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Multifunctional Material Building Blocks from Plant Pollen

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Abstract

With its multifaceted nature, plant pollen serves not only as a key element in the reproductive cycle of seed plants but also as an influential contributor to environmental, human health, safety, and climate-related concerns. Pollen functions as a carrier of nutrients and organisms and holds a pivotal role in sustaining pollinator populations. Moreover, it is vital in ensuring the safety and quality of our food supply while presenting potential therapeutic applications. Pollen, often referred to as the diamond of the organic world due to its distinctive physical structures and properties, has been underappreciated from a material science and engineering standpoint. We propose adopting a more interdisciplinary and comprehensive approach to its study. Recent groundbreaking research has focused on the development of pollen-based building blocks that transform practically indestructible plant pollen into microgel, paper, and sponge, thereby unveiling numerous potential applications. In this review, we highlight the transformative potential of plant pollen as it is converted into a variety of building blocks, thereby unlocking myriad prospective applications through eco-friendly processing.

1. INTRODUCTION

The natural world offers an extensive range of valuable resources, including sunlight, atmosphere, water, land, minerals, plants, and wildlife, which have been prominent subjects of human exploration, processing, and application throughout history. Plants are an essential natural resource that has fulfilled people's basic necessities, including food, clothing, housing, and transportation, since the birth of humanity. The seemingly humble microcomponents of plants, pollens and spores serve as protective carriers to encapsulate and transport genetic materials (1), enabling the biological imperative of plant reproduction (2), and have garnered increasing attention due to their remarkable properties (3). Diversified pollen grains offer various nutrients and therapeutic effects, making them a popular choice as superfood supplements (4, 5) and medicinal materials (6–8). To ensure reproductive success, plants produce excess pollen grains and spores endowed with high endurance in harsh environments (9). Pollens between plant species are differentiated mainly through unique morphologies, whereas those of the same species possess favorable monodispersity (10, 11). Given these superior characteristics, they have been widely used as tools for monitoring of climate and topography changes (9, 12) and forensic analysis (13). From a biological structure perspective, pollen is composed of four layers, namely, pollenkitt, exine, intine, and cytoplasmic content (14, 15). Processing of pollen grains can alter their physical and chemical properties (16), resulting in multifunctional material building blocks that have been applied in many emerging fields, such as drug delivery (17–19), tissue engineering (20, 21), soft robotics (22), biosensors (23, 24) and actuators (25), flexible electronics (26), and environmental remediation (27).

Several reviews on pollen and spores have been published to date, most of which focus on plant biological areas such as cellular (28), molecular (29, 30), genetic (31), and biochemical (32) understanding of biological development or pollen tube guidance in plant biology (14, 33, 34); the effect of pollen and spore transfer and distribution on ecology (35, 36) and allergy (37); the use of fossil pollen and spores in paleobotany and palynology (38); and the physicochemical composition and functionality of bee pollen in health (39) and therapeutic (6–8) products. Additional reviews summarize research progress on pollen and spore materials with either one single structural layer [i.e., exine (16)] or one single application [i.e., drug delivery (40)]. This review focuses on new morphological and chemical structures/features of diverse pollens (11, 15, 41, 42), obtained via environmentally benign processing (43), with mechanically adjustable properties to aid new applications such as 3D printing (44), functional pollen-based papers (45), and ecofriendly sponges (27), from both a materials and chemical science and a sustainability viewpoint (**Figure 1**).

2. PLANT BIOLOGICAL SCIENCE AND APPLICATIONS

2.1. Nutritious Food and Medicine

Bee pollen is widely acknowledged as a natural superfood thanks to its remarkable nutritional and therapeutic properties, which vary significantly according to plant source, growing conditions like soil or climate, and harvesting time (7, 46). Bee pollen contains approximately 250 substances. For air-dried pollen (at 40°C), the main ingredients and their average content are as follows: reducing sugars 40.7% (of which sucrose-3.7%), proteins 32.8% (essential amino acids 11.5%), lipids 12.8%, vitamin C 0.19%, β-carotene 0.07%, and bio-elements 4.0% (6). Administration of pollen affects appetite and helps those suffering from malnutrition and developmental delay due to its high nutritional value (47). Bee pollen is recommended not only as a valuable dietary supplement that helps meet daily nutritional requirements but also as a preferred material for medical treatment, as it exhibits a wide range of bioactivities and has therapeutic qualities, including antioxidative, anti-inflammatory, antibacterial, anti-fungicidal, anti-atherosclerotic, anticarcinogenic,

