over deposition, including the ability to produce conformal coatings on three-dimensional, porous objects. Regions of the substrate in the 'shadows' of the spray may not be coated, and in the worst case the film will form only on the top of a porous mat. Coatings that fully conform to the geometry of fibres and complex, porous architectures have distinct advantages for creating functional catalytic membranes and fabrics with high surface areas.

On page 512 of this issue[6], Paula Hammond and colleagues demonstrate that at low flow rates of spray through porous structures, conformal LbL coating of mats of cylindrical fibres is possible. By varying the extent of the vacuum on the rear side of an electrospun fibre membrane, the flow rate of the spray through the electrospun mat can be controlled to give a conformal polycation/TiO_2 nanoparticle coating on the exterior of the fibres. When a higher vacuum is applied (Fig. 2a), the flow separates from the back of the cylindrical fibres, and only the part of the fibre facing the spray is coated. In contrast, lower flow rates with a lower vacuum allow coating all around the fibre (Fig. 2b). The conformal polycation/TiO_2 nanoparticle films provide a high surface area of TiO_2, which is attractive for photocatalysis. As an example, the Hammond group specifically discuss the photocatalytic degradation of a mustard gas simulant, chloroethyl ethyl sulphide (CEES).

Unfortunately, when conformally coated with polyelectrolyte/TiO_2 films, the fibre membranes catalyse degradation of only 15% of a CEES dose because of the high porosity of the electrospun fibre mat. To confront this problem and to demonstrate the versatility of the spraying process, Hammond and co-workers perform spray-coating in the absence of vacuum-induced convective flow on a mat that has already been coated with a polyelectrolyte/TiO_2 film. Without the vacuum, spray droplets accumulate near the top of the mat so the LbL film does not penetrate deeply into the porous structure, and a second coating forms primarily on the membrane surface. A 50-bilayer film covers nearly

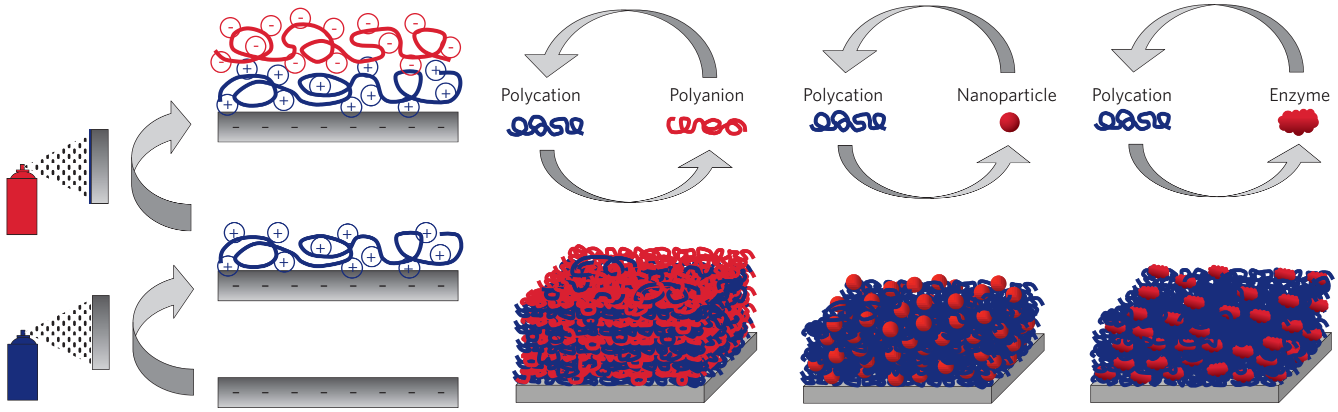

Figure 1 | Schematic drawing of layer-by-layer deposition by alternating spray-coating of polyanions and polycations. (The rinsing between deposition steps is not shown.) Layer-by-layer deposition typically involves immersion of a substrate in alternating solutions, but spray-coating is much faster. These films can incorporate a wide variety of functional materials including nanoparticles and enzymes.

