

Scotland's Rural College

Polydopamine-Enabled Biomimetic Surface Engineering of Materials

Saraf, Mohit; Prateek; Ranjan, Rahul; Balasubramaniam, Bhuvaneshwari; Thakur, Vijay Kumar; Gupta, Raju Kumar

Published in:
Advanced Materials Interfaces

DOI:
[10.1002/admi.202300670](https://doi.org/10.1002/admi.202300670)

First published: 24/12/2023

Document Version
Publisher's PDF, also known as Version of record

[Link to publication](#)

Citation for published version (APA):
Saraf, M., Prateek, Ranjan, R., Balasubramaniam, B., Thakur, V. K., & Gupta, R. K. (2023). Polydopamine-Enabled Biomimetic Surface Engineering of Materials: New Insights and Promising Applications. *Advanced Materials Interfaces*. Advance online publication. <https://doi.org/10.1002/admi.202300670>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Polydopamine-Enabled Biomimetic Surface Engineering of Materials: New Insights and Promising Applications

Mohit Saraf, Prateek, Rahul Ranjan, Bhuvaneshwari Balasubramaniam, Vijay Kumar Thakur,* and Raju Kumar Gupta*

Surface modification is an important approach to modify the properties of materials. Numerous approaches have been adopted to tailor the properties of such materials, which have been proven successful at many scales and parameters. However, most of these techniques are often tedious, poorly adhesive, costly, sometimes hazardous, and surface-specific, hence cannot be extended on a large scale and all kinds of surfaces. These shortcomings have led to the emergence of new dopamine (DA) based green surface modification technique where a thin polydopamine (PDA) layer is deposited on surfaces through a facile polymerization of DA under alkaline conditions to enable the surface for various applications. This surface modification strategy has several advantages over other techniques in deposition processing under mild conditions, cost-effective and straightforward ingredients, and applicability to all kinds of surfaces regardless of their sizes, shapes, and types. Moreover, the PDA layer enhances the surface functionality. Therefore, it can serve as a versatile platform for various secondary reactions for a wide range of applications. Herein, the chemistry of DA is summarized and its polymerized form PDA for the modification of different families of materials' surfaces with an emphasis on energy, environmental and biological applications.

a variety of materials with advanced functionalities.^[2] The emerging fields based on biomimetics' principle, which have gained significant attention in the scientific community include, surfaces for energy conversion and conservation,^[3–5] harvesting,^[6] robotics,^[7] charge transfer,^[8] superhydrophobic surfaces,^[9,10] self-healing^[11] and molecular recognition,^[12,13] self-cleaning surfaces,^[14,15] self-assembly,^[12] super adhesives,^[16,17] crack healing,^[18–20] hierarchical^[21] and high mechanical strength materials and fibres,^[22,23] antireflective surfaces,^[24,25] artificial furs and textiles,^[26–28] and sensory-aid devices,^[29] bio-inspired biomedical devices and implants,^[30,31] to name a few.^[2,32]

While the materials have been the backbone of human civilization, the recent developments in materials science have further elaborated their horizons.^[33,34] The functional properties of materials are usually governed by

the composition and structure of the surface film. Nano-engineering has enabled us to tune materials' properties by varying their size, shape and various other parameters for a wide range of applications.^[35–39] Materials can be modified

1. Introduction

The term biomimetics suggests learning from the nature,^[1] helping the researchers to mimic them to design and fabricate

M. Saraf, Prateek, R. Ranjan, B. Balasubramaniam, R. K. Gupta
 Department of Chemical Engineering
 Indian Institute of Technology Kanpur
 Kanpur, Uttar Pradesh 208016, India
 E-mail: guptark@iitk.ac.in

M. Saraf
 A. J. Drexel Nanomaterials Institute and Department of Materials Science
 and Engineering
 Drexel University
 Philadelphia, Pennsylvania 19104, USA

B. Balasubramaniam
 Department of Chemistry
 Indian Institute of Technology (BHU) Varanasi
 Varanasi, Uttar Pradesh 221005, India

V. K. Thakur
 Biorefining and Advanced Materials Research Center
 SRUC
 Edinburgh EH9 3JG, UK
 E-mail: vijay.thakur@sruc.ac.uk

V. K. Thakur
 School of Engineering
 University of Petroleum & Energy Studies (UPES)
 Dehradun, Uttarakhand 248007, India

R. K. Gupta
 Department of Sustainable Energy Engineering
 Indian Institute of Technology Kanpur
 Kanpur, Uttar Pradesh 208016, India

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/admi.202300670>

© 2023 The Authors. Advanced Materials Interfaces published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/admi.202300670

in numerous ways to improve their properties.^[40] In particular, surface modification of materials has become a common and potential strategy to improve their properties, thus has recently gained wide attention.^[41,42] The properties of materials such as adhesion, hydrophilicity/hydrophobicity, stability, secondary functionalization and biocompatibility can be fine-tuned through the process of surface modification.^[43] Surface modification/manipulation can be realized either by tuning the surface energy or by introducing covalent or strong non-covalent chemical bonds between substrates and modifying layers. Among numerous efforts being made, several physical surface manipulation strategies such as spin-coating, spray-coating, and dip coating have shown great promise. However, an appropriate adhesion between the substrate and modifying layers has been a persistent issue with these techniques. Addressing these issues, chemical vapor deposition (CVD) and atomic layer deposition (ALD) became popular for surface manipulation, however, their high instrumentation and maintenance cost and tedious synthesis protocols make them unfeasible for their widespread use.^[44] Similarly, other techniques such as self-assembled monolayers, layer-by-layer assembly, Langmuir-Blodgett deposition, organosilane chemistry etc. are surface-specific with separate conjugation mechanism,^[45–47] and cannot be extended on a wider range of materials' surfaces. Hence, most of these approaches have often suffered from time-consuming and complex processes as well as substrate-specific applicability. Therefore, a simple, unique, effective, and robust binding agent-based technique and corresponding mechanism was highly desirable for the surface engineering of materials. Moreover, the costs and environmental consequences of such agents/methods must be carefully evaluated without sacrificing the similar performances by approaches that use facile, energy-efficient and sustainable methods.^[48]

According to Anastas and Warner (1998), chemical processes can be regarded as being “greener” over others when they have minimal adverse environmental consequences. Careful analysis of important factors such as the absence of harmful solvents and toxic materials, good energy efficiency and ease of disposing of waste products is also very crucial in calling a method to be comparatively greener. Therefore, current research focuses on designing next-generation sustainable products which are good for human health and the environment while being profitable to the community.^[49,50] In this respect, mussel adhesive proteins (MAPs) can be effective solutions for the modification of surfaces, which not only immobilize strongly to almost all kinds of surfaces (including wet surfaces) but also a high-capacity adhesion can be expected between MAP and surfaces.^[51–53] Vari-

ous catecholic amino acids such as DA and its derivatives are a rich source of MAPs.^[43] Among various forms of DA, PDA has drawn considerable attention thanks to its simple and versatile approach to functionalize material surfaces. PDA has been reported to functionalize surfaces of different families of materials such as metals, metal oxides, ceramics, semiconductors and polymers.^[54,55] The surfaces functionalized with PDA coating are not only more soluble, stable, and multifunctional but also act as smart platforms for various challenging applications.^[56,57] PDA has mussel like properties with good adhesion, and their functional groups provide additional active sites to bind with various molecules. The easy preparation of PDA coupled with good adhesion and controlled thickness, allow the formation of desired structures to be used for desired applications. The biocompatibility of PDA finds applications in many biomedical fields such as biosensing, tissue engineering, drug-delivery etc., and the introduction of PDA is reported to be beneficial for promoting cell adhesion and proliferation on substrates.^[58–62] Besides they have shown great properties in electrocatalysis, photoresponsive agents, and superparamagnetism and an increasing number of reports have been observed on PDA based applications.

In this review, we will be discussing the green modification of materials' surfaces to combat various environmental issues. In particular, we will be highlighting PDA-induced modification of metallic surfaces, ceramics, polymers and hybrid materials, which brings out new prospects in the materials functionality as well as probe new insights into their application potential particularly in energy, environment and biological fields (**Scheme 1**).^[50,63] Furthermore, the role of green modification of materials will be discussed concerning green and sustainable chemistry which is an urgent requirement of not only today's world but also of future generations. It should be emphasized that to obtain desired characteristics, both morphological, as well as the chemical composition of materials surface, should be modified.

2. Dopamine as Innovative Material for Green Surface Modification

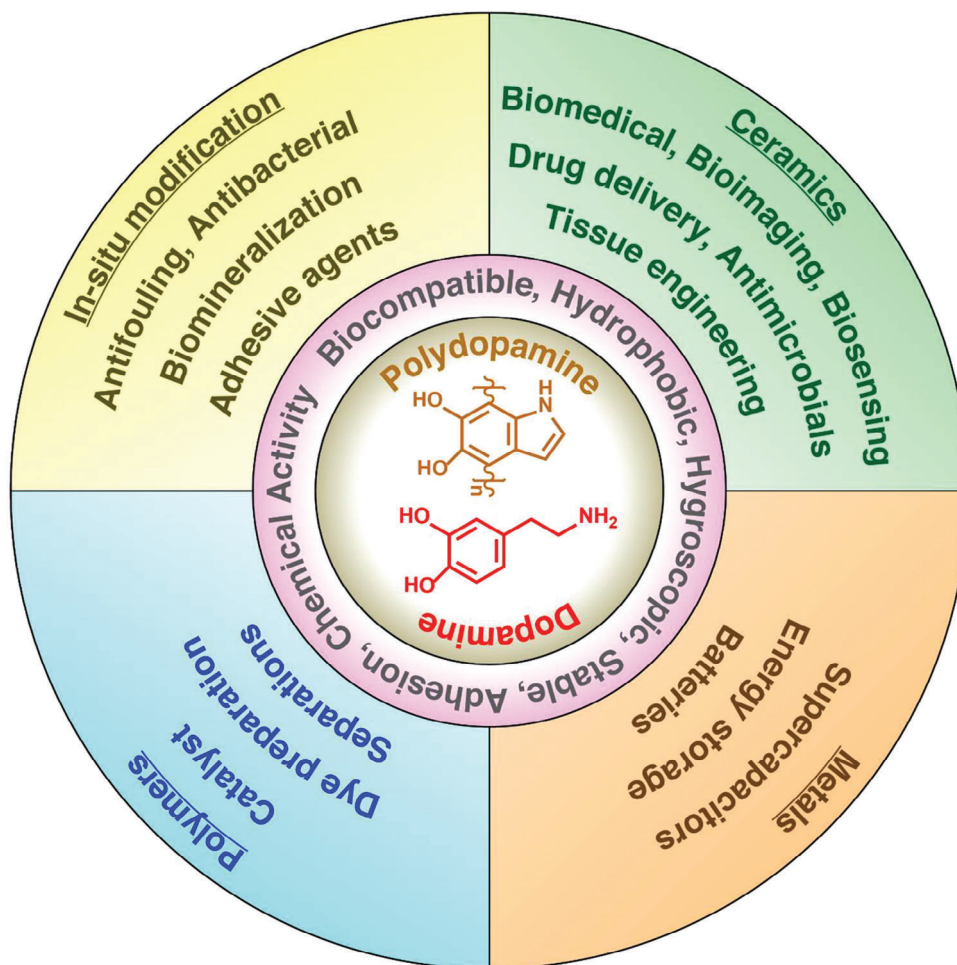
As mentioned earlier, most of the surface modification strategies suffer from some drawbacks either in form of time-consuming and intricate processes or surface specificity, which makes them unsuitable for a wider range of surfaces. Herein, DA being a relatively greener and sustainable agent, can be a promising alternative for the surface modification of the materials.

2.1. Background of DA

DA naturally occurs as a neurotransmitter in the brain, which is an amine or decarboxylated form of L-dopa. By removing a carboxyl group of L-dopa, DA can be synthesized in both brain and kidneys. Furthermore, it can be biosynthesized both directly and indirectly from the tyrosine and phenylalanine amino acids, respectively.

DA has been investigated as a synthetic mimic of MAPs that have gained wide attention over the last few years.^[63–70] Inspired by the composition of adhesive proteins in mussels,^[71] DA was used widely to form thin, robust and adhesive polymer films on

R. K. Gupta
Center for Environmental Science and Engineering
Indian Institute of Technology Kanpur
Kanpur, Uttar Pradesh 208016, India
R. K. Gupta
Chandrakanta Kesavan Centre for Energy Policy and Climate Solutions
Indian Institute of Technology Kanpur
Kanpur, Uttar Pradesh 208016, India
R. Ranjan
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Kharagpur, West Bengal 721302, India



Scheme 1. Dopamine induced modification of different surfaces and their applications.

possibly all kinds of surfaces in alkaline aqueous media.^[72] The polymerization of DA and its derivative have been introduced as a simple and interesting approach for the surface functionalization of materials. The catechol and amino groups of DAs allow it to self-polymerize on different kinds of surfaces to form a conformal coating under ambient conditions. Moreover, the strong interfacial adhesion strength, because of the formation of metal-ligand complexes or hydrogen bonds or quinhydrone charge-transfer complexes, makes it a suitable candidate for the coating of several metals, metal oxides and polymers.^[64,68,73–77]

2.2. Factors Affecting Polymerization of DA Into PDA

The polymerization of DA into a PDA film can easily be achieved under an alkaline and oxidizing environment on almost any virtual surface for surface modification. The concentration of DA plays a key role in regulating the thickness, roughness, morphology and deposition kinetics of the PDA film on the surface, which was verified by Ball et al.^[78] and Liu et al.^[79] through their experiments. Furthermore, buffer,^[80,81] solvent,^[82] pH,^[83] temperature^[84] and oxidants^[80,85] also affect the quality of PDA coatings. Thin-film deposition

of PDA can be obtained very quickly by simply immersing the substrate in a dilute aqueous solution of DA in an alkaline medium. This strategy has been thoroughly used to deposit a variety of ad-layers, including self-assembled monolayers (SAMs),^[86] multilayer films,^[87] surface functionalization of the inorganic materials,^[88–90] drug delivery nanocapsules^[91] and bioinert/bioactive surfaces.^[92] Moreover, this mussel-inspired PDA coating has been successfully realized in building multifunctional surfaces for several challenging applications such as anti-bacterial and antifouling membranes. However, cellulose, polyester, resin and other pH-sensitive/alkaline corrosive materials are not suitable for DA induced modification.^[93] PDA has also shown great potential in post-modification through hydrogen bonds, chelation, electrostatic attraction, and covalent bonds.

2.3. Properties of PDA and its Deposition Process

Thanks to its structure and composition, PDA possesses fascinating properties, including high reactivity and adhesion capability, biocompatibility, photothermal effect and quenching phenomenon, allowing them to be used in a wide range of research

areas and applications.^[57,94–99] Although the PDA coating process is straightforward, the slow kinetics of the polymerization process restricts their large-scale practical implementation. To accelerate the rate of polymerization, various strategies have been adopted. Particularly, the introduction of metal ions or strong chemical oxidizing agents has been demonstrated as an efficient way.^[100] For instance, Zhang et al. developed a $\text{CuSO}_4/\text{H}_2\text{O}_2$ led PDA deposition method exhibiting a very rapid deposition rate at room temperature (10 times of the conventional methods).^[101] Similarly, Ponzio et al.^[85] found a fast route for the homogeneous deposition of PDA films by periodate with a never reported thickness. However, the kind of oxidants used in these methods are hazardous and not environmentally friendly and often contaminate the surface of the PDA film. Moreover, effective control over polymerization is not possible, therefore, a green route for fast and controlled deposition of PDA is highly recommended.

2.4. Polymerization Process and Mechanism

Generally, PDA is prepared through oxidative self-polymerization, besides, some other strategies such as electropolymerization^[102,103] and environment-friendly enzyme polymerization such as eumelanin and pheomelanin have also been reported.^[104,105] However, these methods have their advantages as well as limitations. The polymerization process of DA is quite simple and facile; however, it involves complex redox reactions producing a series of intermediates. In one of the models, the polymerization mechanism of DA was comparable with melanin in living organisms, known as covalent polymerization. In the biosynthesis process of melanin under oxidative reaction, DA is first transformed into 5,6-dihydroxyindole (DHI) followed by covalent polymerization and under weakly alkaline conditions in presence of dissolved oxygen, it is oxidized into DA quinone (**Figure 1**). Subsequently, on deprotonation of amine, the resultant molecule experiences a Michael addition reaction. Herein, DA quinone undergoes intramolecular cyclization and reversible oxidation to form dopaminochrome followed by intramolecular rearrangement to produce DHI (steps A and B in **Figure 1**).^[106–108] In the final step, cross-linking happens because of the dismutation reaction between *o*-quinone and catechol of DHI, yielding PDA.^[109,110] Active functional groups are the abundant source of PDA that can be used for various reactions further. Another model of DA polymerization combines covalent polymerization with noncovalent self-assembly, where the self-assembly process involves various kinds of interactions such as charge transfer, quadrupole-quadrupole, ionic, T-shape, hydrogen-bonding and π - π stacking.^[108,111] Addressing the discrepancy of PDA between covalent polymer or non-covalent aggregate, Delparastan et al.^[112] recently analyzed the PDA films using single-molecule force spectroscopy (SMFS) and found out them to be covalently linked subunits composed of high molecular-weight polymer chains, with weak and irreversible intramolecular non-covalent interactions in the PDA chains. Furthermore, they noticed the PDA films deposition starts possibly at the solid-liquid interface with the adsorption of small oligomers followed by the polymerization to form higher molecular-weight PDA chains.

2.5. Degradation of PDA

Despite its advantageous nature in many advanced functional materials and devices, the degradation behavior and its related mechanism of PDA in the human body are still in debate. Few reports exhibited the degradation behavior and mechanism of PDA through simulated studies.^[113,114] The degradation of PDA was confirmed through color fading of PDA in presence of hydrogen peroxide,^[98] and an in vivo study conducted by Bettinger et al.^[115] also confirmed the complete degradation of implanted PDA in 8 weeks.

Chen et al. studied the PDA degradation by changing the pH value, temperature, and alkali strength of the PDA nanoparticles (PDA NPs) synthesized by oxidation and self-polymerization of its monomer dopamine.^[113] It was found that the degradation of PDA started at pH 11.0 and complete degradation of PDA occurred at high alkaline condition (pH 13.0), which was confirmed through the change in morphology of PDA from sphere shape to nanosheets. It was noted that PDA was completely degraded into monomers and oligomers after 120 h of degradation, and it also showed excellent biocompatibility.

3. The Role of PDA: Mechanistic Approach in Different Applications

PDA, a versatile polymer, is used as one of the bio-Inspired materials to mimic the mussel adhesion mechanism by adopting suitable surface modification methods for various biomedical, energy and environmental-related applications.^[55,116] PDA is an emerging polymer with the synthetic analogue of the naturally occurring melanins.^[56] The melanins are irregular light-absorbing, polyphenolic compounds obtained from the oxidation of tyrosine or DOPA, and found ubiquitous in living organisms that serve a variety of purposes.^[117] Melanin has strong adhesion properties to various surfaces and strong absorption of light, post-polymerization synthetic modification ability, semiconductivity ($\approx 10^{-12} \Omega^{-1} \text{cm}^{-1}$), and antioxidant properties.^[56] PDA also possesses unique adhesiveness, excellent biocompatibility, and mild requirement for synthesis without using an organic solvent. Apart from that, flexibility in controlling essential parameters such as pH, concentration, temperature, oxidants and reaction time, specific and nonspecific interaction to chemical moieties, bonding parameters, surface modification, film thickness control etc. played a greater role in advancing the use of PDA in many emerging applications. In addition, the confluence of nanotechnology and biomimetics approaches have enhanced the PDA in advanced biomedical fields such as drug delivery, wound healing, and tissue engineering. Herein, some pioneering work on DA and PDA have been discussed.