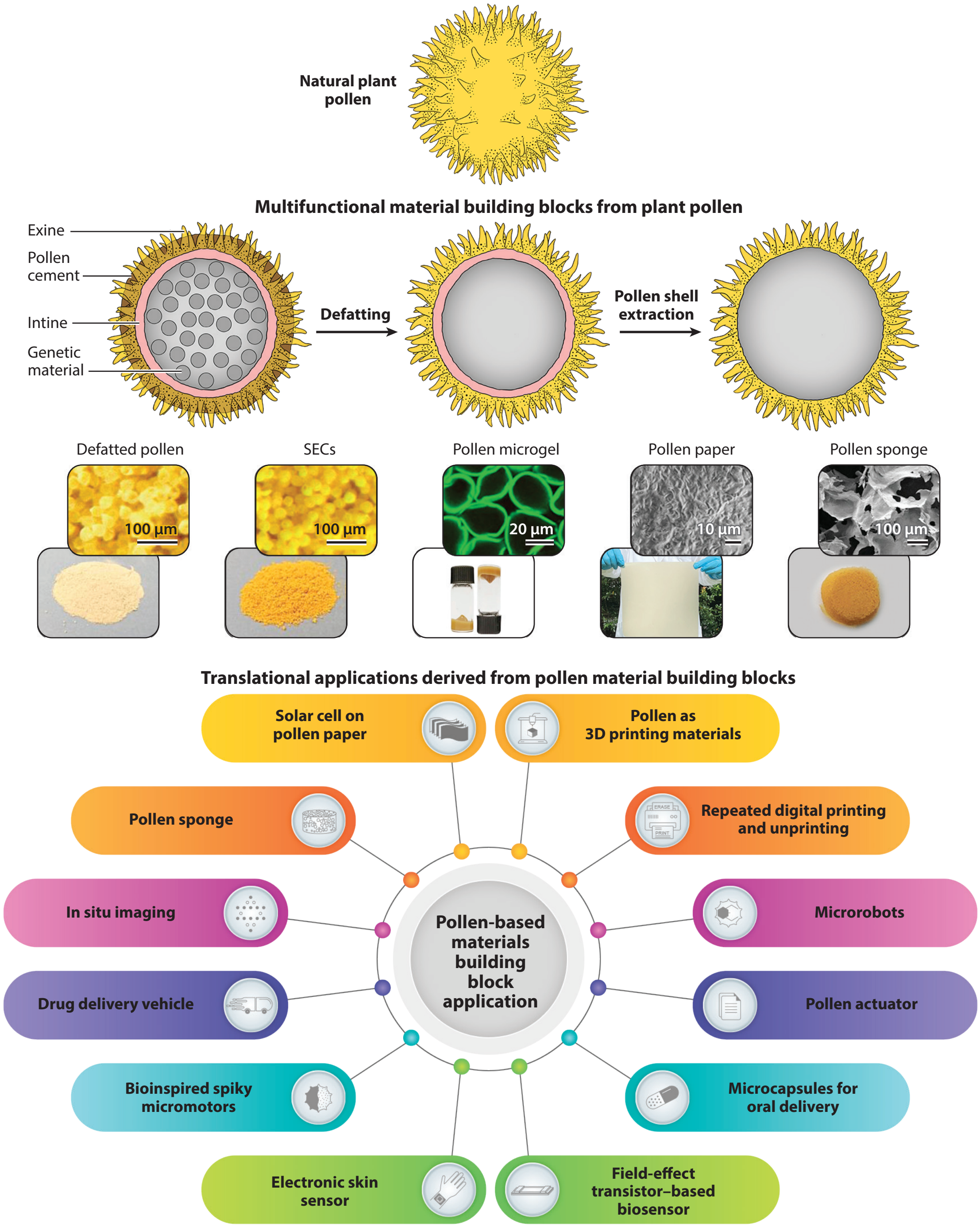

Figure 1

Conversion of plant pollen into diverse building materials, including defatted pollen particles, sporopollenin exine capsules (SECs), microgels, paper, and sponges. This signifies the dawn of a novel application, spanning fields such as biosensors, in situ imaging, drug delivery mechanisms, actuators, microrobots, and various other mainstream commercial uses.

