

over them to make the structure planar and to separate the layers. These steps are repeated as many times as the number of desired layers.

However, many challenges need to be overcome before some of the spectacular applications of metamaterials demonstrated at microwave frequencies, such as perfect lensing and optical cloaking, are realized. Furthermore, it will be a challenge to extend the optical resonance of these structures from the present infrared region into near-infrared and visible parts of the spectrum. Simply scaling down the size of SRRs and therefore reducing the resonance wavelength does not seem to be viable from both fundamental and fabrication standpoints

and, therefore, new geometries may be needed. Another challenge is to combine the electric and magnetic responses in such a way that negative  $\epsilon$  and  $\mu$  are obtained at the same optical frequency range, resulting in a true negative-index material.

Although some two-layer structures in the near-infrared indeed have such NIM properties<sup>7</sup>, they tend not to show strong metamaterials properties and are difficult to fabricate in more than two layers. The fabrication technique developed by Na Liu and colleagues offers the freedom to fabricate multilayer metamaterials that, for example, could be used to construct some of the recently designed subwavelength NIM structures<sup>9</sup>. Regardless of what shape

the future designs of nanoengineered metamaterials are going to take, this powerful fabrication technique is likely to influence the way three-dimensional metamaterials are going to be produced.

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## SURFACE CHEMISTRY

# Mussel power

The adhesive proteins secreted by mussels are the inspiration behind a versatile approach to the surface modification of a wide range of inorganic and organic materials, resulting in the fabrication of multifunctional coatings for a variety of applications.

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**W**hat would you use to join two different materials to form a rigid structure — nails, rivets, screws or glue? In general, the experts advocate adhesion because the interface in such bonded materials contains a myriad of molecular contacts and, as a result, there is better load transfer and lower stress concentration. A great frustration in science and technology, however, is that adhesives do not always work as desired. First, they may not find anything of consequence to bind to on a given surface; second, they may be prevented from binding because of moisture or other contaminants, and third, they may not wear or weather well. The latter two are of particular concern for adhesives and coatings in biomedical applications. One need only think of loose hip implants or dental fillings. Despite the development of numerous pre-adhesive treatments in an attempt to put a more reactive face on uncooperative surfaces, no general strategy has been shown to improve adhesion on all surfaces. But now,



**Figure 1** Dopamine is a small-molecule mimic of the adhesive proteins found in the ‘footprints’ of mussels. **a**, In their natural environment, mussels show strong adhesion to marine surfaces. **b**, Dopamine has a chemical structure comprising both alkylamine (yellow, lysine-like) and catechol (blue, DOPA-like) functionalities.

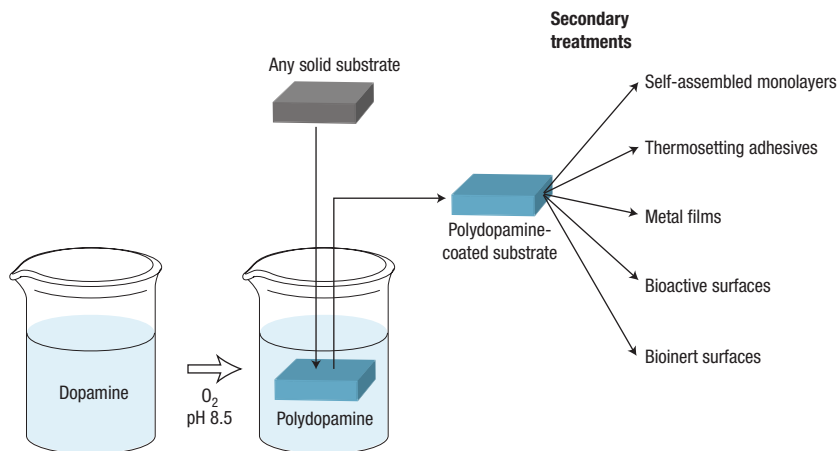
this sticky problem could be solved by a newly developed surface modification method published recently in *Science* by Phillip Messersmith and colleagues<sup>1</sup>. The method draws inspiration from the adhesive proteins found in mussels (Fig. 1a) and the outcome is similar — the adhesive polymer film sticks to almost anything, coating many

different types of surfaces. In addition to the modification of a wide variety of inorganic and organic materials, the resultant surface can react further, and hence the scope for applications widens dramatically.