Lee et al.^[68] have done pioneering work in developing mussel inspired adhesive using DA. Mussels are promiscuous fouling organisms, which even get easily attached to adhesion-resistant materials such as poly(tetrafluoroethylene) (PTFE), as shown in **Figure 2A**. In their approach, they have mimicked the properties of adhesive proteins secreted in mussels as it has the potential to bind to nearly all kinds of materials surfaces such as metals, ceramics, and polymers. The adhesive property of mussels mainly arisen from the lysine amino acids and 3,4-dihydroxy-L-phenylalanine (DOPA) present in the amino acid

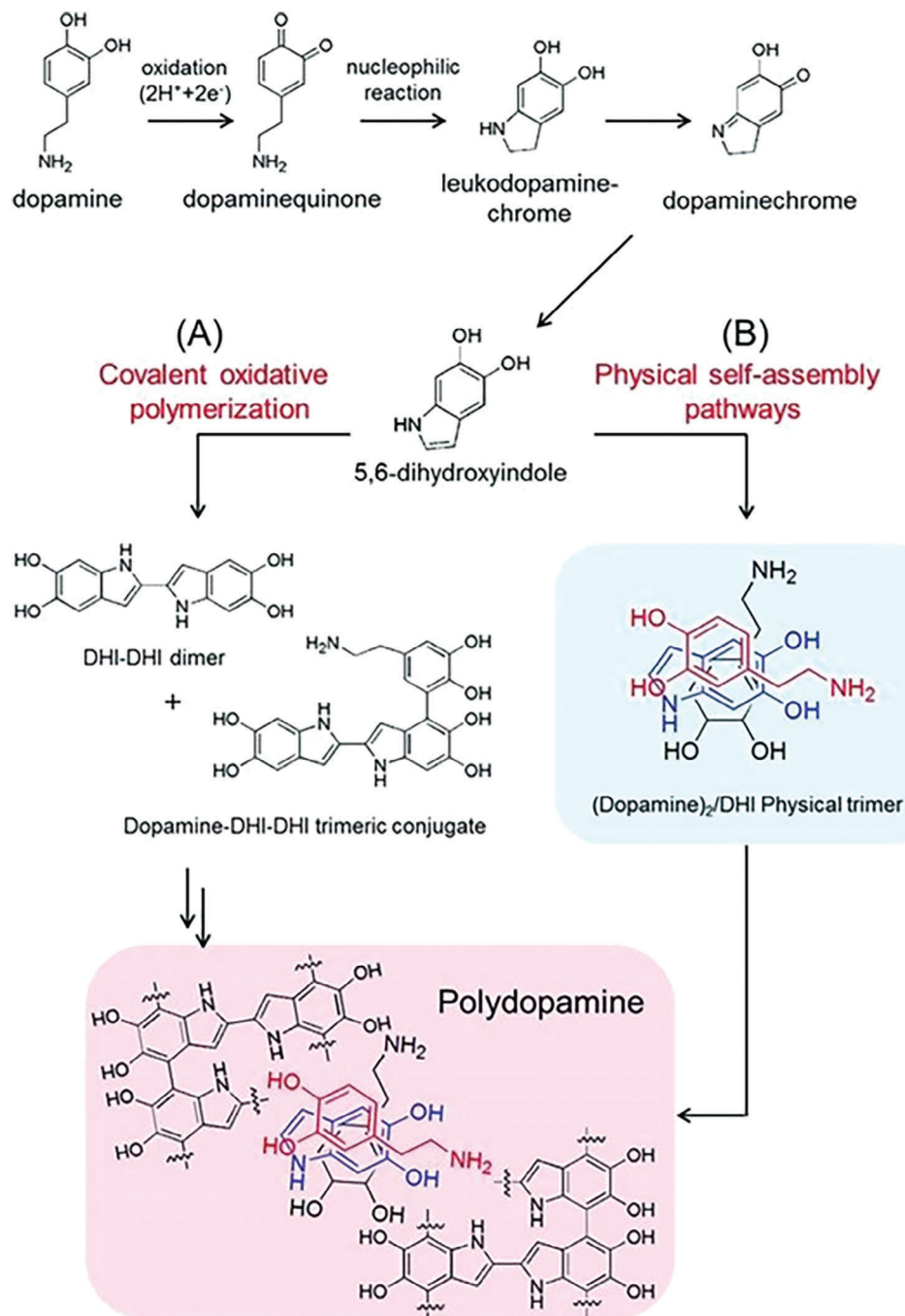


Figure 1. Polydopamine synthesis pathways: a) covalent bond-forming oxidative polymerization, and b) physical self-assembly of dopamine and DHI.^[108] Reproduced with permission.^[108] Copyright 2012, John Wiley and Sons.

proteins (Mefp-5) which are found plaque-substrate interface as shown in Figure 2B–H. During the bulk solidification reaction of the adhesive, strong covalent and noncovalent interactions take place between DOPA and substrates. DOPA and similar catechol compounds show greater binding affinity while coating on inorganic surfaces. The authors have performed a simple dip-coating method for various surfaces by immersing them into a dilute aqueous solution of DOPA with a simulated marine environment (pH 8.5), which always resulted in the spontaneous depo-

sition of thin adherent polymer film on the substrates. The exact mechanism behind the surface adherence of DOPA was not explained, however, it was mentioned that the oxidation of catechol to quinone, with subsequent polymerization, would have been the main reason for the surface coating through covalent and non-covalent binding of DOPA. Hence the polymerized product PDA showed greater and more efficient binding on various substrates. The PDA coating was done on various material surfaces such as noble metals, metals with native oxide surfaces,

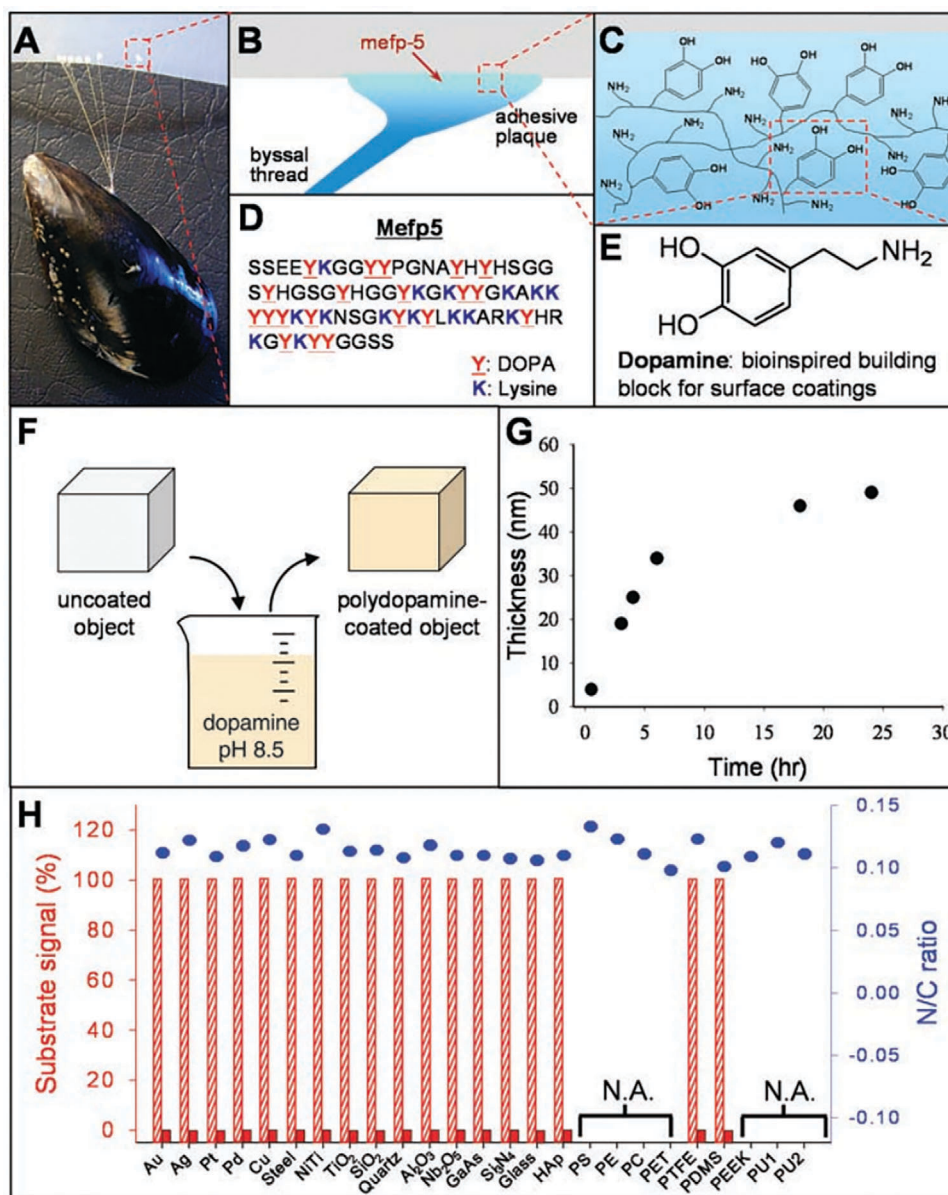


Figure 2. A) Photo exhibiting attachment of a mussel to PTFE. B,C) Interfacial location of Mefp-5 and a simplified molecular representation of characteristic amine and catechol groups. D) The amino acid sequence of Mefp-5. E) Dopamine structure. F) Schematic illustration of thin film deposition of PDA by dip-coating an object in an alkaline DA solution. G) Thickness evolution of PDA coating on Si as measured by AFM of patterned surfaces. H) XPS characterization of 25 different PDA-coated surfaces. The bar graph represents the intensity of characteristic substrate signal before (hatched) and after (solid) coating by PDA. The intensity of the unmodified substrate signal is in each case normalized to 100%. Substrates with characteristic XPS signals indistinguishable from the PDA signal are marked by “N.A.” The blue circles represent the N/C after PDA coating. Reproduced with permission.^[68] Copyright 2007, The American Association for the Advancement of Science.

ceramics, and synthetic polymers {polystyrene (PS), polycarbonate (PC), PTFE, polyethylene (PE), polydimethylsiloxane (PDMS), polyetheretherketone (PEEK), polyethylene terephthalate (PET), and polyurethanes. They have introduced a novel surface modification on DA which leads to the self-polymerization of DA into PDA, which promotes the surface adhesion on various substrates.

Lynge et al.^[116] reviewed the various biomedical applications in the use of synthetic melanin-like polymer, PDA, as a sur-

face coating material. The review includes the design synthesis and characterization of PDA, interfacial mechanisms in coating processes, bonding information related to heterogeneous surfaces, polymerization chemistry, self-assembly, functionalization, reproducibility, and different applications in bio-medical technology such as biosensing, coatings, drug delivery and tissue engineering applications. In addition, sensors, or photoactive/protective materials-based applications of PDA were also discussed. This review was concluded with the present gap in PDA

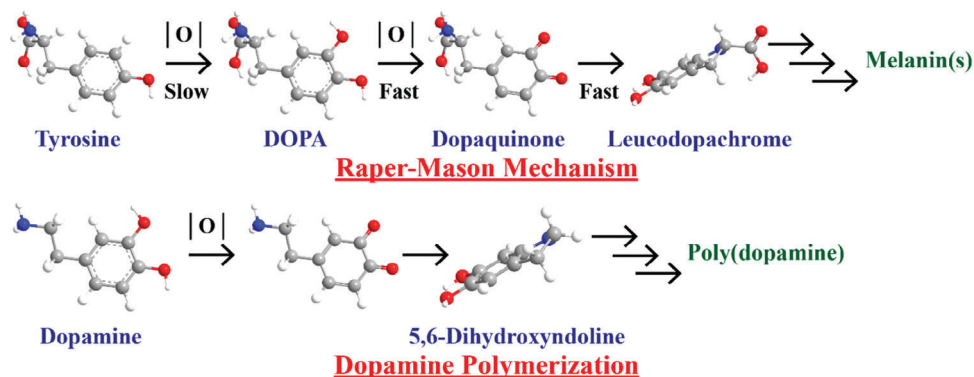


Figure 3. Tyrosinase-catalyzed oxidation and polymerization of tyrosine, according to the Raper–Mason process (top), and a possible polymerization mechanism of dopamine under oxidizing conditions (bottom). Reproduced with permission.^[56] Copyright 2013, Royal Society of Chemistry.

based applications and the future needs to tackle them, thereby fascinating properties of PDA will be realized in the potential technological platforms.

Dreyer and co-workers^[56] presented a short review about the PDA and its extraordinary utility in a range of applications such as biotechnology and biomedicine, surface coatings, and membranes in water purification. The unique characteristics of the PDA film deposition onto a wide range of surfaces plus its inertness to harsh chemical environments made them one of the potential and futuristic polymeric materials. The perspective on PDA, its history, emerging applications, chemical relationship to melanins, were discussed. According to Raper and Mason, the biological melanins are primarily composed of catecholamine monomers, namely tyrosine.^[118–120] The synthetic route of melanin from tyrosine is shown in **Figure 3**. The synthesis route of PDA from DA is also presented. From the synthetic methods of melanin and PDA, it is understood that DA possesses a readily accessible synthetic analogue of the broader class of catecholamine monomers, which would be converted into

melanins easily. Hence, PDA is often described as a model synthetic melanin, as it mimics the melanin physical and chemical properties and is thus subjected to many potential applications. However, at a fundamental level, the structure of PDA remains elusive despite the use of well-defined precursor monomers. So, understanding the fundamental aspects of PDA polymer is the need-of-the-hour for inducing enhanced properties with detailed structure-function relationships.

The two main strategies, i.e., solid or solution state analysis of the polymer product or intermediates, respectively and degradation products, describe the structural parameters of PDA. In conclusion, the coupling reactions between the cyclized intermediates induce the construction of covalent bonding between the monomers in PDA. Few models suggested the mixture of covalent and supramolecular bonding interactions in PDA. The proposed structures of PDA based on three different kinds of interactions are shown in **Figure 4**.^[56,111,121,122]

Han et al.^[123] have synthesized an adhesive with the combination of PDA-clay-polyacrylamide (PDA-clay-PAM) hydrogel,

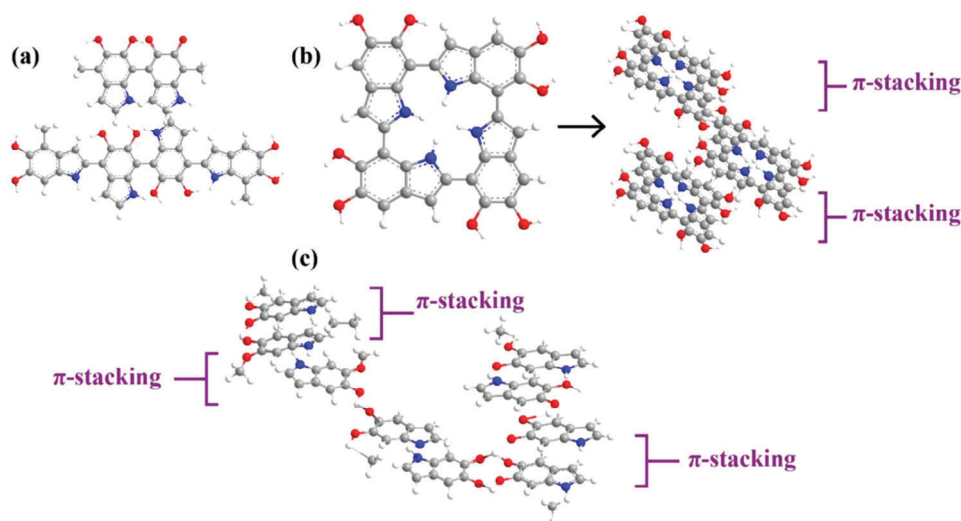


Figure 4. Proposed structures of polydopamine, including a) based on covalent bonding interactions, b) a mixture of supramolecular and covalent bonding interactions, and c) predominately supramolecular bonding interactions. Reproduced with permission.^[56] Copyright 2013, Royal Society of Chemistry.

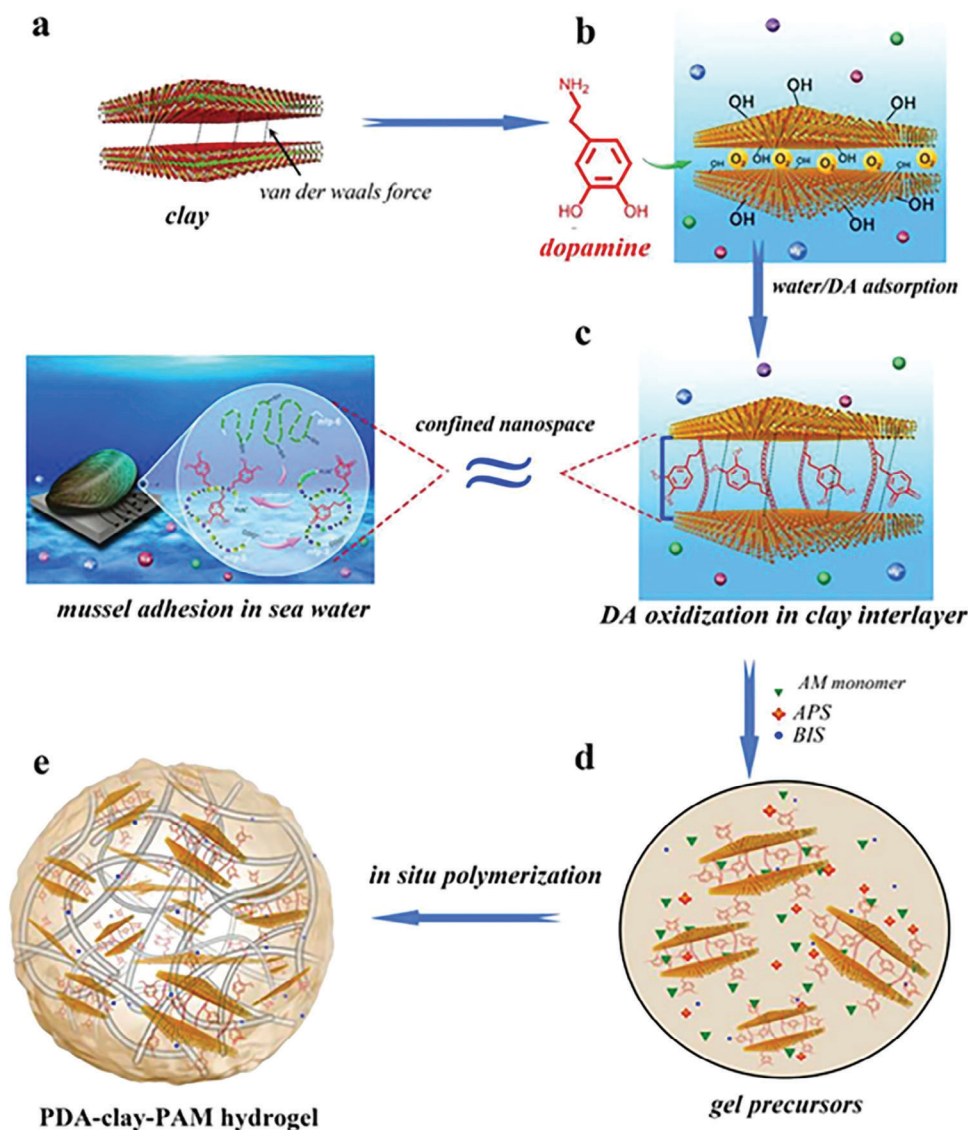


Figure 5. Preparation of PDA-clay-PAM hydrogel. a) The layered structure of clay nanosheets. b) DA molecule intercalated into the nano space between the nanoclay layers. c) Clay-induced DA oxidation to PDA in its nano space, and the interlayer of clay nanosheets mimicked the confined nano space of mussel's plaque. d) AM monomers, cross-linkers (BIS), and initiator (APS) were added into the PDA-intercalated clay suspensions to form gel precursors. e) The PDA-clay-PAM hydrogel was formed by in situ polymerization. Reproduced with permission.^[123] Copyright 2017, American Chemical Society.

to mimic the mussel-inspired adhesion mechanism and the nanocomposite concept while preparing strong adhesive to be used for surgical applications. The design strategy for the preparation of PDA-clay-PAM hydrogel is shown in **Figure 5a–e**. A two-step process was adopted for the preparation of mussel-inspired mechanically strong PDA-clay-PAM hydrogel for tissue repair applications. Initially, DA was intercalated into the layers of clay nanosheets and converted into PDA-intercalated clay nanosheets with free catechol groups. During this step, the oxidation of DA was limited due to the confined nano space of clay layers, thereby intercalation occurs. The nano space of clay layers was restricted by van der Waals attraction which resulted in an insufficient amount of oxygen, which controls the PDA oxidation, further, the dis-

solved ions present in the clay layers provided a sea water environment due to increased alkalinity, which helps the in situ oxidation of DA molecules. In the second step, monomers of acrylamide (AM) were added and then the in situ free-radical polymerizations took place in the presence of cross-linker and initiator molecules. A free-standing and adhesive hydrogel PDA-clay-PAM was obtained after polymerization reaction and the catechol group of PDA present in the nano space of clay layers provides excellent adhesiveness on various surfaces as resulted from the studies conducted. Since PDA was a supramolecular aggregate, noncovalent interactions are prominent to hold together the molecules, which restricts the long-chain formation, and PDA chains are denoted as dotted lines in **Figure 5c**.