hepato-protective, and anti-allergic properties. Diverse primary and secondary metabolites in bee pollen can modify and regulate immune functions, thus making it effective for treating various diseases (see **Supplemental Table 1**).

Supplemental Material >

2.2. Paleoclimate/Paleotopography Reconstruction

The diversity, abundance, and specificity of modern/fossil pollen samples provide rich details for paleoecologists to analyze, infer, and compare vegetation and climate changes through time (48). By tracking plant phenology (time of flowering), establishing species absence/presence, censusing community composition, and capturing changes in trait variation and physiology, researchers have historically used pollen to reconstruct the paleoenvironment (including paleoclimate and paleotopography) (9, 12). The efforts of palynologists over the past century have provided substantial pollen databases for reconstructing the paleoenvironment, including the composition and distribution of paleo-plant communities and features of climate and topography in several continental areas (49). For example, biomes of Africa and the Arabian Peninsula have been mapped over 6,000 years with the assistance of pollen and plant macrofossil data. Only minor biome distribution changes were seen in Madagascar and eastern, southern, and central Africa. In contrast, major changes were seen north of 15°N, where steppes in many low-elevation sites changed to desert, and in temperate xerophytic woods/scrub and warm mixed forest in Saharan mountains. These shifts indicate significant climate changes, especially in precipitation, between 6,000 years and now, reflecting a change in monsoon extent combined with a southward expansion of Mediterranean influence (50). Researchers have used almost 60,000 individual pollen samples to reconstruct the Holocene climate of Europe of the last 12,000 years, including seasonal and annual temperature and precipitation, growing degree days above 5°C, and moisture balance measures. Postglacial isostatic adjustment led to an estimated warming bias of up to +1–2°C for certain regions of Fennoscandia during the early Holocene. Moreover, many features of the Holocene European landscape have since disappeared. For instance, the early-expanded Baltic sea/lake and ancient Doggerland now lie beneath the North Sea (51).

The pollen-based reconstructions of climate and ecosystem variability over the past 10,000 years led to the report that only a 1.5°C warming scenario will permit Mediterranean ecosystems to maintain Holocene variability. Warming of ≥2°C will generate changes unmatched in the Holocene, a period characterized by recurring deficits in precipitation rather than temperature anomalies (12).

2.3. Forensic Analysis

Air-distributed pollen is easily trapped on clothes, hair, nasal cavities, skin, eyebrows, and footwear (13, 52). Geographically unique growing positions, temporally specific flowering seasons, distinctive morphologies, and high robustness render pollen valid and long-lasting evidence for both criminal and civil cases (13). Although pollen species may mix as people pass through different sites, pollen in sediment on footwear has been found to reflect last-site pollen content with a high probability (53). Forensic palynology is now routinely accepted, and courts have tested its application in multiple countries (54).

Pollen analysis has even been used to clarify dramatic historical events. For example, in February 1994, 32 male skeletons were excavated from a common grave in Magdeburg, Germany. The area had been under Gestapo control until Soviet forces took over in 1945. After collecting and analyzing the pollen samples in these skulls, researchers detected high concentrations of plantain (*Plantago*) pollen in the nasal cavities. The plantain pollination season is June–July, coinciding with the timing of a German revolt in 1953. Combined with dental evidence, pollen analysis indicated that the murder victims were Soviet soldiers (55). Compared with traditional forensic palynology, which is limited by the need for expert palynologists, slow identification speed, and relatively poor taxonomic resolution, especially of the plant family or genus level, the emerging technology of pollen DNA barcoding is attracting increasing attention due to its faster and more accurate detection ability (56, 57).