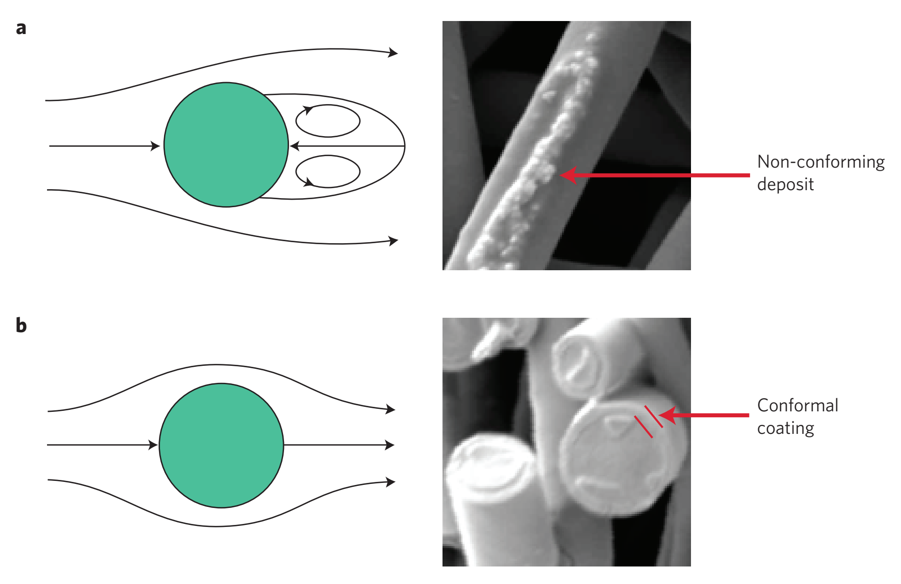

Figure 2 | Layer-by-layer spray-coating of an electrospun fibre with spray forced through a fibre mat by vacuum. The green circle represents a cross-section of a single fibre oriented perpendicular to the spray flow. **a**, At high vacuum (high spray flow rates), the flow field separates from the back of the cylinder, and consequently coating occurs only on the part of the fibre that faces the spray. **b**, At lower vacuum (low spray flow rates), flow around the cylindrical fibres yields a conformal coating.

all of the surface and reduces the flux of CEES through the electrospun membrane. The resulting increase in residence time in the mat increases photodegradation of CEES from 15% in the absence of the surface barrier coating to 74% with this second coating.

If the only purpose of a surface coating were to decrease flux, a variety of materials and films could serve as barriers. But in the case of protective clothing, fabrics that are also permeable to water vapour are indispensable. By selecting polyelectrolytes in which water is highly soluble and CEES is sparingly soluble, Hammond *et al.* construct highly catalytic mats for CEES photodegradation that still allow permeation of water vapour. Remarkably, the water vapour flux through mats coated with 50-bilayer polyelectrolyte films is similar to the flux through cotton fabric. Hence, the combination of the two modes of spraying gives the membrane multiple functions.

Conformal coating requires significantly shorter deposition times (about 15 seconds per layer) than barrier-layer deposition (around 1 minute per layer) because in the conformal case, the vacuum pulls the spray through the mat and the solution does not accumulate. Consequently, conformal coating is particularly attractive. One can readily envisage spray-coating porous membranes with reactive species such as enzymes[7] and catalytic nanoparticles[8] to create a wide range of reactive materials for sensing applications, degradation of pollutants or warfare agents, and even preparative reactions. ❐

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SUPERIONIC CONDUCTION

When small is better

Nanoparticles containing a silver iodine core and a polymer shell have superionic conductance even near room temperature, showing promise for a new generation of electrochemical devices.

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The mobility of ions, such as Ag^+, Li^+, H^+ or O^{2-}, within a static framework is a defining constituent in several proposed energy-related devices for the future. Their subsequent development into a realistic replacement for infrastructure operating on fossil fuels is, in part, reliant on finding innovative materials that free up the ions so that they are more mobile at lower temperatures. On page 476 of this issue, a paper by Makiura *et al.* shows how a canonical high-temperature Ag^+-ion conductor can be manipulated to produce functional conduction under ambient conditions[1]. This is achieved by forming small (11 nm) nanoparticles of AgI coated in a particular polymer that is also known for its ability to conduct Ag^+ ions. The apparent synergy between the inorganic core and the organic shell gives new opportunities in the design, synthesis and production of innovative electrochemical devices such as batteries.

The origin of the ion dynamics in AgI is associated with the 'melting' of the Ag cations at elevated temperatures. There are two reported phases of bulk AgI under ambient conditions, namely β- (Fig. 1b) and γ-, which are isostructural with the ubiquitous hexagonal wurtzite and cubic zincblende structures of ZnS. Both of these structures have ideal packing of the iodine anions, leaving restricted room for silver. On being heated, the structure converts to