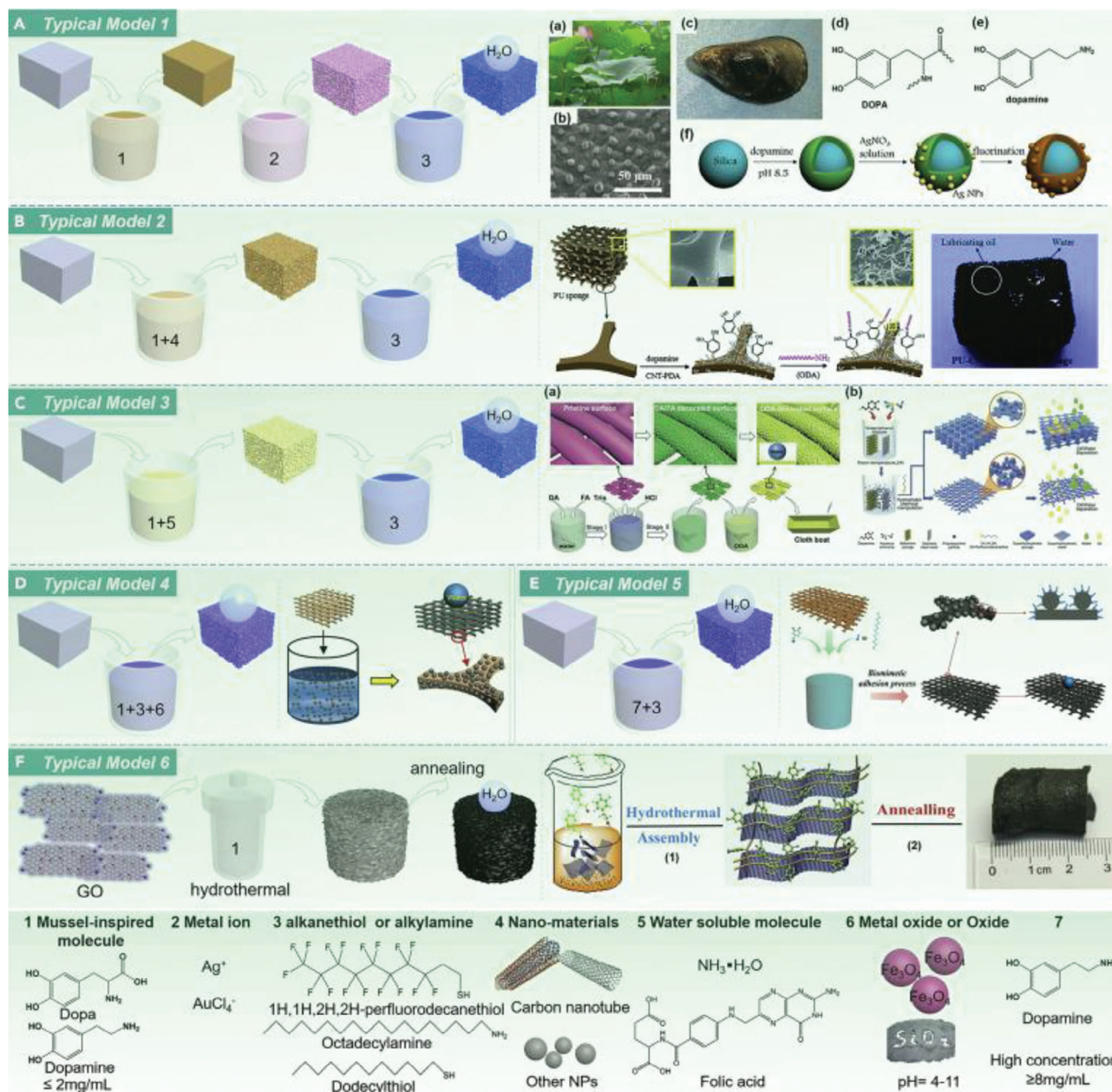


Figure 6. Mussel-inspired strategies for fabricating superhydrophobic materials. Reproduced with permission.^[44] Copyright 2019, Elsevier.

Wang et al.^[44] have reviewed the surface chemistry, synthetic methods, physical properties, superhydrophobization, mechanisms, and various applications of PDA such as oil/water separation, bio-medical, photocatalysis, coatings and water remediation. Authors have correlated the mussel-inspired chemistry with PDA polymer as it is an advanced technique for tailoring the surface properties of materials. An excellent group up on mussel-Inspired strategies adopted for fabricating superhydrophobic materials are summarized in **Figure 6**. The review discussed the various synthetic schemes adopted for PDA from DA and its purity, polymerization mechanism and its complexity, functionality, photothermal ability, adhesion mechanism, long-term stability, and safety protocols when used for practical appli-

cations. It was concluded that significant attention needs to be devoted to the scale-up manufacturing of cost-effective, and environmentally friendly synthesis process of PDA, experimental and theoretical correlations of PDA polymerization, and adhesion mechanisms. It was also stated in the conclusion that mussel-inspired chemistry has immense potential for next-generation technologies such as 3D printing for designing functional materials with high-performance properties. However, proper attention is required to control over both structural and interfacial properties, which may bring up new prospects in this field.

PDA coatings on various polymeric fiber surfaces such as nylon capillary-channeled polymer fibers,^[124] carbon fiber

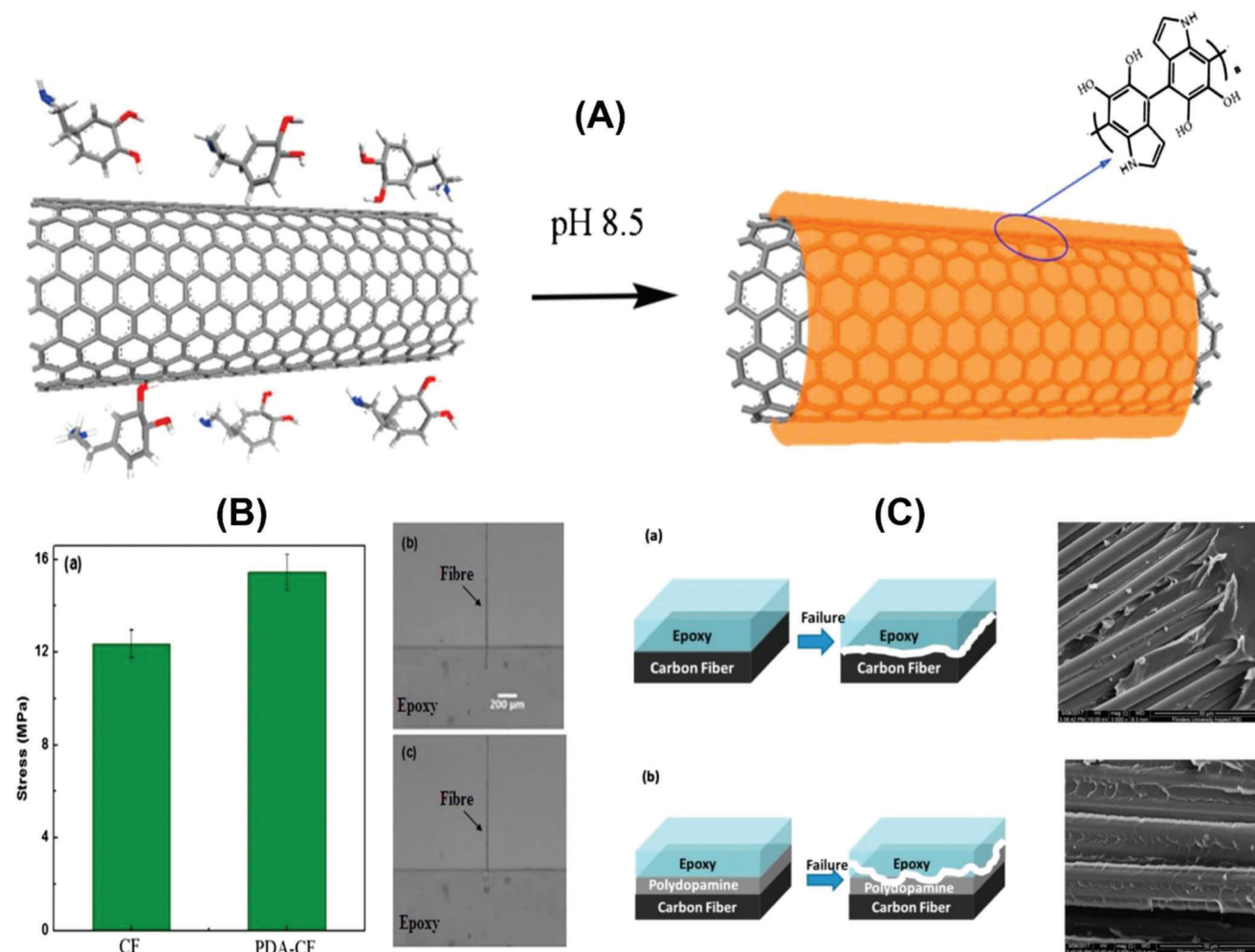


Figure 7. a) Schematic diagram of PDA coating on a CF surface and acting as sizing. b) Interfacial stress for CF and PDA-CF by single fiber pull-out testing and images of a single fiber b) before and c) after pull-out. c) Schematic diagrams and micro-morphologies of interface failure in a) CFRP and b) PDA-CFRP laminates. Reproduced with permission.^[125] Copyright 2018, Elsevier.

(CF) reinforced polymer (CFRP) laminate,^[125] peptide hybrid nanofibers,^[126] poly- ϵ -Caprolactone fibers^[127] and polyphenylene sulfide (PPS) fiber^[128] have been successfully carried out for multiple applications such as mass spectrometric phosphopeptide analysis, high mechanical strength epoxy laminated composites, neuronal growth stimulation and adhesion, bio-electroconductive interfaces fabrication and increased photostability, respectively.

Han et al.^[125] carried out PDA coating on CF fabrics to increase the mechanical properties of CFRP laminates (Figure 7A). It was found that PDA coating on CF escalated the mechanical characteristics of the CFRP laminates with a 20%–25% increment received for Mode I interlaminar fracture toughness over pristine CFRP. Further, interlaminar shear strength, impact strength, and interfacial stress of PDA coated CFRP, were also enhanced similarly. The single fiber pulls out test results were shown in Figure 7B, indicates that the interfacial stress for CF/epoxy and PDA-CF/epoxy was found to be 12.36 and 15.44 MPa, respectively. It shows that a 25% increment in interfacial stress for the PDA/CF epoxy was witnessed. Improved crack propagation was

evidenced as the Mode I interlaminar fracture toughness showed relatively smooth curves for the PDA coated CFRP. PDA coating increased the interfacial bonding between the epoxy resin and CF, hence load transfer was improved between the polymer matrix and CFs. The interfacial failure in CFRP and PDA-CFRP laminates is shown through a pictorial representation (Figure 7C).

4. Dopamine Induced Modification of Materials for Energy, Biological and Environment Applications

The thin layer of PDA coating can be deposited onto various inorganic and organic materials, including metals, oxides, and ceramics through self-polymerization of DA. The thickness of PDA film can be controlled by adjusting deposition time and conditions. Furthermore, this deposition rate can be increased by various techniques.^[129–131] PDA shows promising contributions in enhancing the functionalities of these materials and enable them for a large number of energy, environment and biological applications,^[132–236] which are discussed below.

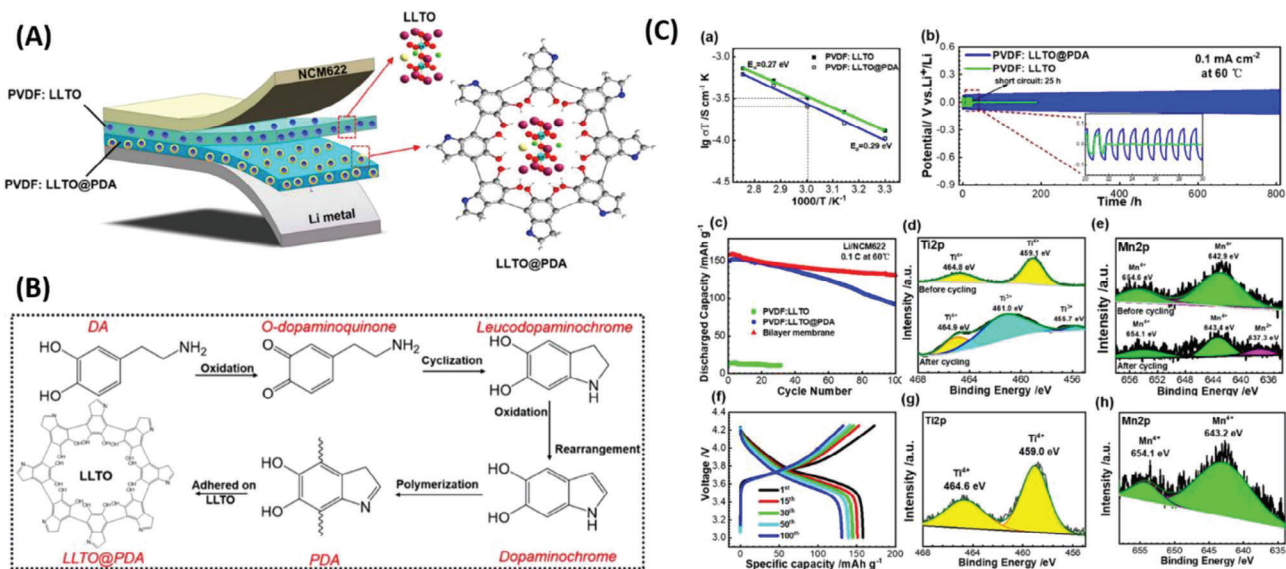


Figure 8. A) Structure of the bilayer membrane electrolyte. B) Possible synthetic mechanism of LLTO@PDA particles. C) a) cycling performances, b) discharge capacity of Li/NCM622 cells with different membrane electrolytes. d) XPS analysis. Reproduced with permission.^[136] Copyright 2020, American Chemical Society.

4.1. Energy Applications

4.1.1. Energy Storage

PDA possesses high stability and great adhesion on materials because of which it has been incorporated as modified layers in lithium-based batteries for better cycling stability.^[132–135] Jia et al.^[136] synthesized PDA coated perovskite-structured $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLTO) particles (LLTO@PDA) and dispersed them into poly(vinylidene fluoride) (PVDF) matrix having high ionic conductivity as well as high voltage tolerance and mechanical robustness. One of the major roles of PDA is to provide LLTO stability against Li metal by forming a composite electrolyte with PVDF. Inspired by the reductive ability of PDA, the bilayer membranes were designed in such a way that PVDF: LLTO membranes contact cathodes, while PVDF: LLTO@PDA membranes link with Li anodes for maintaining the high-voltage tolerance and stable anode/electrolyte interface, respectively (Figure 8A). The catechol and imino groups in PDA membrane electrolytes drive an effective interfacial contact leading to a great interfacial bonding between the LLTO filler and the PVDF matrix (Figure 8B). As per experimental investigations couple with XPS analysis, the Li/ $\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (Li/NCM62) cells demonstrate a good specific capacity of 158.2 mAh g^{-1} excellent cycling with 83% capacity retention after 100 cycles at 0.1 C and rate capacity, having $35 \mu\text{m}$ thickness of membrane electrolytes and total areal specific resistance below $15 \Omega\text{cm}^2$. Furthermore, the prepared cells exhibit superior flexibility and stretchability having the ability to power a lamp even under bending, twisting and stretching of several extreme conditions (Figure 8C). This study highlights the important role of PDA to improve the stability of LLTO Against Li in a simple, cost-effective and environmentally friendly manner.^[136] Similarly, PDA coating has been used for other energy storage devices such as supercapacitors etc.^[137–142]

The researchers have used PDA as an electrode material for other advanced electrochemical applications.^[228–230] Liu et al.^[230] have harvested in situ DA polymerization in developing redox-active organic cathodes for Na- and Li-ion batteries or hybrid capacitors. They used hydrothermal reaction ($180 \text{ }^\circ\text{C}/6 \text{ h}$) in which graphene oxide worked as an oxidant and a template, thereby assisting in the polymerization and conformal growth of PDA. It has been found that graphene oxide self-assembly varied with the GO content (2, 0.05, and 0 mg mL^{-1}) while keeping the DA concentration fixed to 2 mg mL^{-1} . Figure 9a shows that at a higher GO concentration of 2 mg mL^{-1} , GO sheets convert into reduced graphene followed by self-assembled graphene hydrogels and oxidative polymerization of DA to form PDA functionalized graphene (PDG) electrodes. The ultra-low concentration of GO (0.05 mg mL^{-1}) restricted the self-assembly of graphene and promoted a thin and conformal PDA coating of thickness 10–15 nm (Figure 9b,d). In the absence of GO, the DA colorless solution was converted into PDA nanoparticles of $\approx 100 \text{ nm}$ (Figure 9c,e). Thus, the GO substrate controls the heterogeneous polymerization reaction of PDA. Thus, the PDA coating prevented active materials through dissolution and retained excellent cycling stability ($\approx 95\%$ efficiency over 1000 cycles). Furthermore, the Na and Li-cells exhibited excellent capacities of ≈ 211 and $\approx 230 \text{ mAh g}^{-1}$.

In another study, Chen et al.^[231] have designed multifunctional interfaces through in situ DA polymerization on the cellulose textile substrate. The transition from PDA to nitrogen-doped interface is simultaneously used as a binder, conductive additive, and active material. The strong binding between them even after pyrolysis was ascribed to the functional groups on GO (hydroxyl, carboxyl, and epoxide) and PDA (catechol and amino). This interface resulted in an enhanced specific areal capacitance of 3100 mF cm^{-2} .

4.1.2. Flexible and Wearable Devices

PDA also plays a vital role in developing flexible biosensing materials for their medical devices and wearable detectors applications.^[232] For example, Xie et al.^[233] have demonstrated a flexible bioelectrode comprising conductive bacterial cellulose (BC)/PDA biocomposite for electrophysiological signal detection. They proposed that PDA formed by non-covalent interaction between the hydroxyl groups on BC and catechol and amino functional groups on DA via hydrogen bonding. The in situ self-polymerization happened in multiple stages, as shown in **Figure 10a**. Initially, the reaction started from the surface of the BC. Since the PDA particle is a smaller size than BC, it infiltrated into the 3D network of BC. The PDA particles finally cover the whole BC with an increase in concentration to 20%. The PDA addition increased the conductivity of 10^{-3} S cm^{-1} which was speculated to be the π -bond interaction among stacked layers of DA molecules (**Figure 10b**). The tensile strength also increased to 0.87 MPa which was double that of pure BC. Apart from increased electrical and mechanical properties, the BC/PDA composite also exhibited excellent antibacterial properties having the inhibition zones and inhibitory rates of >20 mm and >98%, respectively for Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*).

4.1.3. Electric and Ferroelectric Properties

PDA has found application in improving the electric and ferroelectric properties of various functional surfaces to create highly efficient flexible capacitors for the modernization of power systems. In a recent study, Yin et al used a facile and nature-

friendly strategy to prepare flexible cellulose-based dielectric films of regenerated cellulose (RC) and 1D BaTiO₃ nanofiber (BTNF) based composite (**Figure 11A**), in which they further modified BTNF surface by DA to yield PDA modified BTNF (PDA@BTNF) for improving the distributional homogeneity and compatibility of the matrix.^[143] Compared to RC and RC/BTNF, the RC/PDA@BTNF composite films exhibit lower dielectric loss and higher dielectric constant and breakdown strength because of introducing PDA (**Figure 11B**). Particularly, a thin film consisting of 2 vol% PDA@BTNF labelled as RC-2PDA@BTNF exhibited a high discharged energy density of 17.1 J cm^{-3} at 520 MV m^{-1} , exceedingly over 40% than RC-2BTNF at 460 MV m^{-1} with good efficiency of 91% after constantly working for more than 10 000 times at 200 and 300 MV m^{-1} , respectively (**Figure 11C**). Furthermore, it shows good retention of dielectric properties after storing the thin films in a vacuum for a longer period. Therefore, PDA based surface modification strategy has become important for the development of high-performing dielectric capacitors. This work highlights a novel and efficient strategy of introducing biomass materials for improved dielectric energy storage systems. Similarly, numerous other materials and compositions were designed to improve the electrical energy density.^[77,144–150]

In another study, Mayeen et al.^[54] incorporated electrospinning technique for the preparation of ceramics polymer-based flexible ferroelectric nanofibers, where DA functionalized barium titanate (DBTO), zirconium titanate (DBZTO) and barium zirconate (DBZO) act as fillers and PVDF as the polymer matrix (**Figure 12A,B**). The concentration of DA functionalized nanoparticles was fixed at 10 wt%, which was added to the polymeric solution (15 wt%). The results highlight an important

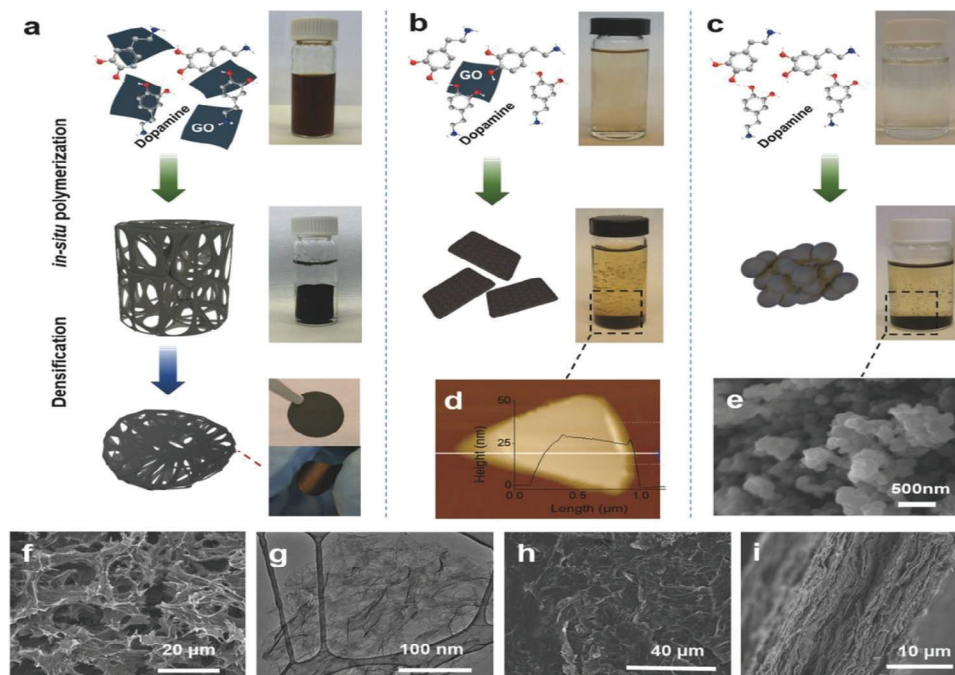


Figure 9. Schematic preparation of a) PDA-functionalized graphene film, b) PDA-coated graphene flake, and c) pristine PDA particles through hydrothermal polymerization of DA. d) AFM image of the PDA-coated graphene flake. e) SEM image of the pristine PDA particles. Reproduced with permission under the terms of the Creative Commons CC BY license.^[230] Copyright 2017, the Authors. Published by Royal Society of Chemistry.