3. ECOFRIENDLY AND SUSTAINABLE PROCESSING METHODS

As extraordinary substances in nature, spores and pollen are abundant and ubiquitous (58). They possess unique multifunctionality for encapsulating, protecting, and transporting male gametes of plants (59), inspiring researchers to transform (44, 60) and functionalize (23, 24) them to construct diverse engineered pollen- or spore-derived materials. Before the functional use of the humble natural spore and pollen grains, proper processing methods should be applied to clean the raw grains and modify their structural layers to obtain desired microcapsules according to the application requirements (**Figure 2**). Though natural spores and pollen are inexpensive, readily available, and renewable, the economic efficiency and viability of processing should also be considered and incorporated to realize the goals of materials innovation and sustainable practices.

3.1. Defatting Raw Spores and Pollens

The first step is to remove the sticky oil-based layer that coats pollen and spore exines. *Lycopodium clavatum* is the most widely studied plant spore species due to its abundance, commercial availability, monodispersity, and chemical stability (61). The conventional defatting method involves solvent refluxing in acetone for up to 12 h (62). This process has been optimized further, decreasing the duration from 12 h to 6 h (76, 77). Pollens differ from spores in structure and composition, leading to different defatting processes. A strategy was proposed to improve removal of pollenkitt from pollens, using both acetone and diethyl ether (19). The pollen grains were refluxed first in acetone, after which diethyl ether was used to defat the pollen sequentially. The diethyl ether defatting step is repeated twice with fresh diethyl ether in each cycle. Finally, the pollen sample is dispersed in fresh diethyl ether and stirred overnight to obtain the defatted pollen. This process has been successful in defatting pollen from camellia (*Camellia sinensis*) and sunflower (*Helianthus annuus*) (22, 63). Pine pollen has an intriguing triple-cavity structure, which can be defatted directly by diethyl ether without use of acetone (64).

3.2. Extracting Sporopollenin Exine Capsules

Removing cytoplasmic material, pollen coat, and the cellulosic intine layer from the defatted spores and pollen produces hollow sporopollenin exine capsules (SECs) for different applications, such as drugs and vaccines vehicles. The most prevalent SEC extraction method involves alkaline refluxing in 6% potassium hydroxide (KOH) at 120°C for up to 12 h, followed by acid refluxing in 85% phosphoric acid at 180°C for up to 7 days and a comprehensive washing process (61, 62). However, in terms of energy efficiency and environmental impact, high temperatures and long extraction periods significantly impair process profitability and sustainability. This complex process was improved by eliminating the alkaline refluxing step and treating with only 85% phosphoric acid for 30 h at 70°C to remove the sporoplasm and intine layer from defatted spores (65). The chemical structure and exine morphology of sporopollenin exine material vary slightly among spore and pollen species, resulting in different levels of resistance to harsh processing techniques. Thus, processing conditions for each species must be optimized to achieve desired results. The conventional method used for spores, involving alkali treatment and acidolysis, failed to obtain structurally intact SEC from sunflower (*H. annuus*) and short ragweed (*Ambrosia artemisiifolia*)