The adhesive film is formed from dopamine, a catecholic (1,2-dihydroxybenzene) compound with a

primary amine functional group (Fig. 1b). This small molecule is better known as the neurotransmitter whose deficiency leads to Parkinson's disease. The materials to be coated are dipped directly into an aqueous dopamine solution at pH 8.5 (approximately marine pH), autopolymerization occurs and the substrates become coated with a polydopamine film up to 50 nm thick (Fig. 2). Surface-active polydopamine readily adhered to all surfaces tested by Messersmith and colleagues, including noble metals (Au and Ag), metals with native oxide surfaces (Cu and stainless steel), oxides (TiO<sub>2</sub> and SiO<sub>2</sub>), semiconductors (GaAs) and glass. But this is just the first stage of the process — the robust dopamine-derived films can subsequently support a variety of secondary reactions and, as a consequence, a wide range of functional surfaces can be created including self-assembled monolayers (SAMs), metal films, bioactive and bioinert surfaces. These secondary treatments include reaction of the surface with alkanethiols to form SAM-like coatings, amino organosilanes for conventional adhesive thermosets, amino polyethylene glycol for non-fouling surfaces and hyaluronate-coated surfaces for bioimplants. The versatility reflects not only the wide variety of surfaces coated but the variety of possible treatments — also, the approach seems to be simple, inexpensive, quick and 'green'.

Inspiration for the dopamine-derived adhesive platform is attributed to the adhesive proteins of marine organisms such as mussels and sandcastle worms. As a consequence of their wave-swept habitats, mussels and other sessile organisms have perfected the art of adhering quickly, opportunistically and tenaciously to all manner of wet and slippery surfaces. Advances in soft ionization mass spectrometry have enabled the characterization of the adhesive 'footprints' of mussels on smooth substrates. This exploration has revealed an unusual assortment of proteins — including *Mytilus* foot protein 5 (Mfp-5), of which 30% of the residues in the sequence are 3,4-dihydroxyphenyl-L-alanine (DOPA), a catechol-containing compound, and 15% are lysine, an amino acid with a side-chain ending in a primary amine group<sup>2</sup>. Messersmith and colleagues combine the catecholic and amino functionalities of Mfp-5 in their use of dopamine as a minimalist alternative to nature's designer adhesive. Although this homage to mussels seems appropriate, a more immediate inspiration has been overlooked — the bruised banana. Bananas are rich in dopamine, which oxidizes to form dihydroxyindole oligomers and



**Figure 2** The polymer-coating and secondary treatment processes. Dopamine autopolymerizes in solution at pH 8.5 and the resultant polymers readily coat any exposed surface. After drying, the coated surfaces provide a reactive platform for several secondary treatments, and produce a variety of functional materials.

the polymer, melanin, when the fruit is damaged<sup>3</sup>. These oligomers and polymers help stabilize damaged tissue by binding cellulose and other fibres as well as retarding microbial attack. This binding role seems to be strikingly similar to the use of dopamine in this new polymer-coating technique.

Although the reduction of complex aspects of mussel adhesion to a simple molecule like dopamine seems astonishing, it shouldn't be. The astringency of red wine, the treatment of animal skins with condensed tannins to produce leather and the durability of tea stains on the kitchen counter are a few reminders of how well polycatechols stick to surfaces and resist moisture. In a previous mechanistic study using single-molecule atomic force microscopy (AFM), Messersmith and colleagues<sup>4</sup> showed the versatility of adsorbed DOPA on different surfaces — ranging from covalent crosslinks on amine-functionalized surfaces, to chelate complexes on metal oxides, and hydrogen bonds on polar polymers. In other words, the apparent universality of polydopamine as a coating platform is not predicated on a single type of molecular interaction with underlying surfaces, but rather on a multiplicity of chemical options.

Although there is no question about the practical appeal of this versatile adhesive platform, the study raises many fundamental questions about the formation mechanism and structure of the dopamine polymer. In the formation mechanism of eumelanin, a type of melanin found throughout nature, for which both DOPA and dopamine serve as precursors, the general agreement is that the committed step involves oxidation of dopamine to dihydroxyindole and indolequinone. The

latter two compounds then couple in a stepwise fashion, through several carbon atoms on the indole structure, to form sprawling oligomeric mats, which stack four to six high to form melanin<sup>5</sup>. Using mass-spectrometry techniques, the Northwestern team detect the presence of dihydroxyindole oligomers in the adsorbed dopamine polymer, therefore it is evident that a similar oxidation mechanism is involved in the dopamine-derived polymer coating.

The mechanism aside, questions remain: Is there a critical molecular weight of dopamine polymer for optimal coating? As the dopamine-derived dihydroxyindole oligomers ultimately self-assemble into insoluble and highly aggregative particles having diameters of 100–200 nm (ref. 6), is there a limit where coating does not occur? Using AFM techniques, Messersmith and colleagues<sup>4</sup> showed that on metal oxides, the quinone was only a tenth as effective in binding to TiO<sub>2</sub> as the hydroquinone. Does this mean the ratio of the quinone/hydroquinone can be adjusted to tune adhesion? Finally, how do polycatechols evict water from even highly solvated surfaces and keep it from returning? Answers to these and other questions will amplify the utility of this discovery and also advance fields as diverse as plant science, neuropathology and pigmentation chemistry.

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