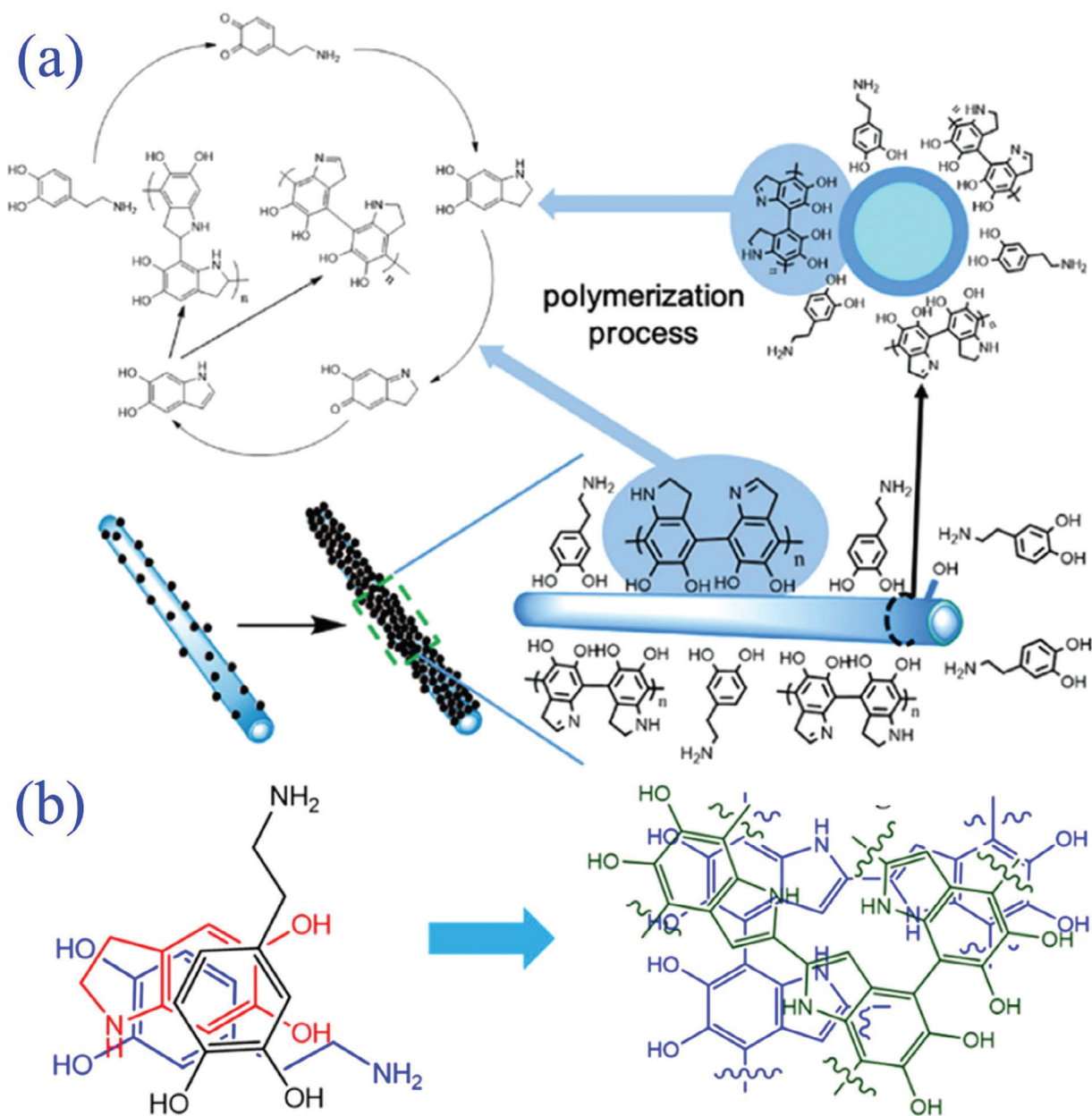


Figure 10. a) Schematic diagram of the polymerization process of DA and PDA aggregation on the surface of BC and b) diagram of the interaction between PDA molecules by the p-p interaction. Reproduced with permission.^[233] Copyright 2018, American Chemical Society.

role of DA, where an improved ferroelectric β -crystalline phase of PVDF was observed on the addition of fillers (Figure 12C). Moreover, systematic analysis reveals improved electric, ferroelectric and mechanical properties of electrospun fibres on the addition of DA functionalized nanoparticles, which can be extended for many potential applications in electronics as storage media and in ferroelectric random access memories (FeRAM) etc.

Similarly, various other attempts were made to improve the electrical and ferroelectric properties of various materials through surface modifications by DA or its polymerized form PDA. For eg., Xie et al.^[144] fabricated a stretchable nanocomposite by cross-linking PVDF filled with PDA encapsulated

BaTiO₃ for high energy density and low-loss dielectric capacitor. Liu et al.^[151] constructed a ceramic-polymer nanocomposite of high aspect ratio electrospun DA functionalized BaTiO₃ nanofibers with PVDF matrix for high energy-storage density.

4.2. Biological Applications

Apart from energy applications, the strategy of PDA deposition has been applied for creating functionalized surfaces for various biological applications^[57,95,116,170–173] and environment applications.^[174–183]

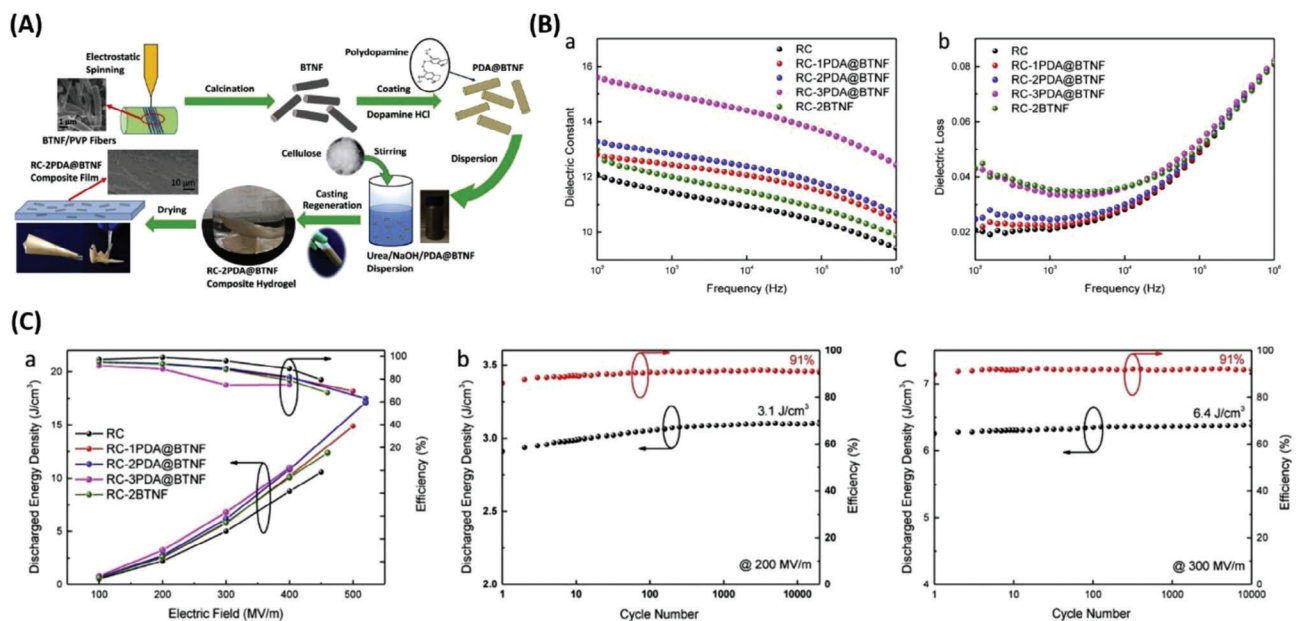


Figure 11. A) Schematic of preparation of BTNF, PDA@BTNF and RC-PDA@BTNF. B) Frequency dependence of the a) dielectric constant and b) dielectric loss for the RC, RC-2BTNF and RC-PDA@BTNF composite films with different loadings, respectively. C) a) Discharged energy density and charge-discharge efficiency cycle performance at b) 200 MV m⁻¹, and c) 300 MV m⁻¹. Reproduced with permission.^[143] Copyright 2020, Elsevier.

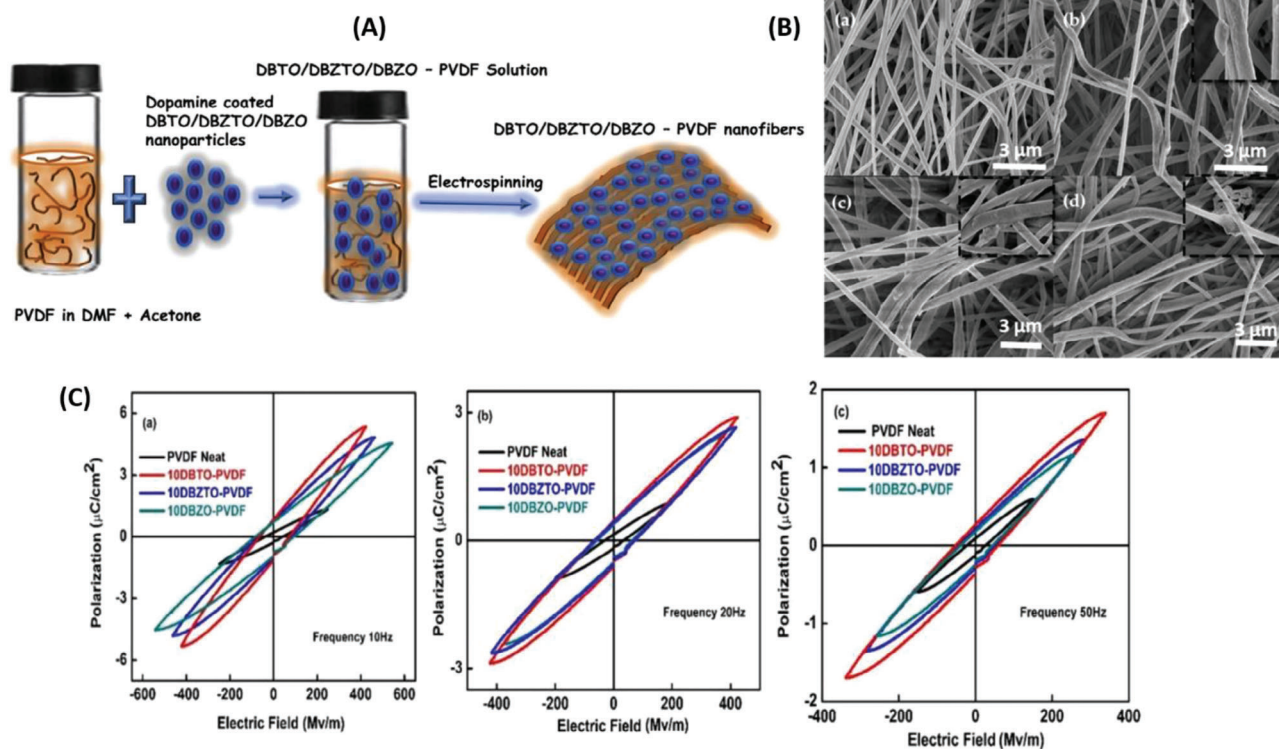


Figure 12. A) Scheme of fabricating ceramics polymer-based flexible ferroelectric nanofibers. B) SEM images of a) PVDF, b) 10DBTO-PVDF, c) 10DBZTO-PVDF, and d) 10DBZO-PVDF composite nanofibers. C) P-E loop of DBTO/DBZTO/DBZO-PVDF nanofibers at different frequencies. Reproduced with permission.^[54] Copyright 2020, Elsevier.

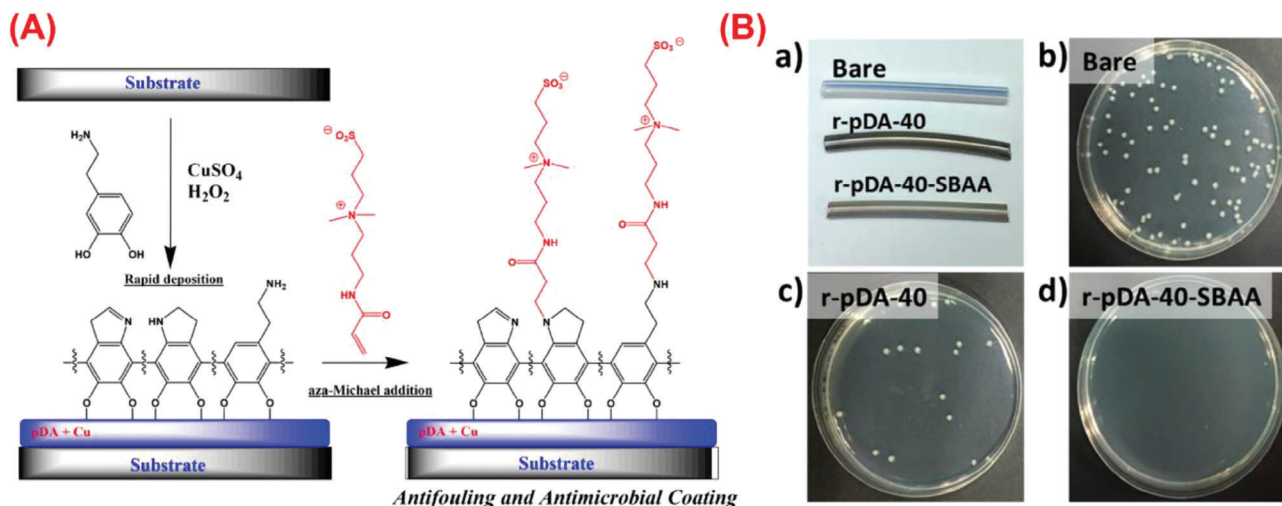


Figure 13. A) Schematic representation of Dual Antifouling and Antimicrobial Coatings Preparation Process, B) Snapshot of silicone-based urinary catheters before and after surface modification a). Plate-counting assays for *S. epidermidis* released from catheters before modification b) and after modification of r-pDA-40 c) and r-pDA-40-SBAA d). (r-pDA-40 denoted as the coating prepared from the CuSO₄/H₂O₂-triggered rapid deposition with 40 min deposition time).^[184] Reproduced with permission.^[184] Copyright 2019, American Chemical Society.

4.2.1. Antimicrobial Coatings, Tissue Engineering and Bone Scaffolds

PDA is also envisioned as one of the prime chemicals in drug delivery, photothermal therapy, bone tissue engineering, cell adhesion and patterning, and antimicrobial / antifouling-based applications.^[55,58–61,184–187] Yu-Jhen Fan et al.^[184] developed the dual functionality enabling PDA based bioinspired antimicrobial and antifouling coatings to tackle the important issues of biomaterials-associated infections (BAIs). The famous chemical reaction namely aza-Michael addition reaction was adopted to synthesize the bioinspired coatings. In the synthesis process, rapid deposition of functional PDA and copper ions with antimicrobial properties was conducted followed by conjugation of zwitterionic sulfobetaine (SB) moieties with antifouling characteristics. Zwitterionic acrylamide-based molecules (SBAA) were used to create the formation of β -amino carbonyl linkage. The synthesis scheme was shown in **Figure 13A**. *E. coli* and *S. epidermidis* were employed to understand the antimicrobial properties of the TiO₂ substrates. Surface modifications were employed for improving the antimicrobial properties of the coatings. Trials were made to scrutinize the release of bactericidal copper ions toward killing the residual number of adsorbed bacteria on the substrate. The findings based on viability tests for fibroblast cells represent the superior biocompatibility of the medical coatings developed. To display the real-world applications, the antifouling and antimicrobial coatings were applied on silicone-based commercially available urinary catheters **Figure 13B**. The bacteria's existence was evaluated through plate-counting assay, and the results indicated the undetectable level of living bacteria. So, the conclusion states that the prepared bioinspired PDA based dual functional medical coating provides a promising approach to counter the BAIs for practical applications.

Recent reviews highlighted the importance and futuristic applications of PDA in tissue engineering applications.^[188–190] Due to its biocompatibility, superior surface functional properties on transferring the bioinert surface to bioactive surface, and flexibil-

ity in immobilizing biomolecules, PDA was extensively used in bone scaffold making process.^[191–194] Mussel-inspired PDA coating was famous in implants design based bioengineering applications, which serves the platform to understand the process of Osteogenic differentiation and Osseointegration of the implants designed.

Wang et al.^[194] studied the effects of PDA coating on different representative substrates of biopolymer, biometal, and bio-ceramic based materials such as polyetheretherketone (PEEK), Ti6Al4 V (Ti) and hydroxyapatite (HA) respectively, to analyze the cell responsive behaviors (in vitro) and the capacity of bond formation (in vivo). Results proved the increased hydrophilicity properties of surfaces after PDA coating, improved cell adhesion, and proliferation. The authors chose FAK and p38 signaling pathways to estimate the osteogenic differentiation of bone marrow derived mesenchymal stromal cells (BMSCs) (**Figure 14**). The study concluded that the PDA coatings enhanced the osseointegration performance resulting in new bone formations according to the evidence arrived from in vivo study.

Feng et al.^[195] investigated the bone scaffolds made up of PDA modified polycaprolactone toward its biomineralization capacity. Based on the results, it was concluded that the PDA modifications improved the hydrophilicity, cell adhesion and biomineralization capacity of the bone scaffolds. Li et al.^[196] conducted the studies to improve the bioactivity of chitosan (CS) anchored porous poly(ϵ -caprolactone) (PCL)/ bioactive glass (BG) composite polymeric scaffold using PDA coating as a bridging layer. In vivo results demonstrated that cranial bone regeneration was highly promoted due to the covalent immobilization of CS onto the polymeric scaffold surface. Hence, the fabricated artificial bioactive scaffolds were an excellent potential source for bone tissue engineering application. Farnaz Ghorbani et al.^[197] fabricated the PDA coated electrospun polyurethane/graphene oxide nanofibers as scaffolds for bone tissue engineering applications. Results find that the excellent improvement on wettability, both cell attachment

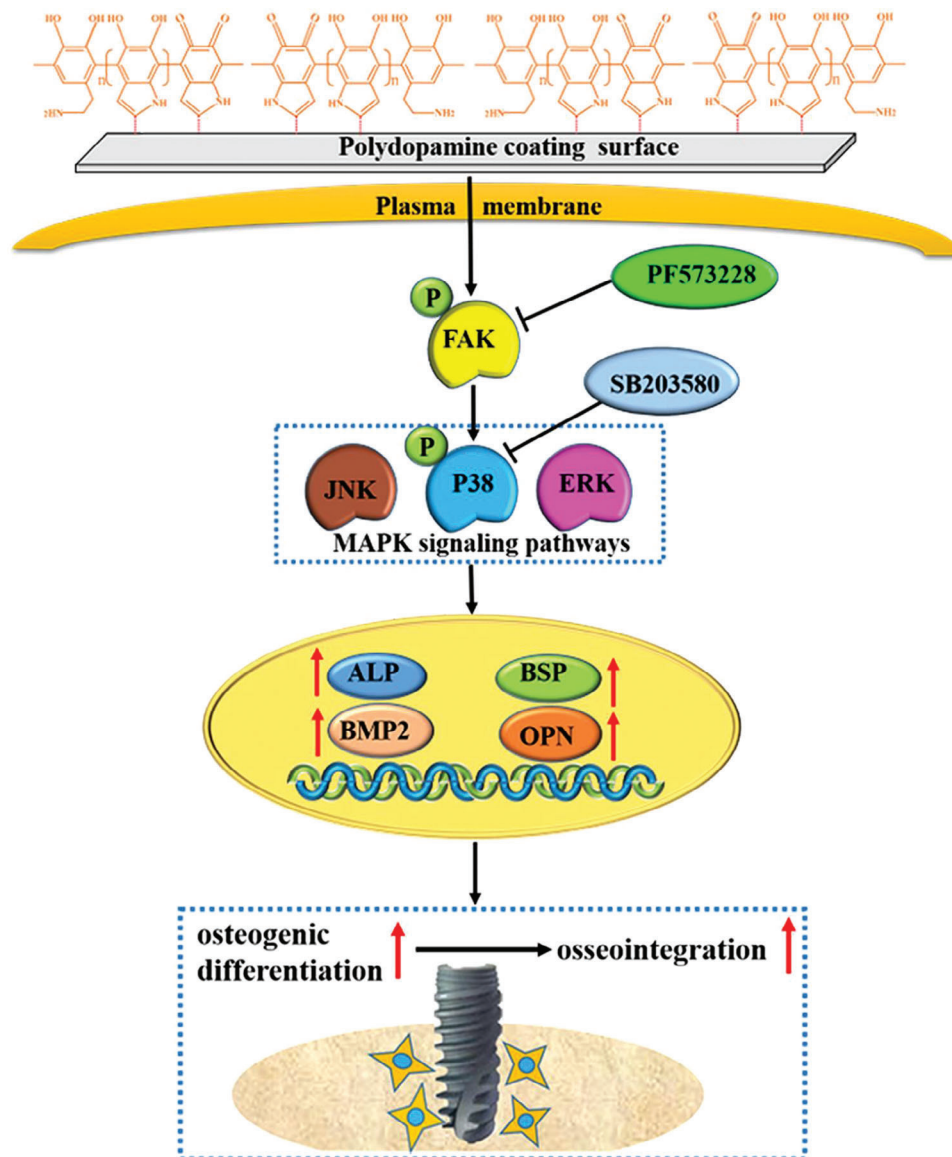


Figure 14. Schematic diagram of PDA coating on osteogenic differentiation and osseointegration. Reproduced with permission.^[194] Copyright 2019, American Chemical Society.

and proliferation and water absorption characteristics of the electrospun scaffolds comparatively and significant improvement in the osteogenic differentiation property was noticed than the scaffold without PDA coating. Deng et al.^[198] fabricated osteopromotive electrospun polymeric scaffolds through co-electrospinning of polycaprolactone (PCL) with PDA nanoparticles (PDA NPs). The fiber size, chemical composition and mechanical properties of PCL/PDA fibrous membranes significantly improved because of the inclusion of PDA NPs. Results from the cell experiment assessed that the polymeric fibrous membranes would facilitate the reproduction, spreading, and in vitro osteogenic commitment of hMSCs. The in vivo preclinical study quantitatively demonstrates the newly formed bone with 2% PDA/PCL fibrous membranes compared to its pure PCL counterpart.