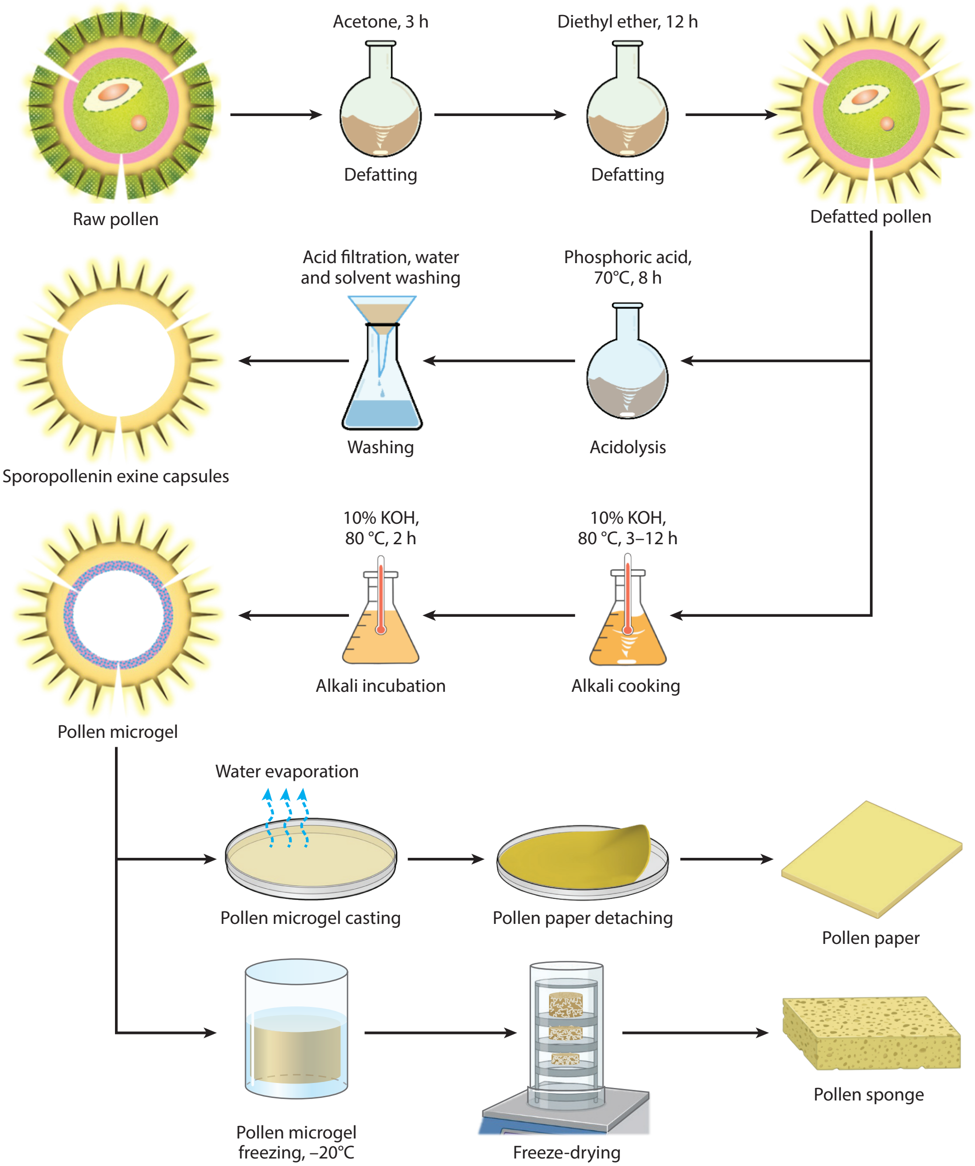

Figure 2

An outline of the stages involved in transforming raw pollen into defatted pollen, sporopollenin exine capsules, and pollen microgels. The resulting pollen microgels can act as microprecursors, which can then be meticulously crafted into pollen paper and sponge, catering to a range of subsequent applications.

pollens. To address this issue, Mundargi et al. (66) circumvented the alkali step and directly used phosphoric acid to isolate sunflower SECs, successfully extracting them without damaging the native microstructure and surface ornamentation. However, this method led to relatively high residual protein content. Gill and coauthors (67–69) developed a new approach that switched the sequence of alkali and acid treatment steps, obtaining clean, intact, and protein-free SECs for numerous applications.