4.2.2. Photothermal Applications, Separation of Ions and MRI Activities

PDA can easily functionalize various ranges of surfaces including metal and metal oxides thus enhancing their solubility and increasing their stability. The most common metal used is Fe_3O_4 for the modification of the surface with PDA. Since Fe_3O_4 has magnetic properties, they are simply purified and collected using an external magnetic field and thus these nanoparticles can be applied in nanomedicine.

Wu et al.^[199] prepared Fe_3O_4 @PDA nanoparticles in the range of 50–60 nm, which were embedded with natural killer cells and in vivo experiments were conducted. Thus, by using an external magnetic field, they can increase the accumulation of Fe_3O_4 @PDA labelled NK in the tumor region and inhibits

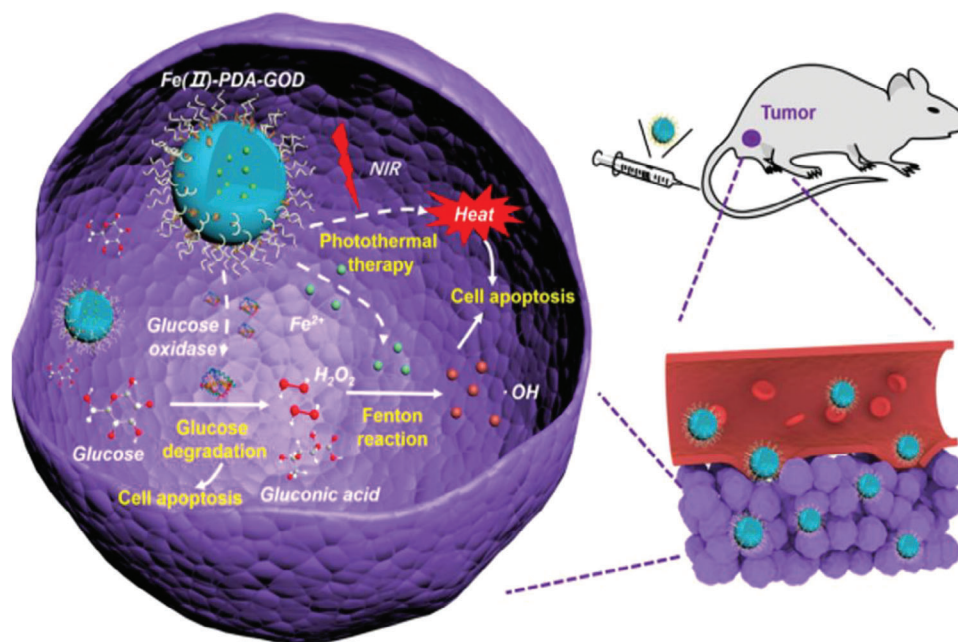


Figure 15. Schematic illustration of TME-Based Fe(II)–PDA–GOD nanosystems for efficient cancer therapy by combining glucose degradation, the Fenton reaction, and photothermal therapy. Reproduced with permission.^[207] Copyright 2019, American Chemical Society.

tumor growth. PDA was also used for the modification of Fe_3O_4 nanoparticle clusters, and a core-shell system was synthesized keeping Fe_3O_4 nanoparticle clusters as the core and PDA as the shell (SPION cluster@PDA) having 4 nm of PDA layer, thus constituting a whole nanocomposite diameter of 50 nm. Thus, the crystallized iron oxide and PDA layer showed enhanced photothermal properties when used in killing cancer cells.^[200] Zheng et al.^[201] further investigated in a similar direction by synthesizing PDA-coated Fe_3O_4 clusters and compared them with single Fe_3O_4 and PDA nanoparticles. They concluded that the enhanced photothermal effect due to PDA-coated Fe_3O_4 clusters is due to enhanced NIR absorption. Li et al.^[202] fabricated Fe_3O_4 @Au@PDA nanocomposites. Fe_3O_4 nanoparticles were first covered with Au to form Fe_3O_4 @Au, then these clusters were coated with a PDA layer. Thus, they were used for analysis and separation of Cu^{2+} .

Ge et al.^[203] synthesized PDA-capped Fe_3O_4 (Fe_3O_4 @PDA) superparticles using preassembled Fe_3O_4 nanoparticles (NPs) at its cores thus enhancing both the superparamagnetism and photothermal performance. They made nanodevices based on these Fe_3O_4 @PDA superparticles and showed enhanced magnetic resonance imaging (MRI)-guided photothermal efficiency. Also, various attempts have been made to improve the sensitivity of MRI scans. Particularly, several MR contrast agents have emerged to change the longitudinal (T1) or transverse (T2) relaxation times of surrounding water protons and increase the contrast of the target from the background. Also, the progress in developing new T1/T2 dual-mode contrast agents (DMCAs) is also at a swift speed. PDAs having good coordination capability can act as anchoring sites for iron ions. When Fe-chelated PDAs face organic bridging ligands benzene-1,3,5-tricarboxylic acid (H3btc), the biodegradable coordination polymer (CP) forms on the surface of PDAs. Herein, the Fe-chelated PDAs act as T1 contrast

agents while pure CP synthesized from Fe and H3btc acts as a T2 contrast agent. Thus, PDAs@CP3 showed combined properties and serves as a T1/T2 dual-mode contrast agent for MRI.^[204]

4.2.3. Photodynamic Therapy, Theranostics, and Related Biomedical Applications

Dong et al.^[206] prepared biodegradable as well as biocompatible hollow CaCO_3 -PDA NPs and incorporated them as a multifunctional molecular-loading platform for image-guided cancer photodynamic therapy. They utilized the DA-mediated biomimetalization method to develop CaCO_3 -PDA hollow nanoparticles. Further, these nanoparticles can be attached with different metal ions (e.g., Fe^{3+} , Zn^{2+} , Mn^{2+} , and Co^{2+}), thus these nanocomposites can be utilized with multimodal imaging functionality. Thus, after PEGylation, it can be used to utilize imaging of ions (e.g., Mn^{2+}) as well as therapeutic molecules (e.g., Ce6) upon simple mixing.

Zhu et al.^[207] synthesized a PDA-based tumor microenvironment (TME) responsive nanosystem, which utilizes the Fenton reaction (glucose degradation), and photothermal therapy (PTT) used in cancer therapy (Figure 15). Natural glucose oxidase (GOD) grafted on Fe(II)–PDA–GOD can catalyze a high amount of glucose in TME into gluconic acid and H_2O_2 . Thus, the concomitant generation of H_2O_2 will increase the efficiency of the sequential Fenton reaction and abundant hydroxyl radicals ($\bullet\text{OH}$) will be produced for cancer therapy. Hence, Fe(II)–PDA–GOD showed a favorable synergistic activity of glucose degradation, the Fenton reaction, and PTT against tumor growth.

Ge et al.^[208] synthesized theranostics nanodevices using Cu^{2+} -loaded PDA NPs (CuPDA NPs). When Cu^{2+} ions were loaded on PDA, the molar extinction coefficient of PDA NPs was

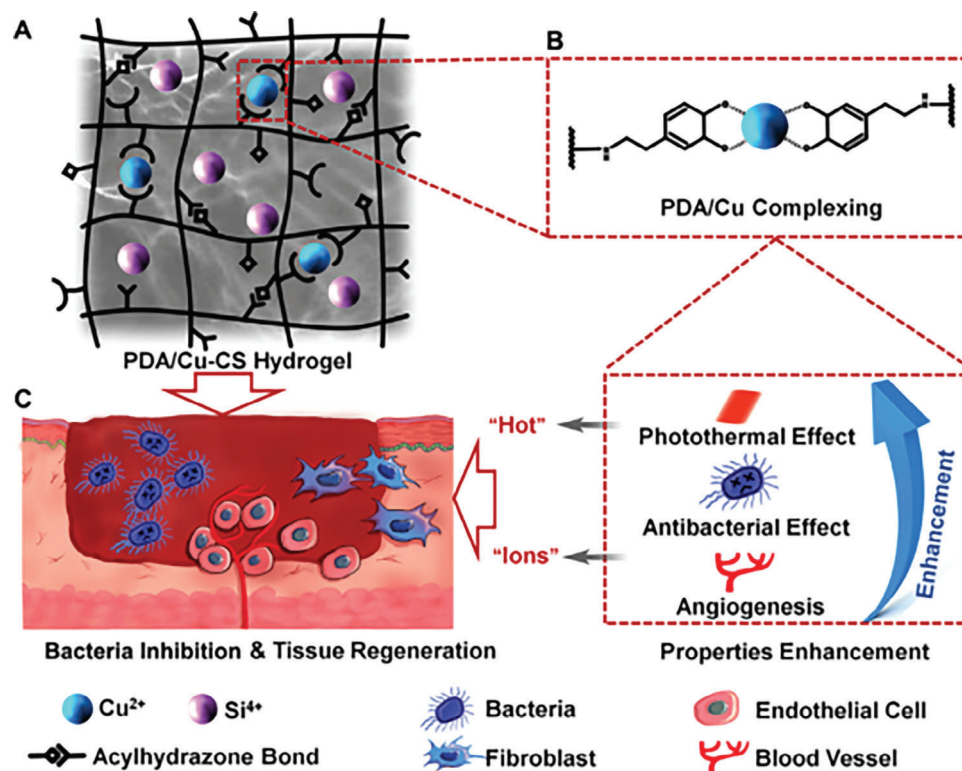


Figure 16. A) Structures of composite hydrogel networks. B) Complexation of PDA and Cu ions (PDA/Cu complexing). C) Composite hydrogel with "hot ions effect". Reproduced with permission.^[209] Copyright 2020, American Chemical Society.

enhanced by 4 times, thus increasing its efficiency toward PTT. These NPs were used in MRI-guided thermochemotherapy (TCT). Though Cu²⁺ ions being toxic, it gets a release in an acidic environment (pH ≈ 6.5–6.8), and during chemotherapy, it effectively avoids the systematic toxicity. Recently, a composite hydrogel consisting of PDA and Cu-doped calcium silicate ceramic (Cu-CS) (PDA/Cu-CS) was prepared by Xu et al.,^[209] which was shown to improve the photothermal performance and antibacterial activity. Due to the heating of Cu ions through the photothermal effect thanks to the "hot ions effect", the hydrogel exhibited better efficiency and long-term inhibition of methicillin-resistant *Staphylococcus aureus* and *Escherichia coli*. Further results showed disappeared infection in the wound area and promoted angiogenesis and collagen deposition during wound healing because of the "hot ions effect" of PDA/Cu-CS hydrogel (Figure 16A–C).

Dai et al.^[210] synthesized a three-layer core-shell-shell nanocomposite (NaYF₄:Nd³⁺@NaLuF₄@PDA). For photoluminescence emission and CT imaging, the NaLuF₄ layer was used, and an outer layer of PDA for photothermal therapy was optimized and showed that 20 nm of PDA shell showed enhanced photothermal efficiency. Thus, this core-shell-shell exhibited NIR-II/CT spatial- and temporal-specific tumor imaging, an outstanding photothermal conversion capability and biocompatibility. As it is a known fact that PDA is used as a universal coating material for many materials and biomolecules. Using it with biocompatible DNA can be used in various applications such as sensing, material fabrication and intracellular delivery. Zandieh et al. used different transition metals (Mn²⁺, Co²⁺, Zn²⁺ and Ni²⁺) to bridge between DNA and PDA and compared its

efficiency with Ca²⁺ for promoting DNA adsorption. DNA phosphate played an important role in adsorption for all these metals. These transition metals showed greater binding compared to Ca²⁺ and Ni²⁺ showed the tightest DNA adsorption. The ability of PDA to adsorb DNA decayed gradually upon ageing and Zn²⁺ or Ni²⁺ could considerably relieve the ageing effect and at low temperature has slowed down ageing.^[211] In 25%–30% of clinical MRI procedures, Magnevist (Gd–DTPA), a Gadolinium (Gd)–chelator complexes are used as MR contrast agents. However, there is always the risk of releasing Gd ions that are toxic, also it has low relaxivity. Keeping this in mind, Wang et al.^[212] used a radionuclide-Cu labelled doxorubicin-loaded PDA–gadolinium–metalofullerene core-satellite nano theranostics agent (denoted as CDPGM) for MR/photoacoustic (PA)/positron emission tomography (PET) multimodal imaging-guided combination cancer therapy. This system showed strong NIR absorption, the low release of Gd ions, high relaxivity (r1 = 14.06 mM⁻¹ s⁻¹) and good biocompatibility. In vivo, MR/PA/PET multimodal imaging was done which showed implicit tumor accumulation of the CDPGM NPs. The further tumor was eliminated when NIR laser therapy was used.

The human skeleton and teeth are made of hydroxyapatite (HAP) which can be utilized as a suitable carrier. Cao et al.^[213] synthesized hybrid microcapsules of hollow hydroxyapatite/polydopamine/gold nanorods (H-HAP/PDA/AuNRs) for multi-responsive drug delivery. PDA/AuNRs hybrid shell was used to prevent initial burst during drug release and showed enhanced photothermal conversion capacity, photothermal stability and excellent absorption in the NIR region. Further mesoporous

H-HAP along with PDA, Au NPs showed good loading capability which can be utilized as novel smart drug carriers for remotely controllable drug delivery.

4.2.4. Antibacterial Properties

Silver (Ag) NPs exhibit great characteristics in terms of antibacterial property by destroying bacteria cell walls. These Ag NPs agglomerates which eclipse their inherent antimicrobial property. These should be stabilized with polymers and surfactants, thus complicating the process. Templates of polystyrene-PDA nanospheres were used to synthesize Ag NPs using the electrodeless metallization process. Besides acting as templates for growth of these particles, PDA gives way for the development of antibacterial and antifouling coating strategies.^[214]

To prevent Ag leaching and to enhance the antibacterial property of Ag, Jatoi et al.^[215] used TiO_2 @PDA-Ag in nanofibers made of cellulose acetate thus enhancing the antibacterial property also. It was seen that this CA/ TiO_2 /Ag nanofiber inhibits the bacterial growth till 72 h. The antibacterial property of Ag was further studied with different structure such as nanosilver embedded in SiO_2 @PDA nanoparticles, rodlike Silica containing Ag-incorporated PDA.^[216] On the same line, Chen et al.^[217] prepared lysozyme-imprinted Fe_3O_4 @ SiO_2 @PDA NPs. Due to photothermal activity PDA, it can release the lysozyme when activated by NIR. These lysozymes due to their antimicrobial properties destroy the *E. Coli* cell walls. Meeker et al.^[218] used Au nanoparticle coated with PDA and loaded it with antibiotic thus achieved the photoactivable nanodrugs to target methicillin-resistant *S. aureus*. Au@Ag nanorods were used by Black et al. to destroy bacteria cells walls. PDA on the Au NRs surface triggered the localize Ag releasing when irradiated and due to plasmonic heating cells walls get ruptured.^[219]

The inorganic and organic materials used separately often have a lack of characteristics for specific functions. So, the researchers have adopted hybrid materials that comprise the properties of both inorganic and organic compounds. An International Union of Pure and Applied Chemistry (IUPAC) defined hybrid materials as “A hybrid material is composed of an intimate mixture of inorganic components, organic components, or both types of components. Note: The components usually interpenetrate on a scale of less than $1\ \mu\text{m}$ ”.^[220] The present section will cover the PDA modified surface chemistry of hybrid nanomaterials and their applications in various fields.

4.2.5. Bioelectronics and Related Bio Applications

The PDA has also been used in hydrogels formulation for bioelectronics applications. The researchers have harvested the PDA functionalized, demonstrated self-adhesive glycerol-hydrogel (G-hydrogel)^[234] and hybrid patches^[235] for antifreeze and skin wound healing applications, respectively. In another study, Han et al.^[236] have reported conductive hydrogels via in situ PDA formation in doped polypyrrole (PPy) nanofibrils interwoven in a polyacrylamide (PAM) network. The PDA exhibited a high affinity for monomers (hydrophilic) and PPy (hydrophobic) and formed hydrophilic and conductive PDA-PPy NPs. The re-

sulting hydrogel exhibited high conductivity ($12\ \text{S m}^{-1}$), transmittance (70%), UV-shielding ability, flexibility, and stretchability ($>2000\%$). More importantly, the self-adhesiveness property helped adhere to the human body and detect biosignals. Thus, in situ PDA polymerization is extensively utilized in hybrid materials for various applications, including membranes, electrochromatography, electrochemical, biosensing, bioelectronics, etc.

4.3. Environment and Other Important Applications

4.3.1. Antifouling, Filtration and Dye Separation Properties

Li et al. generated in situ PDA microspheres via cluster phenolic hydroxyl effect on PVDF membranes for achieving super-hydrophilicity, antifouling, and hemocompatibility membranes.^[221] They suggested that “The effect enhancement over and beyond what would be expected from the presence of amounts of hydroxyl groups on a large number of PDA microspheres surface.” The presence of PDA microspheres throughout the membrane (top, bottom, a cross-section along with pore walls) leads to the formation of phenolic hydroxyl groups, as seen in **Figure 17**, and causes improved hydrophilicity. The contact angle was tailored from 103.1 and 105.3° to 9.7 and 13.5° for the upper and lower surfaces, respectively suggesting that PDA strongly impacted the membrane properties.

Also, **Figure 17-iB** shows the driving force during filtration. Here, the forces F_1 and F_2 are the adhesive and repulsive forces between solid walls and water flow, while F_3 surface tension of the liquid water flows making an angle θ with the gravity force G . The resultant force from F_1 and F_3 causes a net flow with the increased velocity in the downward direction (F_2 is neglected because the PDA solid microspheres have high hydrophilicity).^[222,223] Thus, the pristine PVDF membrane exhibited the lowest permeate flux ($8.4\ \text{L m}^{-2}\ \text{h}^{-1}$) and increased with the PDA addition to $8.4\ \text{L m}^{-2}\ \text{h}^{-1}$. Further, these PDA/PVDF films also have applications in biomedical fields. Their non-hemolytic nature and resistance to the non-specific adsorption of proteins proved them to be an ideal biomaterial.

Tu and co-workers^[224] have constructed PDA modified UiO-66 NPs/GO hybrid membranes for dye separation, enhanced water permeability, and antifouling property. They harvested the PDA potential to partially reduce the GO and stabilize the composites. The reason for improved properties is that both GO and PDA have enormous polar hydroxyl and carboxyl groups that form a hydrogen bond with water molecules and promote their penetration. The dye removal is ascribed to the adsorption, electrostatic interaction, and physical sieving during the penetration. The more hydrophilicity of PDA/RGO/UiO-66 leads to a highly pure water flux of $167.14\ \text{L}/(\text{m}^2\cdot\text{h})$, 256.91% higher than that of the PDA/RGO along with a high dye separation performance of 99.54% and 87.36% for MB and CR, respectively. The higher values for MB are attributed to the negatively charged membrane causing the Donnan effect.

Recently, Fu and co-workers^[225] have explored PDA's role as a stationary phase in the open-tubular capillary electrochromatography (OT-CEC). The CEC utilizes highly efficient capillary electrophoresis (CE) and highly selective high-performance liquid chromatography (HPLC).^[164,226] **Figure 18i**

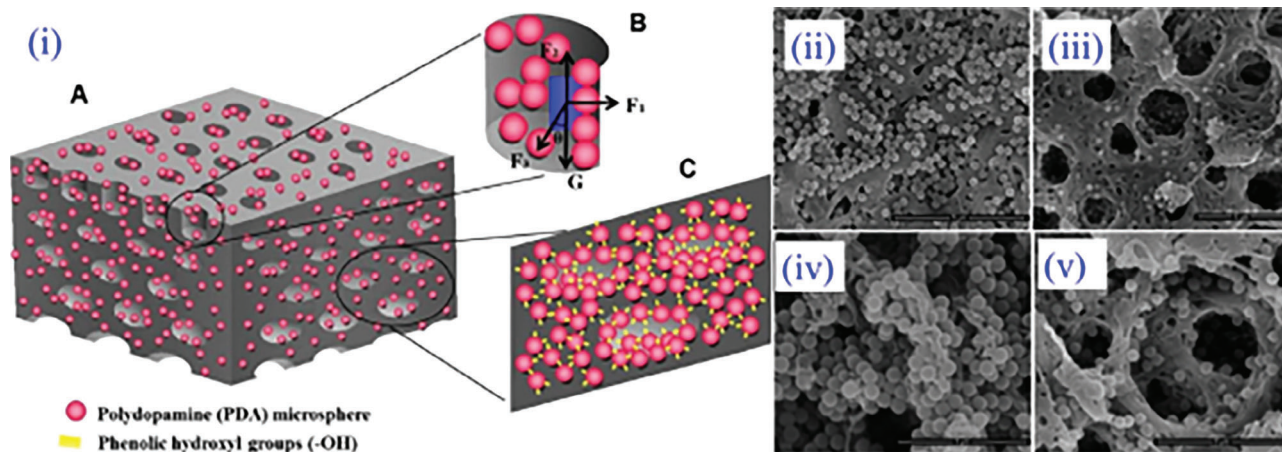


Figure 17. i) Scheme of the distributions of PDA microspheres on the surface and cross-section of the membrane A) and the partial enlarged image C), and the schematic diagram of driving forces on the cross-section of the membrane during the self-driven filtration B). ii) Morphologies and structures of enlarged SEM images of the upper surface, iii) lower surface, iv) cross-section, and v) membrane pore structure of the lower surface. Reproduced with permission.^[221] Copyright 2018, Elsevier.

shows PDA/octadecylamine (ODA) co-deposition steps of capillary columns using Michael addition reaction and in situ one-pot synthesis. ODA simultaneously triggers the DA polymerization and covalently immobilized via organic amine onto PDA coated substrate. This property of ODA makes the self-polymerization and in-situ hybrid coating of ODA-DA feasible on the capillary inner wall. It has been found that the contact angle significantly increased with increasing the number of layers and follows the order as quartz plate ($32.3 \pm 0.2^\circ$) < PDA coated ($60.1 \pm 0.2^\circ$) < PDA/ODA coated ($139.3 \pm 0.5^\circ$) < three-layer coated ($152.2 \pm 0.7^\circ$). The increase in contact angle is attributed to the hydrophilic silanol groups' masking and long chains of hydrophobic ODA attached to DA. The columns exhibited good separation efficiencies with alkylbenzenes and steroids and followed the reversed-phase chromatographic retention mechanism. However, the work's drawback is the multiple preparation steps and time-consuming coating process and thereby reduces the practicality of the process.

The same group^[227] developed an effective approach using a one-step in situ solvothermal-assisted rapid coating strategy. The high temperature and pressure of the solvothermal process speed up the PDA/ODA polymerization and coating processes (Figure 18ii). Here, the water contact angles also vary in a similar manner with different time intervals up to 60 min and decreased after 90 min of co-deposition: ($31.6 \pm 0.2^\circ$) < 30 min ($103.8 \pm 0.3^\circ$) < 60 min ($143.9 \pm 0.4^\circ$) < 90 min ($121.9 \pm 0.8^\circ$). The decreased value after 90 min was ascribed to the fact that the carbonized PDA partially detached and lead to deteriorated stability at longer times of coating. So, the PDA finds application in chromatographic separation techniques.

4.3.2. Adhesive Agents and Flame Retardant Properties

DA and its derivatives have been applied as interfacial adhesive agents. Despite some fascinating mechanical properties, chemical/thermal stability and applicative potential in various fields,

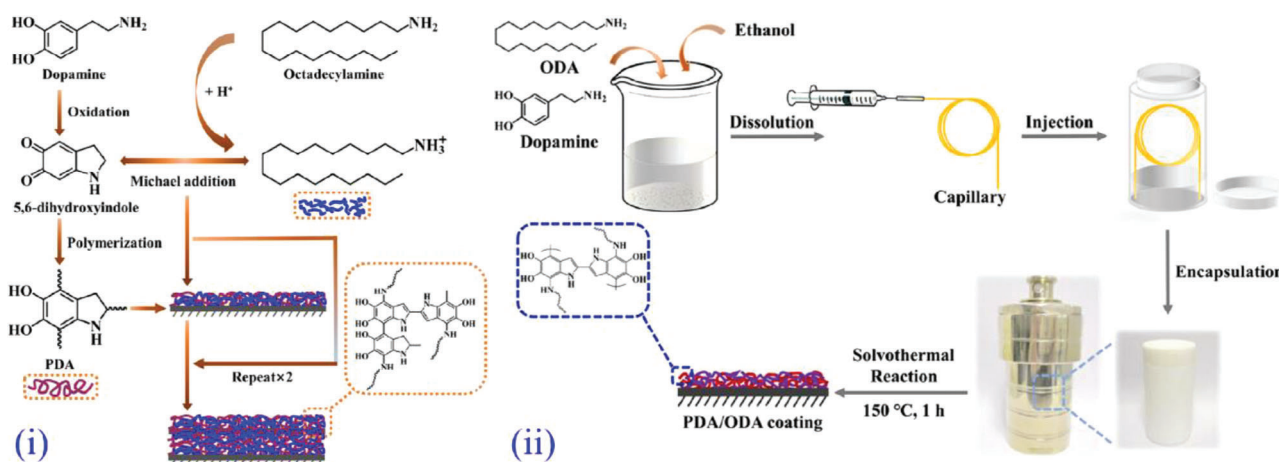


Figure 18. Schematic of the preparation of PDA/ODA i) co-deposited. Reproduced with permission.^[225] Copyright 2020, Elsevier. ii) Solvothermal-assisted hybrid coating columns. Reproduced with permission.^[227] Copyright 2020, Elsevier.

Table 1. Different classes of materials and their implications with PDA for the most promising applications.

| Class of Materials | Nanomaterials with PDA | Applications |
|--------------------|--|---|
| Metal/Metal oxide | Fe ₃ O ₄ @PDA | Photothermal therapy |
| | Fe ₃ O ₄ @Au@PDA | Analysis of Cu ²⁺ |
| | CaCO ₃ -PDA | Imaging |
| | Fe(II)-PDA-GOD | Chemical treatment |
| | (Cu-CS) (PDA/Cu-CS) | Photothermal, antimicrobial |
| | TiO ₂ @PDA-Ag | Antimicrobial |
| | Lysozyme-imprinted Fe ₃ O ₄ @SiO ₂ @PDA | Photothermal therapy |
| | Au@PDA | Photothermal, antimicrobial |
| Hybrid Materials | PDA modified UiO-66 NPs/GO hybrid membranes | Dye separation, enhanced water permeability, and antifouling property |
| | PDA/octadecylamine (ODA) | Capillary electrophoresis (CE) and highly selective high-performance liquid chromatography (HPLC) |
| | PDA functionalized graphene (PDG) electrodes | Na- and Li-ion batteries |
| | PDA on the cellulose textile substrate | Binder |
| | conductive bacterial cellulose (BC)/PDA biocomposite | Electrophysiological signal detection |
| | PDA in doped polypyrrole (PPy) nanofibrils | UV-shielding |
| Polymer | PDA coating on carbon fibre fabrics | Improved mechanical strength |
| Ceramics | PVDF: LLTO@PDA | Improving anode flexibility in batteries |
| | perovskite-structured Li _{0.33} La _{0.557} TiO ₃ (LLTO) | |
| | PDA@BTNF | Improving ferroelectric properties |
| | BaTiO ₃ nanofiber (BTNF) | |
| | PVDF filled with PDA encapsulated BaTiO ₃ | High energy density and low-loss dielectric capacitor |
| | PDA functionalized BaTiO ₃ nanofibers with PVDF matrix | High energy-storage density |
| | Meta-aramid (MPIA) fibers with PDA films | Adhesive property |

the applicability of traditionally used aramid fibers has been greatly restricted due to its smooth and chemically inert surface allowing a very poor adhesion.^[152,153] Addressing this issue, numerous strategies were developed to enhance the interfacial adhesion such as chemical etching, grafting,^[154–157] plasma treatment,^[158] ultrasonic treatment,^[159] γ -ray irradiation^[160] and ultraviolet radiation,^[161] which primarily focuses on attaching active functional groups like amino, hydroxyl and carbonyl through reduction or nitration or chlorosulfonation. However, these techniques are often costly, tedious, time-consuming, dangerous and require sophisticated instrument approaches. Therefore, to mimic the mussel's adhesion, DA has been applied as an adhesive agent to modify the surfaces of various materials. For an instance, Sa et al.^[162] developed a novel biomimetic surface modification method of meta-aramid (MPIA) fibers with PDA films and observed improved adhesion. In this process, they simply immersed MPIA fibers in a DA solution under ambient conditions, followed by an epoxy functionalized silane (KH560) grafting, to introduce an epoxy group, on the PDA coated MPIA surface. This can be processed either through a "one-step" or "two-step" method (Figure 19A). The adhesion strength of MPIA fibers with the rubber matrix was examined through a single-fiber pull-out test, which suggests 62.5% increase in adhesion strength of silane treated PDA coated fibers compared with the untreated one. The possible self-polymerization of DA can be expressed as shown in Figure 19B, where catechol oxidized into benzoquinone

as per the standard reaction of melanin formation. This allows the formation of covalent bonds on the matrix leading to PDA deposition. Similarly, some other attempts have been made to improve the adhesion properties of various functional surfaces through PDA deposition chemistry.^[163–169]

The development of non-toxic and highly efficient flame retardants for polymer composites is one of the challenging fields so that fire-related accidents can be retarded. The char formation and free-radical scavenging actions of PDA coatings decrease the heat release rate. The Fe(III)-chelated PDA coatings with high free-radical scavenging and catalytic carbonization abilities act as an efficient flame retardant in gaseous as well as condensed phase. Zhang et al. prepared iron-loaded PDA (Fe-PDA) nanospheres through a one-pot reaction and employed them as flame retardant for epoxy resin (EP). They found that the free radical scavenging action contributes to flame extinguishment in the gas phase.^[205] Table 1 shows a summary of applications where PDA has been used with different families of materials which have been discussed in detail in the above sections.

5. Conclusions and Perspectives

The above discussion highlights the potential applicability of PDA in the surface modification of various materials not just to create abundant functionality but reactivity also. This enhances

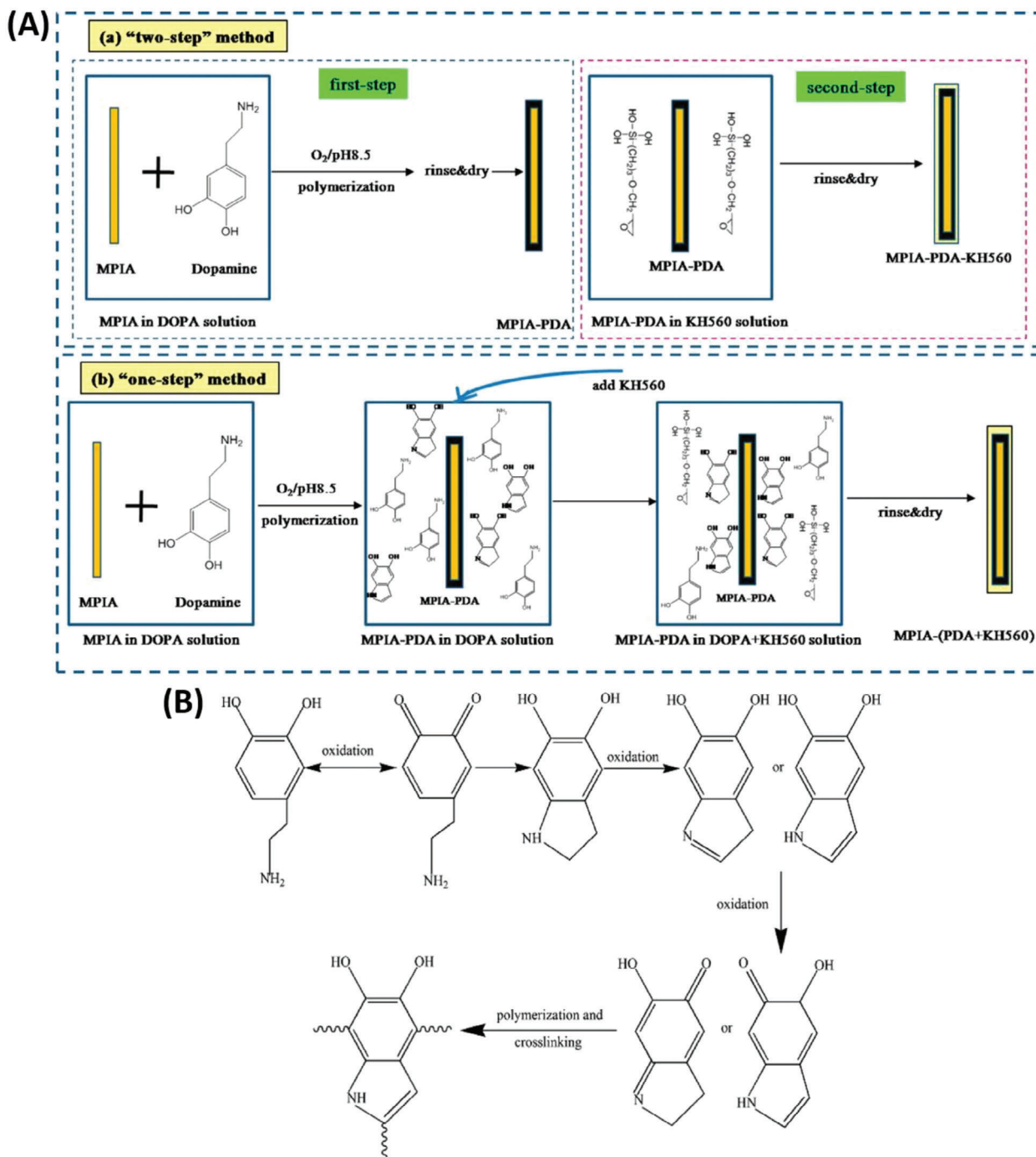
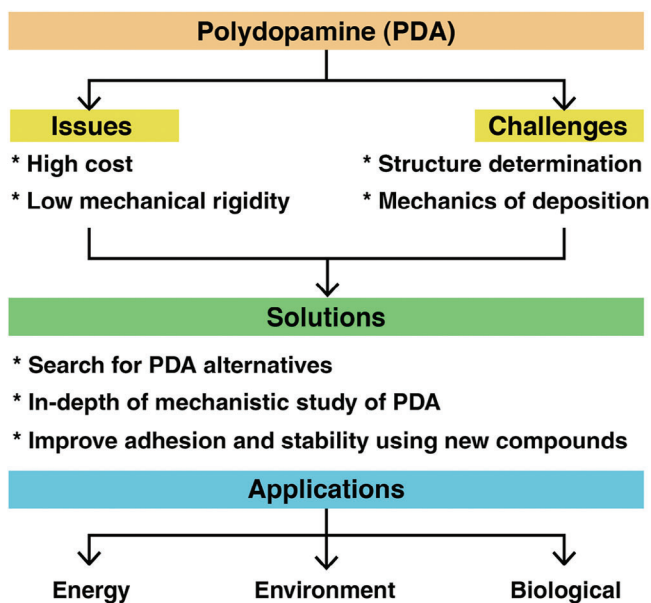


Figure 19. A) Illustration of procedures for preparing a) MPIA-PDA-KH560 fibers and b) MPIA-(PDA+KH560) fibers. B) Possible polymerization mechanism of DA. Reproduced with permission.^[162] Copyright 2020, American Chemical Society.

the applicability of modified surfaces, making them suitable for a wide range of practical applications such as electrochemical energy storage, conversion, conversion, photothermal therapy, bioengineering, adhesives, separation, purification, sensors, environment protection.^[237–247] Moreover, the DA polymerization technique of PDA deposition is quite straightforward, cost-effective, has a material-independent coating ability and does not require high-maintenance sophisticated instruments, unlike

many other thin film deposition techniques.^[237] A good adhesion can also be observed between the substrate and thin film in the DA assisted modification technique. The thickness of PDA coating and subsequently its properties can be adjusted easily by varying deposition parameters including DA concentration, pH, solvent, coating time and introducing metal ions. Despite these advantages, the high cost of DA may be a possible restriction for its wide practical utility on a larger scale. Furthermore, the



Scheme 2. Issues, challenges, and possible solutions of PDA induced modification of surfaces to make them useful in different applications.

determination of the chemical structure of PDA, mechanistic aspects of the deposition process, improving mechanical rigidity and extension of this process to chemically diverse species in plants have been some of the challenging issues (Scheme 2). Therefore, a paradigm shift has been observed recently in incorporating facile, cost-effective, green, and environmentally friendly methods to develop mussel-inspired functional materials. In this respect, nitrogen-free catechol, gallic acid and polyphenols compounds such as tannic acid, epigallocatechin gallate, epigallocatechin gallate and epigallocatechin gallate can be alternative coating materials and suitable substitutes of DA. However, the surface specificity, stability and versatility of such coating materials should be thoroughly investigated. Another important outlook is to develop effective strategies of DA polymerization on the materials' surface only to avoid the waste as a large amount of DA self-polymerizes in the solution only.^[62] It is anticipated that with advancements in this area, some fascinating candidates consisting of properties like PDA will emerge, which will find multifunctional applicability in a diverse range of applications including energy, environment, biomedical, sensor and agricultural sectors.

Acknowledgements

R.K.G. acknowledges financial assistance from Department of Science and Technology (DST), India, through the INSPIRE Faculty Award (Project No. IFA-13 ENG-57) and Grant No: DST/TM/WTI/2K16/23(G); DST and Indo-U.S. Science & Technology Forum (IUSSTF), India for funding Indo-U.S. Virtual Networked Joint Center (Project No. IUSSTF/JC-025/2016). B.B. acknowledges the SEED grant provided by Indian Institute of Technology (BHU) Varanasi.

Conflict of Interest

The authors declare no conflict of interest

Keywords

biomimetics, dopamine, polydopamine, polymerization, surface modifications

Received: August 11, 2023

Revised: October 15, 2023

Published online:

- [1] B. Bhushan, *Philos. Trans. Royal Soc. A* **2009**, 367, 1445.
- [2] R. R. Naik, S. Singamaneni, *Chem. Rev.* **2017**, 117, 12581.
- [3] D. A. Lavan, J. N. Cha, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, 103, 5251.
- [4] K. Kalyanasundaram, M. Graetzel, *Curr. Opin. Biotechnol.* **2010**, 21, 298.
- [5] A. A. Boghossian, M.-H. Ham, J. H. Choi, M. S. Strano, *Energy Environ. Sci.* **2011**, 4, 3834.
- [6] A. Pieper, M. Hohgardt, M. Willich, D. A. Gacek, N. Hafi, D. Pfennig, A. Albrecht, P. J. Walla, *Nat. Commun.* **2018**, 9, 666.
- [7] Z. Gao, Q. Shi, T. Fukuda, C. Li, Q. Huang, *Neurocomputing* **2019**, 332, 339.
- [8] M. Corva, F. Mohamed, E. Tomsic, M. Rinaldi, C. Cepek, N. Seriani, M. Peressi, E. Vesselli, *J. Phys. Chem. C* **2019**, 123, 3916.
- [9] G. Wen, Z. Guo, W. Liu, *Nanoscale* **2017**, 9, 3338.
- [10] J. Lin, Y. Cai, X. Wang, B. Ding, J. Yu, M. Wang, *Nanoscale* **2011**, 3, 1258.
- [11] D. Wan, Q. Jiang, Y. Song, J. Pan, T. Qi, G. L. Li, *ACS Appl. Polym. Mater.* **2020**, 2, 879.
- [12] A. Pizzi, C. Pigliacelli, G. Bergamaschi, A. Gori, P. Metrangolo, *Coord. Chem. Rev.* **2020**, 411, 213242.
- [13] P. C. Knipe, S. Thompson, A. D. Hamilton, in *Macrocyclic and Supramolecular Chemistry*, (Eds.: R. M. Izatt), John Wiley & Sons, **2016**, p. 146.
- [14] C. Yu, S. Sasic, K. Liu, S. Salameh, R. H. A. Ras, J. R. Van Ommen, *Chem. Eng. Res. Des.* **2020**, 155, 48.
- [15] P. Gould, *Mater. Today* **2003**, 6, 44.
- [16] H. J. Meredith, C. L. Jenkins, J. J. Wilker, *Adv. Funct. Mater.* **2014**, 24, 3259.
- [17] M. G. Mazzotta, A. A. Putnam, M. A. North, J. J. Wilker, *J. Am. Chem. Soc.* **2020**, 142, 4762.
- [18] B. Bhuvaneshwari, G. Palani, N. R. Iyer, *J. Struct. Eng.* **2011**, 38, 1.
- [19] V. R. Kumar, B. Bhuvaneshwari, S. Maheswaran, G. Palani, K. Ravisankar, N. R. Iyer, *Curr. Sci.* **2011**, 101, 741.
- [20] S. Maheswaran, S. Dasuru, A. R. C. Murthy, B. Bhuvaneshwari, V. R. Kumar, G. Palani, N. R. Iyer, S. Krishnamoorthy, S. Sandhya, *Curr. Sci.* **2014**, 106, 50.
- [21] H. Zhu, Z. Guo, W. Liu, *Chem. Commun.* **2016**, 52, 3863.
- [22] S.-M. Chen, H.-L. Gao, Y.-B. Zhu, H.-B. Yao, L.-B. Mao, Q.-Y. Song, J. Xia, Z. Pan, Z. He, H.-A. Wu, S.-H. Yu, *Natl. Sci. Rev.* **2018**, 5, 703.
- [23] A. Heidebrecht, L. Eisoldt, J. Diehl, A. Schmidt, M. Geffers, G. Lang, T. Scheibel, *Adv. Mater.* **2015**, 27, 2189.
- [24] J. Sun, X. Wang, J. Wu, C. Jiang, J. Shen, M. A. Cooper, X. Zheng, Y. Liu, Z. Yang, D. Wu, *Sci. Rep.* **2018**, 8, 5438.
- [25] Y. Li, J. Zhang, B. Yang, *Nano Today* **2010**, 5, 117.
- [26] L. Eadie, T. K. Ghosh, *J. R. Soc. Interface* **2011**, 8, 761.
- [27] J. Wood, *Biomimetics* **2019**, 4, 16.
- [28] P. Mohammadi, A. S. Aranko, C. P. Landowski, O. Ikkala, K. Jaudzems, W. Wagermaier, M. B. Linder, *Sci. Adv.* **2019**, 5, eaaw2541.
- [29] Y. Lee, J.-H. Ahn, *ACS Nano* **2020**, 14, 1220.
- [30] P. Dorishetty, R. Balu, S. S. Athukoralalage, T. L. Greaves, J. Mata, L. De Campo, N. Saha, A. C. W. Zannettino, N. K. Dutta, N. R. Choudhury, *ACS Sustainable Chem. Eng.* **2020**, 8, 2375.