3.3. Transforming Hard Pollen into Soft Microgels

Previous processing strategies aimed to remove the proteinaceous material and soft cellulosic intine, retaining only the stiff sporopollenin exine as a clean, naturally occurring microshell for subsequent steps. However, these ignored the preservation of their composite architectures. The collaborative properties and functions of the exine and intine as composite materials, together with their fundamental materials science, are critical and remain largely unexplored. Recently, Fan et al. (60) developed a simple, highly effective chemical processing method—akin to the basic steps in traditional soapmaking—to transform hard pollen grains into soft microgel particles, which retain both a tough exine and soft intine. This process, called alkaline hydrolysis, involves pollen shell extraction and subsequent incubation in an alkaline medium. Specifically, to remove the internal cytoplasmic content, the defatted pollen is subjected to 10 wt/vol% KOH treatment at 80°C and stirred for 2 h. It is then incubated in fresh 10 wt/vol% KOH at 80°C for a specific duration (3, 6, or 12 h) to allow for extensive hydrolysis, converting the hard pollen into microgel particles with lower mechanical strength. Stable pollen microgel suspensions are obtained through subsequent neutralization and centrifugation. Integrating the exine and intine, along with the apertures, creates pollen microgel particles that retain their unique geometrical and morphological features and exhibit exceptional long-term stability. Moreover, they can sense, respond to, and adapt to environmental perturbations (70, 71).

3.4. Building Higher-Dimensional Pollen Assemblies

Owing to the pliability and enhanced exposure of functional groups capable of hydrogen bonding during alkaline hydrolysis, the as-prepared pollen microgels can be readily adapted to self-assembly into higher-dimensional material forms as potential micro-building blocks, analogous to other biopolymers like cellulose, lignin, and chitosan. A straightforward and environmentally friendly film casting has enabled the pollen microgels to self-assemble into pollen film or paper (25). At the beginning of the fabrication process, dilute pollen microgels are cast effortlessly into the mold with desired shapes. As water continuously evaporates, pollen particle concentration increases, leading to their agglomeration and formation of continuous assemblies. Prolonged incubation in KOH results in considerably reduced mechanical stiffness of pollen microgels, enabling the flattening of the particles during evaporation-induced dehydration in the pollen papermaking process. Compared to conventional processing methods for paper production (i.e., from a wood source) that involve multiple energy-intensive processes, transformation of raw pollen grains to end paper products follows a simple, four-step, aqueous solution–based approach, with minimized energy input and emissions (45). Additionally, a macroscopic 3D sponge can be produced by freeze-drying the aggregated pollen microgels (27). Like other freeze-dried biopolymers, the pollen microgel is first frozen at −20°C overnight or in liquid nitrogen for 15 min, which induces pollen wall lamination owing to ice crystal nucleation. Following lyophilization, sublimation of ice crystals under vacuum results in 3D porous architectures. The freezing temperature strongly influences pollen sponge fabrication quality, and more homogeneous sponge structures are obtained at –20°C with few defects and smooth walls.

4. APPLICATIONS BASED ON PLANT POLLEN BUILDING BLOCKS

4.1. Defatted Pollen Applications in Eco-/Bioengineering

Defatted pollen grains are formed after being stripped off pollenkitt, which contains lipids and proteins. Without allergic proteins, the pollens are biocompatible and safe for oral consumption, hence their use as components in biological supplements and herbal medicines (72). After lipid