- [31] N. J. Kanu, E. Gupta, U. K. Vates, G. K. Singh, *RSC Adv.* **2019**, *9*, 38209.
- [32] H. Ko, A. Javey, *Acc. Chem. Res.* **2017**, *50*, 691.
- [33] M. Saraf, R. Rajak, S. M. Mobin, *J. Mater. Chem. A* **2016**, *4*, 16432.
- [34] M. Saraf, K. Natarajan, S. M. Mobin, *ACS Appl. Mater. Interfaces* **2018**, *10*, 16588.
- [35] Prateek, V. K. Thakur, R. K. Gupta, *Chem. Rev.* **2016**, *116*, 4260.
- [36] M. Saraf, K. Natarajan, S. M. Mobin, *ACS Sustainable Chem. Eng.* **2018**, *6*, 10489.
- [37] M. Saraf, K. Natarajan, S. M. Mobin, *RSC Adv.* **2017**, *7*, 309.
- [38] M. Saraf, M. Tavakkoli Yaraki, Y. N. T. Prateek, R. K. Gupta, *ACS Appl. Nano Mater.* **2021**, *4*, 911.
- [39] B. Balasubramaniam, Prateek, S. Ranjan, M. Saraf, P. Kar, S. P. Singh, V. K. Thakur, A. Singh, R. K. Gupta, *ACS Pharmacol. Transl. Sci.* **2021**, *4*, 8.
- [40] M. Saraf, R. Rajak, S. M. Mobin, *ChemistrySelect* **2019**, *4*, 8142.
- [41] J. R. Conrad, J. L. Radtke, R. A. Dodd, F. J. Worzala, N. C. Tran, *J. Appl. Phys.* **1987**, *62*, 4591.
- [42] H. Chouirfa, H. Bouloussa, V. Migonney, C. Falentin-Daudré, *Acta Biomater.* **2019**, *83*, 37.
- [43] W. Cheng, X. Zeng, H. Chen, Z. Li, W. Zeng, L. Mei, Y. Zhao, *ACS Nano* **2019**, *13*, 8537.
- [44] Z. Wang, H.-C. Yang, F. He, S. Peng, Y. Li, L. Shao, S. B. Darling, *Matter* **2019**, *1*, 115.
- [45] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.
- [46] B. Yameen, M. Ali, M. Álvarez, R. Neumann, W. Ensinger, W. Knoll, O. Azzaroni, *Polym. Chem.* **2010**, *1*, 183.
- [47] S. R. Whaley, D. S. English, E. L. Hu, P. F. Barbara, A. M. Belcher, *Nature* **2000**, *405*, 665.
- [48] M. A. Hubbe, O. J. Rojas, L. A. Lucia, *BioResources* **2015**, *10*, 112.
- [49] P. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, *39*, 301.
- [50] S. Kalia, K. Thakur, A. Celli, M. A. Kiechel, C. L. Schauer, *J. Environ. Chem. Eng.* **2013**, *1*, 97.
- [51] K. J. Coyne, X.-X. Qin, J. H. Waite, *Science* **1997**, *277*, 1830.
- [52] J. H. Waite, M. L. Tanzer, *Science* **1981**, *212*, 1038.
- [53] N. Holten-Andersen, J. H. Waite, *J. Dent. Res.* **2008**, *87*, 701.
- [54] A. Mayeen, M. S. Kala, S. Sunija, D. Rouxel, R. N. Bhowmik, S. Thomas, N. Kalarikkal, *J. Alloys Compd.* **2020**, *837*, 155492.
- [55] A. Jin, Y. Wang, K. Lin, L. Jiang, *Bioact. Mater.* **2020**, *5*, 522.
- [56] D. R. Dreyer, D. J. Miller, B. D. Freeman, D. R. Paul, C. W. Bielawski, *Chem. Sci.* **2013**, *4*, 3796.
- [57] M. Liu, G. Zeng, K. Wang, Q. Wan, L. Tao, X. Zhang, Y. Wei, *Nanoscale* **2016**, *8*, 16819.
- [58] R. Batul, T. Tamanna, A. Khaliq, A. Yu, *Biomater. Sci.* **2017**, *5*, 1204.
- [59] Z. Li, Y. Yang, H. Wei, X. Shan, X. Wang, M. Ou, Q. Liu, N. Gao, H. Chen, L. Mei, X. Zeng, *J. Controlled Release* **2021**, *338*, 719.
- [60] X. Zeng, M. Luo, G. Liu, X. Wang, W. Tao, Y. Lin, X. Ji, L. Nie, L. Mei, *Adv. Sci.* **2018**, *5*, 1800510.
- [61] F. Zhang, G. Lu, X. Wen, F. Li, X. Ji, Q. Li, M. Wu, Q. Cheng, Y. Yu, J. Tang, L. Mei, *J. Controlled Release* **2020**, *326*, 131.
- [62] Q. Huang, J. Chen, M. Liu, H. Huang, X. Zhang, Y. Wei, *Chem. Eng. J.* **2020**, *387*, 124019.
- [63] V. K. Thakur, M.-F. Lin, E. J. Tan, P. S. Lee, *J. Mater. Chem.* **2012**, *22*, 5951.
- [64] V. K. Thakur, D. Vennerberg, M. R. Kessler, *ACS Appl. Mater. Interfaces* **2014**, *6*, 9349.
- [65] S. L. Phua, L. Yang, C. L. Toh, S. Huang, Z. Tsakadze, S. K. Lau, Y.-W. Mai, X. Lu, *ACS Appl. Mater. Interfaces* **2012**, *4*, 4571.
- [66] L. Yang, S. L. Phua, J. K. H. Teo, C. L. Toh, S. K. Lau, J. Ma, X. Lu, *ACS Appl. Mater. Interfaces* **2011**, *3*, 3026.
- [67] S. i. L. Phua, L. Yang, C. L. Toh, D. Guoqiang, S. K. Lau, A. Dasari, X. Lu, *ACS Appl. Mater. Interfaces* **2013**, *5*, 1302.
- [68] H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007**, *318*, 426.
- [69] V. K. Thakur, J. Yan, M.-F. Lin, C. Zhi, D. Golberg, Y. Bando, R. Sim, P. S. Lee, *Polym. Chem.* **2012**, *3*, 962.
- [70] V. K. Thakur, D. Vennerberg, S. A. Madbouly, M. R. Kessler, *RSC Adv.* **2014**, *4*, 6677.
- [71] J. H. Waite, X. Qin, *Biochemistry* **2001**, *40*, 2887.
- [72] S. M. Kang, J. Rho, I. S. Choi, P. B. Messersmith, H. Lee, *J. Am. Chem. Soc.* **2009**, *131*, 13224.
- [73] B. Luo, X. Wang, Y. Wang, L. Li, *J. Mater. Chem. A* **2014**, *2*, 510.
- [74] Y. Song, Y. Shen, H. Liu, Y. Lin, M. Li, C.-W. Nan, *J. Mater. Chem.* **2012**, *22*, 8063.
- [75] L. Jiang, A. Betts, D. Kennedy, S. Jerrams, *Mater. Des.* **2015**, *85*, 733.
- [76] Z. Wang, T. Wang, C. Wang, Y. Xiao, Y. Pu, *Mater. Lett.* **2017**, *198*, 152.
- [77] Q. Chi, T. Ma, Y. Zhang, Y. Cui, C. Zhang, J. Lin, X. Wang, Q. Lei, *J. Mater. Chem. A* **2017**, *5*, 16757.
- [78] V. Ball, D. D. Frari, V. Toniazzo, D. Ruch, *J. Colloid Interface Sci.* **2012**, *386*, 366.
- [79] X. Liu, J. Cao, H. Li, J. Li, Q. Jin, K. Ren, J. Ji, *ACS Nano* **2013**, *7*, 9384.
- [80] F. Bernsmann, V. Ball, F. Addiego, A. Ponche, M. Michel, J. J. D. A. Gracio, V. Toniazzo, D. Ruch, *Langmuir* **2011**, *27*, 2819.
- [81] N. F. Della Vecchia, A. Luchini, A. Napolitano, G. D'errico, G. Vitiello, N. Szekely, M. D'ischia, L. Paduano, *Langmuir* **2014**, *30*, 9811.
- [82] M.-H. Ryou, Y. M. Lee, J.-K. Park, J. W. Choi, *Adv. Mater.* **2011**, *23*, 3066.
- [83] W. Zheng, H. Fan, L. Wang, Z. Jin, *Langmuir* **2015**, *31*, 11671.
- [84] P. Zhou, Y. Deng, B. Lyu, R. Zhang, H. Zhang, H. Ma, Y. Lyu, S. Wei, *PLoS One* **2014**, *9*, 113087.
- [85] F. Ponzio, J. Barthès, J. Bour, M. Michel, P. Bertani, J. Hemmerlé, M. D'ischia, V. Ball, *Chem. Mater.* **2016**, *28*, 4697.
- [86] H. Lee, Y. Lee, A. R. Stutz, J. Rho, T. G. Park, P. B. Messersmith, *Adv. Mater.* **2008**, *20*, 1619.
- [87] F. Bernsmann, L. Richert, B. Senger, P. Lavalle, J.-C. Voegel, P. Schaaf, V. Ball, *Soft Matter* **2008**, *4*, 1621.
- [88] Y. Lee, H. Lee, Y. B. Kim, J. Kim, T. Hyeon, H. Park, P. B. Messersmith, T. G. Park, *Adv. Mater.* **2008**, *20*, 4154.
- [89] F. Bernsmann, A. Ponche, C. Ringwald, J. Hemmerlé, J. Raya, B. Bechinger, J.-C. Voegel, P. Schaaf, V. Ball, *J. Phys. Chem. C* **2009**, *113*, 8234.
- [90] J. Ryu, S. H. Ku, H. Lee, C. B. Park, *Adv. Funct. Mater.* **2010**, *20*, 2132.
- [91] B. Yu, D. A. Wang, Q. Ye, F. Zhou, W. Liu, *Chem. Commun.* **2009**, 6789, <https://pubs.rsc.org/en/content/articlelanding/2009/CC/b910679k>.
- [92] T. A. Morris, A. W. Peterson, M. J. Tarlov, *Anal. Chem.* **2009**, *81*, 5413.
- [93] Q. Wei, F. Zhang, J. Li, B. Li, C. Zhao, *Polym. Chem.* **2010**, *1*, 1430.
- [94] I. L. Medintz, M. H. Stewart, S. A. Trammell, K. Susumu, J. B. Delehanty, B. C. Mei, J. S. Melinger, J. B. Blanco-Canosa, P. E. Dawson, H. Mattoussi, *Nat. Mater.* **2010**, *9*, 676.
- [95] R. Mrówczyński, *ACS Appl. Mater. Interfaces* **2018**, *10*, 7541.
- [96] J. Park, T. F. Brust, H. J. Lee, S. C. Lee, V. J. Watts, Y. Yeo, *ACS Nano* **2014**, *8*, 3347.
- [97] W. Qiang, W. Li, X. Li, X. Chen, D. Xu, *Chem. Sci.* **2014**, *5*, 3018.
- [98] Y. Liu, K. Ai, J. Liu, M. Deng, Y. He, L. Lu, *Adv. Mater.* **2013**, *25*, 1353.
- [99] V. Shanmugam, S. Selvakumar, C.-S. Yeh, *Chem. Soc. Rev.* **2014**, *43*, 6254.
- [100] Z. Wang, C. Xu, Y. Lu, G. Wei, G. Ye, T. Sun, J. Chen, *Polym. Chem.* **2017**, *8*, 4388.
- [101] C. Zhang, Y. Ou, W.-X. Lei, L.-S. Wan, J. Ji, Z.-K. Xu, *Angew. Chem., Int. Ed.* **2016**, *55*, 3054.
- [102] J.-L. Wang, B.-C. Li, Z.-J. Li, K.-F. Ren, L.-J. Jin, S.-M. Zhang, H. Chang, Y.-X. Sun, J. Ji, *Biomaterials* **2014**, *35*, 7679.
- [103] J. Cai, J. Huang, M. Ge, J. Iocozzia, Z. Lin, K.-Q. Zhang, Y. Lai, *Small* **2017**, *13*, 1604240.

- [104] N. Li, H.-B. Wang, L. Thia, J.-Y. Wang, X. Wang, *Analyst* **2015**, *140*, 449.
- [105] D. Fan, C. Wu, K. Wang, X. Gu, Y. Liu, E. Wang, *Chem. Commun.* **2016**, *52*, 406.
- [106] S. Gidanian, P. J. Farmer, *J. Inorg. Biochem.* **2002**, *89*, 54.
- [107] T. Luczak, *Electrochim. Acta* **2008**, *53*, 5725.
- [108] S. Hong, Y. S. Na, S. Choi, I. T. Song, W. Y. Kim, H. Lee, *Adv. Funct. Mater.* **2012**, *22*, 4711.
- [109] F. Yu, S. Chen, Y. Chen, H. Li, L. Yang, Y. Chen, Y. Yin, *J. Mol. Struct.* **2010**, *982*, 152.
- [110] M. B. Peterson, S. P. Le-Masurier, K. Lim, J. M. Hook, P. Martens, A. M. Granville, *Macromol. Rapid Commun.* **2014**, *35*, 291.
- [111] N. F. Della Vecchia, R. Avolio, M. Alfè, M. E. Errico, A. Napolitano, M. D'ischia, *Adv. Funct. Mater.* **2013**, *23*, 1331.
- [112] P. Delparastan, K. G. Malollari, H. Lee, P. B. Messersmith, *Angew. Chem., Int. Ed.* **2019**, *58*, 1077.
- [113] X. Chen, W. Yang, J. Zhang, L. Zhang, H. Shen, D. Shi, *Polym. Bull.* **2021**, *78*, 4439.
- [114] Z. Khan, R. Shanker, D. Um, A. Jaiswal, H. Ko, in *Electrically Conductive Polymer and Polymer Composites*, (Eds.: A. Khan, M. Jawaid, A. A. P. Khan, A. M. Asiri), John Wiley & Sons, Ltd, **2018**, p. 1.
- [115] C. J. Bettinger, J. P. Bruggeman, A. Misra, J. T. Borenstein, R. Langer, *Biomaterials* **2009**, *30*, 3050.
- [116] M. E. Lyng, R. Van Der Westen, A. Postma, B. Städler, *Nanoscale* **2011**, *3*, 4916.
- [117] P. A. Riley, *Int. J. Biochem. Cell Biol.* **1997**, *29*, 1235.
- [118] H. S. Mason, *J. Biol. Chem.* **1948**, *172*, 83.
- [119] H. S. Raper, *Biochem. J.* **1927**, *21*, 89.
- [120] H. S. Raper, *Physiol. Rev.* **1928**, *8*, 245.
- [121] M. D'ischia, A. Napolitano, A. Pezzella, *Eur. J. Org. Chem.* **2011**, *2011*, 5501.
- [122] M. D'ischia, A. Napolitano, A. Pezzella, P. Meredith, T. Sarna, *Angew. Chem., Int. Ed.* **2009**, *48*, 3914.
- [123] L. Han, X. Lu, K. Liu, K. Wang, L. Fang, L.-T. Weng, H. Zhang, Y. Tang, F. Ren, C. Zhao, G. Sun, R. Liang, Z. Li, *ACS Nano* **2017**, *11*, 2561.
- [124] H. K. Trang, R. K. Marcus, *Electrophoresis* **2020**, *41*, 215.
- [125] W. Han, H.-P. Zhang, J. Tavakoli, J. Campbell, Y. Tang, *Composites, Part A* **2018**, *107*, 626.
- [126] S. Sieste, T. Mack, C. V. Synatschke, C. Schilling, C. Meyer Zu Reckendorf, L. Pendi, S. Harvey, F. S. Ruggieri, T. P. J. Knowles, C. Meier, D. Y. W. Ng, T. Weil, B. Knöll, *Adv. Healthcare Mater.* **2018**, *7*, 1701485.
- [127] S. Zuppolini, I. Cruz-Maya, V. Guarino, A. Borriello, *J. Funct. Biomater.* **2020**, *11*, 19.
- [128] X. Yang, L. Duan, X. Ran, *Polym. Bull.* **2017**, *74*, 641.
- [129] L. Jia, F. Han, H. Wang, C. Zhu, Q. Guo, J. Li, Z. Zhao, Q. Zhang, X. Zhu, B. Li, *J. Orthop. Translat.* **2019**, *17*, 82.
- [130] Z. Wang, Y. Zou, Y. Li, Y. Cheng, *Small* **2020**, *16*, 1907042.
- [131] J. Miao, W. Geng, P. J. J. Alvarez, M. Long, *Environ. Sci. Technol.* **2020**, *54*, 8473.
- [132] C. Shi, J. Dai, S. Huang, C. Li, X. Shen, P. Zhang, D. Wu, D. Sun, J. Zhao, *J. Membr. Sci.* **2016**, *518*, 168.
- [133] Z. Huang, W. Pang, P. Liang, Z. Jin, N. Grundish, Y. Li, C.-A. Wang, *J. Mater. Chem. A* **2019**, *7*, 16425.
- [134] Y. Liu, M. Zhu, M. Chen, L. Ma, B. Yang, L. Li, W. Tu, *Chem. Eng. J.* **2019**, *359*, 47.
- [135] X. Zhang, S. Wang, C. Xue, C. Xin, Y. Lin, Y. Shen, L. Li, C.-W. Nan, *Adv. Mater.* **2019**, *31*, 1806082.
- [136] M. Jia, Z. Bi, C. Shi, N. Zhao, X. Guo, *ACS Appl. Mater. Interfaces* **2020**, *12*, 46231.
- [137] M. Jia, N. Zhao, Z. Bi, Z. Fu, F. Xu, C. Shi, X. Guo, *ACS Appl. Mater. Interfaces* **2020**, *12*, 46162.
- [138] S. Jia, J. Long, J. Li, S. Yang, K. Huang, N. Yang, Y. Liang, J. Xiao, *J. Mater. Sci.* **2020**, *55*, 14907.
- [139] K. Zhang, W. Xiao, X. Li, J. Liu, C. Yan, *J. Power Sources* **2020**, *468*, 228403.
- [140] Z. Liu, Y. Jiang, Q. Hu, S. Guo, L. Yu, Q. Li, Q. Liu, X. Hu, *Energy Environ. Mater.* **2021**, *4*, 336.
- [141] L. Liu, Y. Wang, C. Gao, C. Yang, K. Wang, H. Li, H. Gu, *J. Membr. Sci.* **2019**, *592*, 117368.
- [142] F. Wang, M. Wu, T. Zhang, Z. Wen, *ACS Appl. Mater. Interfaces* **2019**, *11*, 5123.
- [143] Y. Yin, C. Zhang, J. Chen, W. Yu, Z. Shi, C. Xiong, Q. Yang, *Carbohydr. Polym.* **2020**, *249*, 116883.
- [144] Y. Xie, Y. Yu, Y. Feng, W. Jiang, Z. Zhang, *ACS Appl. Mater. Interfaces* **2017**, *9*, 2995.
- [145] L. Zhang, F. Song, X. Lin, D. Wang, *Mater. Chem. Phys.* **2020**, *241*, 122373.
- [146] L. Guan, L. Weng, X. Zhang, Z. Wu, Q. Li, L. Liu, *J. Mater. Sci.* **2020**, *55*, 15238.
- [147] Y. Sheng, X. Zhang, H. Ye, L. Liang, L. Xu, H. Wu, *Colloids Surf., A* **2020**, *585*, 124091.
- [148] M. Feng, C. Li, M. He, Y. Huang, J. Luo, *Ceram. Int.* **2020**, *46*, 19181.
- [149] B. Li, Q. Su, L. Yu, D. Wang, S. Ding, M. Zhang, G. Du, B. Xu, *ACS Appl. Mater. Interfaces* **2019**, *11*, 42206.
- [150] Y. e Yang, H. Pan, G. Xie, Y. Jiang, C. Chen, Y. Su, Y. Wang, H. Tai, *Sens. Actuators, A* **2020**, *301*, 111789.
- [151] S. Liu, S. Xue, W. Zhang, J. Zhai, *Ceram. Int.* **2014**, *40*, 15633.
- [152] S.-H. Zhang, G.-Q. He, G.-Z. Liang, H. Cui, W. Zhang, B. Wang, *Appl. Surf. Sci.* **2010**, *256*, 2104.
- [153] A. Andres Leal, J. M. Deitzel, S. H. Mcknight, J. W. Gillespie, *Polymer* **2009**, *50*, 1228.
- [154] K. Imielinska, L. Guillaumat, *Compos. Sci. Technol.* **2004**, *64*, 2271.
- [155] R. J. Day, K. D. Hewson, P. A. Lovell, *Compos. Sci. Technol.* **2002**, *62*, 153.
- [156] T. K. Lin, S. J. Wu, J. G. Lai, S. S. Shyu, *Compos. Sci. Technol.* **2000**, *60*, 1873.
- [157] P. A. Tarantili, A. G. Andreopoulos, *J. Appl. Polym. Sci.* **1997**, *65*, 267.
- [158] S. R. Wu, G. S. Sheu, S. S. Shyu, *J. Appl. Polym. Sci.* **1996**, *62*, 1347.
- [159] L. Liu, Y. D. Huang, Z. Q. Zhang, Z. X. Jiang, L. N. Wu, *Appl. Surf. Sci.* **2008**, *254*, 2594.
- [160] Y. H. Zhang, Y. D. Huang, L. Liu, K. L. Cai, *Appl. Surf. Sci.* **2008**, *254*, 3153.
- [161] L. Ghosh, M. H. Fadhilah, H. Kinoshita, N. Ohmae, *Polymer* **2006**, *47*, 6836.
- [162] R. Sa, Y. Yan, Z. Wei, L. Zhang, W. Wang, M. Tian, *ACS Appl. Mater. Interfaces* **2014**, *6*, 21730.
- [163] X. Yang, Q. Tu, X. Shen, M. Pan, C. Jiang, P. Zhu, Y. i Li, P. Li, C. Hu, *Polym. Test.* **2019**, *78*, 105985.
- [164] X. Niu, S. Ding, W. Wang, Y. Xu, Y. Xu, H. Chen, X. Chen, *J. Chromatogr. A* **2016**, *1436*, 109.
- [165] H. Kang, X. Song, Z. Wang, W. Zhang, S. Zhang, J. Li, *ACS Sustainable Chem. Eng.* **2016**, *4*, 4354.
- [166] Z. Li, B. Liu, H. Kong, M. Yu, M. Qin, C. Teng, *Polymers* **2018**, *10*, 820.
- [167] M. Yi, H. Sun, H. Zhang, X. Deng, Q. Cai, X. Yang, *Mater. Sci. Eng., C* **2016**, *58*, 742.
- [168] Y. Li, Q. Chen, M. Yi, X. Zhou, X. Wang, Q. Cai, X. Yang, *Appl. Surf. Sci.* **2013**, *274*, 248.
- [169] Y. Liu, Y. Fang, X. Liu, X. Wang, B. Yang, *Compos. Sci. Technol.* **2017**, *151*, 164.
- [170] T. Su, W. Zhao, L. Wu, W. Dong, X. Qi, *Int. J. Biol. Macromol.* **2020**, *163*, 366.
- [171] H. Jiang, Q. Xia, D. Liu, K. Ling, *Anal. Chim. Acta* **2020**, *1121*, 1.
- [172] S. Cheng, D. Wang, J. Ke, L. Ma, J. Zhou, H. Shao, H. Zhu, L. Liu, Y. Zhang, F. Peng, X. Liu, *Colloids Surf., B* **2020**, *194*, 111176.

- [173] X. Zhang, Y. Nie, Q. Zhang, Z. Liang, Q. Ma, *J. Mater. Chem. C* **2020**, *8*, 8592.
- [174] Y. Liu, K. Ai, L. Lu, *Chem. Rev.* **2014**, *114*, 5057.
- [175] H. Gao, Y. Sun, J. Zhou, R. Xu, H. Duan, *ACS Appl. Mater. Interfaces* **2013**, *5*, 425.
- [176] R. Qu, W. Zhang, N. Liu, Q. Zhang, Y. Liu, X. Li, Y. Wei, L. Feng, *ACS Sustainable Chem. Eng.* **2018**, *6*, 8019.
- [177] Y. Qian, Y. Yuan, H. Wang, H. Liu, J. Zhang, S. Shi, Z. Guo, N. Wang, *J. Mater. Chem. A* **2018**, *6*, 24676.
- [178] F. Meng, F. Song, Y. Yao, G. Liu, S. Zhao, *ACS Sustainable Chem. Eng.* **2020**, *8*, 10928.
- [179] M. Qu, Y. Qin, Y. Sun, H. Xu, D. W. Schubert, K. Zheng, W. Xu, F. Nilsson, *ACS Appl. Mater. Interfaces* **2020**, *12*, 42140.
- [180] X. Yang, Y. Zhou, Z. Sun, C. Yang, D. Tang, *Environ. Chem. Lett.* **2020**, *19*, 743.
- [181] H. Chen, Y. Zhou, J. Wang, J. Lu, Y. Zhou, *J. Hazard. Mater.* **2020**, *389*, 121897.
- [182] L. Cheng, H. Wu, J. Li, H. Zhao, L. Wang, *Corros. Sci.* **2021**, *178*, 109064.
- [183] M. Liang, C. He, J. Dai, P. Ren, Y. Fu, F. Wang, X. Ge, T. Zhang, Z. Lu, *J. Mater. Chem. B* **2020**, *8*, 8232.
- [184] Y.-J. Fan, M. T. Pham, C.-J. Huang, *Langmuir* **2019**, *35*, 1642.
- [185] N. P. Shumbula, S. S. Nkabinde, Z. B. Ndala, S. Mpelane, M. P. Shumbula, P. S. Mdluli, Z. Njengele-Tetyana, P. Tetyana, T. Hlatshwayo, M. Mlambo, N. Moloto, *Arabian J. Chem.* **2022**, *15*, 103798.
- [186] C. Muller, E. Berber, G. Lutzweiler, O. Ersen, M. Bahri, P. Lavalle, V. Ball, N. E. Vrana, J. Barthes, *Front. Bioeng. Biotechnol.* **2020**, *8*, 982.
- [187] I. Singh, G. Dhawan, S. Gupta, P. Kumar, *Front. Microbiol.* **2021**, *11*, 607099.
- [188] Y. Tang, Y. Tan, K. Lin, M. Zhu, *Front. Chem.* **2021**, *9*, 727123.
- [189] S. Huang, N. Liang, Y. Hu, X. Zhou, N. Abidi, *Biomed Res. Int.* **2016**, *2016*, 2389895.
- [190] N. Kaushik, L. Nhat Nguyen, J. H. Kim, E. H. Choi, N. Kumar Kaushik, *Int. J. Mol. Sci.* **2020**, *21*, 6544.
- [191] Y. Yang, Y. Cheng, F. Deng, L. Shen, Z. Zhao, S. Peng, C. Shuai, *Bio-Des. Manuf.* **2021**, *4*, 452.
- [192] F. Qi, Z. Zeng, J. Yao, W. Cai, Z. Zhao, S. Peng, C. Shuai, *Mater. Sci. Eng., C* **2021**, *126*, 112129.
- [193] P. Palladino, F. Bettazzi, S. Scarano, *Anal. Bioanal. Chem.* **2019**, *411*, 4327.
- [194] H. Wang, C. Lin, X. Zhang, K. Lin, X. Wang, S. G. Shen, *ACS Appl. Mater. Interfaces* **2019**, *11*, 7615.
- [195] P. Feng, M. Liu, S. Peng, S. Bin, Z. Zhao, C. Shuai, *J. Mater. Res. Technol.* **2021**, *15*, 3375.
- [196] X. Li, H.-M. Yin, K. Su, G.-S. Zheng, C.-Y. Mao, W. Liu, P. Wang, Z. Zhang, J.-Z. Xu, Z.-M. Li, G.-Q. Liao, *ACS Biomater. Sci. Eng.* **2019**, *5*, 2998.
- [197] F. Ghorbani, A. Zamanian, A. Aidun, *J. Appl. Polym. Sci.* **2019**, *136*, 47656.
- [198] Yi Deng, W.-Z. Yang, D. Shi, M. Wu, X.-L. Xiong, Z.-G. Chen, S.-C. Wei, *NPG Asia Mater* **2019**, *11*, 39.
- [199] L. Wu, F. Zhang, Z. Wei, X. Li, H. Zhao, H. Lv, R. Ge, H. Ma, H. Zhang, B. Yang, J. Li, J. Jiang, *Biomater. Sci.* **2018**, *6*, 2714.
- [200] M. Wu, D. Zhang, Y. Zeng, L. Wu, X. Liu, J. Liu, *Nanotechnology* **2015**, *26*, 115102.
- [201] R. Zheng, S. Wang, Y. Tian, X. Jiang, D. Fu, S. Shen, W. Yang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 15876.
- [202] Y. Li, L. Huang, W. He, Y. Chen, B. Lou, *Polymers* **2018**, *10*, 570.
- [203] R. Ge, X. Li, M. Lin, D. Wang, S. Li, S. Liu, Q. Tang, Y. Liu, J. Jiang, L. Liu, H. Sun, H. Zhang, B. Yang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 22942.
- [204] Y. Chen, K. Ai, J. Liu, X. Ren, C. Jiang, L. Lu, *Biomaterials* **2016**, *77*, 198.
- [205] L. Zhang, Q. Wang, R.-K. Jian, D.-Y. Wang, *J. Mater. Chem. A* **2020**, *8*, 2529.
- [206] Z. Dong, L. Feng, Y. Hao, M. Chen, M. Gao, Y. Chao, H. Zhao, W. Zhu, J. Liu, C. Liang, Q. Zhang, Z. Liu, *J. Am. Chem. Soc.* **2018**, *140*, 2165.
- [207] Y. Zhu, N. Xin, Z. Qiao, S. Chen, L. Zeng, Y. Zhang, D. Wei, J. Sun, H. Fan, *ACS Appl. Mater. Interfaces* **2019**, *11*, 43018.
- [208] R. Ge, M. Lin, X. Li, S. Liu, W. Wang, S. Li, X. Zhang, Y. Liu, L. Liu, F. Shi, H. Sun, H. Zhang, B. Yang, *ACS Appl. Mater. Interfaces* **2017**, *9*, 19706.
- [209] Q. Xu, M. Chang, Y. Zhang, E. Wang, M. Xing, L. Gao, Z. Huan, F. Guo, J. Chang, *ACS Appl. Mater. Interfaces* **2020**, *12*, 31255.
- [210] Y. Dai, D. Yang, D. Yu, C. Cao, Q. Wang, S. Xie, L. Shen, W. Feng, F. Li, *ACS Appl. Mater. Interfaces* **2017**, *9*, 26674.
- [211] M. Zandieh, J. Liu, *Langmuir* **2020**, *36*, 3260.
- [212] S. Wang, J. Lin, Z. Wang, Z. Zhou, R. Bai, N. Lu, Y. Liu, X. Fu, O. Jacobson, W. Fan, J. Qu, S. Chen, T. Wang, P. Huang, X. Chen, *Adv. Mater.* **2017**, *29*, 1701013.
- [213] Y. Cao, J. Shi, Z. Wu, J. Li, S. Cao, *Powder Technol.* **2020**, *372*, 486.
- [214] Y. Cong, T. Xia, M. Zou, Z. Li, B. Peng, D. Guo, Z. Deng, *J. Mater. Chem. B* **2014**, *2*, 3450.
- [215] A. W. Jatoui, I. S. Kim, Q.-Q. Ni, *Carbohydr. Polym.* **2019**, *207*, 640.
- [216] Y. Song, H. Jiang, B. Wang, Y. Kong, J. Chen, *ACS Appl. Mater. Interfaces* **2018**, *10*, 1792.
- [217] J. Chen, S. Lei, Y. Xie, M. Wang, J. Yang, X. Ge, *ACS Appl. Mater. Interfaces* **2015**, *7*, 28606.
- [218] D. G. Meeker, S. V. Jenkins, E. K. Miller, K. E. Beenken, A. J. Loughran, A. Powless, T. J. Muldoon, E. I. Galanzha, V. P. Zharov, M. S. Smeltzer, J. Chen, *ACS Infect. Dis.* **2016**, *2*, 241.
- [219] K. C. L. Black, T. S. Sileika, J. Yi, R. Zhang, J. G. Rivera, P. B. Messersmith, *Small* **2014**, *10*, 169.
- [220] I. Cooperstein, E. Sachyani-Keneth, E. Shukrun-Farrell, T. Rosental, X. Wang, A. Kamyshny, S. Magdassi, *Adv. Mater. Interfaces* **2018**, *5*, 1800996.
- [221] J.-H. Li, X.-X. Ni, D.-B. Zhang, H. Zheng, J.-B. Wang, Q.-Q. Zhang, *Appl. Surf. Sci.* **2018**, *444*, 672.
- [222] D. Camel, B. Drevet, N. Eustathopoulos, *J. Mater. Sci.* **2016**, *51*, 1722.
- [223] O. Vincent, A. Szenicer, A. D. Stroock, *Soft Matter* **2016**, *12*, 6656.
- [224] Y. Liu, D. Gan, M. Chen, L. Ma, B. Yang, L. Li, M. Zhu, W. Tu, *Sep. Purif. Technol.* **2020**, *253*, 117552.
- [225] Y. Huang, G. Yi, B. Ji, D. Gao, Y. Bai, Y. Liu, L. Wang, Z. Xia, Q. Fu, *J. Chromatogr. A* **2020**, *1610*, 460559.
- [226] F. M. Tarongoy, P. R. Haddad, J. P. Quirino, *Electrophoresis* **2018**, *39*, 34.
- [227] G. Yi, J. He, B. Ji, D. Gao, K. Zhang, L. Wang, J. Zeng, Z. Xia, Q. Fu, *J. Chromatogr. A* **2020**, *1628*, 461436.
- [228] B. Fei, B. Qian, Z. Yang, R. Wang, W. C. Liu, C. L. Mak, J. H. Xin, *Carbon* **2008**, *46*, 1795.
- [229] T. Sun, Z.-J. Li, H.-G. Wang, D. Bao, F.-L. Meng, X.-B. Zhang, *Angew. Chem., Int. Ed.* **2016**, *55*, 10662.
- [230] T. Liu, K. C. Kim, B. Lee, Z. Chen, S. Noda, S. S. Jang, S. W. Lee, *Energy Environ. Sci.* **2017**, *10*, 205.
- [231] R. Chen, Y. Yang, Q. Huang, H. Ling, X. Li, J. Ren, K. Zhang, R. Sun, X. Wang, *Energy Storage Mater.* **2020**, *32*, 208.
- [232] C. Xie, X. Wang, H. He, Y. Ding, X. Lu, *Adv. Funct. Mater.* **2020**, *30*, 1909954.
- [233] Y. Xie, Y. Zheng, J. Fan, Y. Wang, L. Yue, N. Zhang, *ACS Appl. Mater. Interfaces* **2018**, *10*, 22692.
- [234] L. Wu, L. Li, M. Qu, H. Wang, Y. Bin, *ACS Appl. Polym. Mater.* **2020**, *2*, 3094.

- [235] S. Du, N. Zhou, Y. Gao, G. Xie, H. Du, H. Jiang, L. Zhang, J. Tao, J. Zhu, *Nano Res.* **2020**, *13*, 2525.
- [236] L. Han, L. Yan, M. Wang, K. Wang, L. Fang, J. Zhou, J. Fang, F. Ren, X. Lu, *Chem. Mater.* **2018**, *30*, 5561.
- [237] J. H. Ryu, P. B. Messersmith, H. Lee, *ACS Appl. Mater. Interfaces* **2018**, *10*, 7523.
- [238] A. B. Asha, Y. Chen, R. Narain, *Chem. Soc. Rev.* **2021**, *50*, 11668.
- [239] A. B. Asha, Y. Chen, H. Zhang, S. Ghaemi, K. Ishihara, Y. Liu, R. Narain, *Langmuir* **2019**, *35*, 1621.
- [240] Y. Xu, J. Hu, J. Hu, Y. Cheng, X. Chen, Z. Gu, Y. Li, *Prog. Polym. Sci.* **2023**, *146*, 101740.
- [241] N. Li, Q. Zhang, L. Han, J. Huang, X. Luo, X. Li, *Int. J. Hydrog.* **2023**, *48*, 7004.
- [242] T. Wang, P. Wang, L. Pan, Z. He, L. Dai, L. Wang, S. Liu, S. C. Jun, B. Lu, S. Liang, J. Zhou, *Adv. Energy Mater.* **2023**, *13*, 2203523.
- [243] Z. Shi, H. Zeng, Y. Yuan, N. Shi, L. Wen, H. Rong, D. Zhu, L. Hu, L. Ji, L. Zhao, X. Zhang, *Adv. Funct. Mater.* **2023**, *33*, 2213042.
- [244] Y. Liu, S. Liu, X. Xie, Z. Li, P. Wang, B. Lu, S. Liang, Y. Tang, J. Zhou, *InfoMat* **2023**, *5*, e12374.
- [245] W. Ma, X. Zhang, Y. Liu, L. Fan, J. Gan, W. Liu, Y. Zhao, L. Sun, *Adv. Sci.* **2022**, *9*, 2103370.
- [246] X. Qi, Y. Huang, S. You, Y. Xiang, E. Cai, R. Mao, W. Pan, X. Tong, W. Dong, F. Ye, J. Shen, *Adv. Sci.* **2022**, *9*, 2106015.
- [247] Q. Xin, D. Hu, L. Zhou, G. Yang, S. Liang, J. Lin, *ACS Appl. Electron. Mater.* **2023**, *5*, 3756.



Mohit Saraf earned his Ph.D. in metallurgical engineering & materials science from the Indian Institute of Technology Indore in 2019. He also holds an Integrated Bachelor's-Master's degree in Nanotechnology from the University of Rajasthan, Jaipur. Recently, he successfully completed his Fulbright-Nehru postdoctoral fellowship at the A. J. Drexel Nanomaterials Institute, Department of Materials Science and Engineering at Drexel University, USA. Dr. Saraf's notable achievements include an impressive publication record, active participation in peer review processes, and a range of other accomplishments that highlight his scientific aptitude and leadership qualities. His current research focuses on 2D MXenes for energy storage applications.



Prateek is a postdoctoral research associate in the Watkins Research Group at the Department of Polymer Science & Engineering, University of Massachusetts Amherst, USA. He graduated in biochemical engineering (B. Tech. 2011) from Harcourt Butler Technological Institute, Kanpur, and chemical engineering (M. Tech. 2013) from the Indian Institute of Technology (IIT) Roorkee, India. He obtained his Ph.D. in chemical engineering (2020) from the Indian Institute of Technology Kanpur, India. His research interests are dielectrics, polymer nanocomposites, and energy storage devices.



Rahul Ranjan is currently working as an assistant professor in the Department of Chemical Engineering at the Indian Institute of Technology Kharagpur (IIT KGP). Before joining IIT KGP, he was a Marie-Curie fellow at ICHF, Polish Academy of Science, Poland, and EPFL, Switzerland. He completed his Ph.D. from the Indian Institute of Technology Kanpur in 2019. He is working on the perovskite solar cells (PSC) area, primarily focusing on the large area fabrication on the electron and hole transport layers.



B. Bhuvaneshwari is currently working as an assistant professor in the Department of Chemistry at the Indian Institute of Technology (BHU) Varanasi, India. She holds her Ph.D. in chemistry and has more than seven years of post-doctoral experience. She obtained several research awards and handled many scientific projects as principal investigator, team leader, and team member. Her research expertise includes polymer nanocomposites, corrosion, fuel cells, supercapacitors, artificial intelligence, and functional biomaterials.



Vijay Kumar Thakur is a professor and founding head of the Biorefining and Advanced Materials Research Centre at SRUC, Edinburgh, UK. Before commencing his tenure at SRUC, he held faculty positions at Cranfield University, UK, Washington State University, USA, and Nanyang Technological University, Singapore. His research activities span the disciplines of biorefining, chemistry, manufacturing, materials science, nanotechnology, and sustainable and advanced materials. He has published over 360 SCI journal articles, 2 patents, 54 books, and 45 book chapters. He sits on the editorial board of several SCI journals as an EiC/Associate Editor/ Editorial advisory board member.



Raju Kumar Gupta is currently a professor at the Department of Chemical Engineering, Indian Institute of Technology Kanpur, India. Prof. Gupta's research interests are photocatalysis for water remediation and CO₂ conversion to fuels, desalination, perovskite solar cells, and energy storage devices based on batteries. He has been the recipient of several fellowships and awards for his outstanding career in academic and research fields. Prof. Gupta is an editorial board member of several international journals, as well as a member of scientific bodies. Some of his significant appointments include Founding Editor for 'Sustainable Chemistry One World' and Associate Editor for 'Solar Energy'.