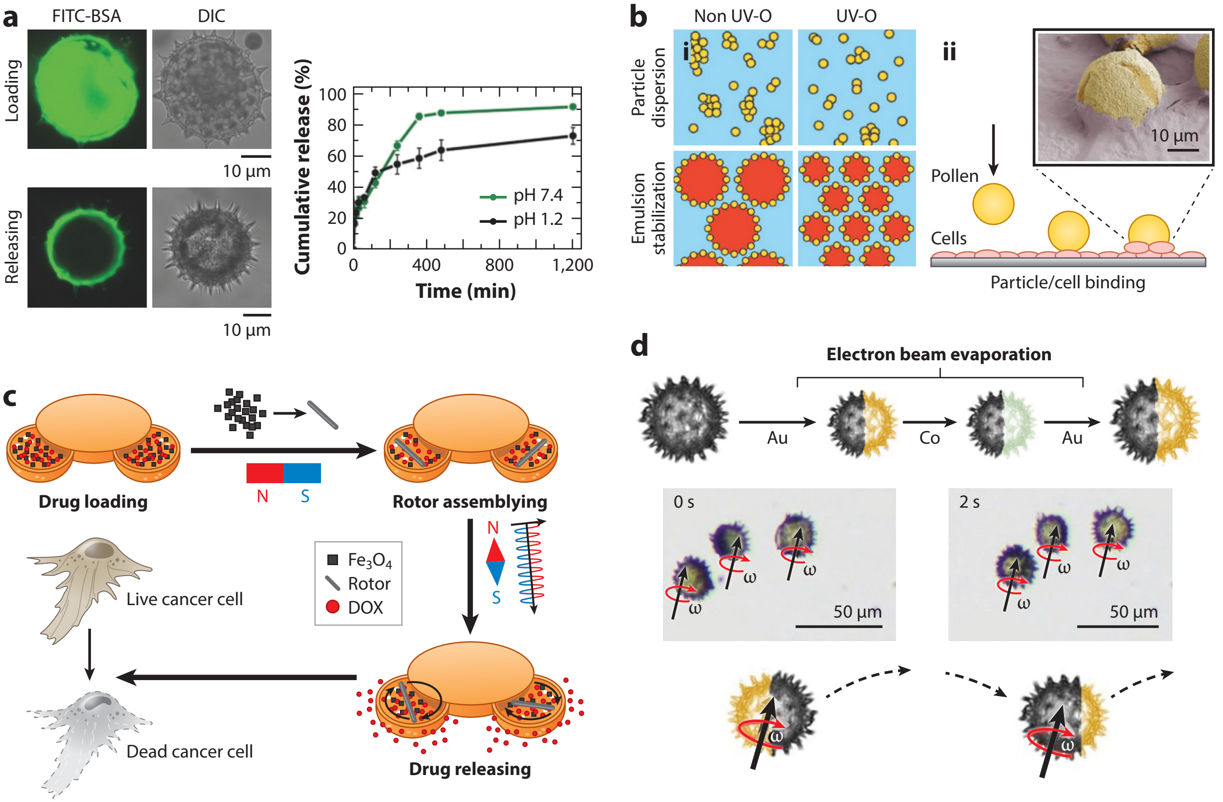

Figure 3

The drug delivery and micromotor applications of defatted pollens. (*a*) BSA-loaded pollen grains and their in vitro release (reproduced with permission from Reference 19; copyright 2016 John Wiley and Sons). (*b*) Defatted *Camellia* pollen with UV–O treatment for (*i*) Pickering emulsions and (*ii*) cell binding (reproduced with permission from Reference 63; copyright 2018 John Wiley and Sons). (*c*) The targeted drug delivery and controlled release of pine pollen–based micromotors (reproduced with permission from Reference 72; copyright 2019 Royal Society of Chemistry). (*d*) The locomotion of the sunflower pollens after asymmetric deposition of Au, Co, and Au on one side (reproduced with permission from Reference 22; copyright 2022 John Wiley and Sons). Abbreviations: BSA, bovine serum albumin; DIC, differential interference contrast; DOX, doxorubicin; FITC, fluorescein isothiocyanate conjugate.

removal, pollen surface wettability improves greatly, and the porous structure in exine is exposed, thereby enhancing water permeability and absorption and providing nanochannels for substance encapsulation and release. To date, defatted pollen has been used for drug delivery (19) and as cell carriers (63), electroactive building blocks (73), and microrobots/micromotors (22).

Mundargi et al. (19) investigated the use of defatted sunflower pollen as a drug delivery vehicle and tested its release profile, toxicity, and biocompatibility. They demonstrated that defatted sunflower pollen could load bovine serum albumin (BSA) effectively and release it in simulated intestinal (pH 7.4) and gastric (pH 1.2) fluid (**Figure 3*a***). Application of an alginate coating slowed BSA release. Tan et al. (63) reported on the light-induced surface modification of defatted *C. sinensis* pollen for colloidal science and cell adhesion applications. The ultraviolet–ozone-treated pollen showed increased surface hydrophilicity, enhanced particle dispersibility and tunable control over Pickering emulsions, and improved cell adhesion (**Figure 3*b***). Defatted pine pollen was also used for macromolecular encapsulation (64), providing efficient and controllable drug loading and release.

As for artificial micromotors, defatted pollen grains usually are loaded with specific functional components that can propel the entities under external stimuli such as light, heat, magnetism, and chemical fuels. This has spurred remarkable progress in targeted drug delivery and sensing (64). There are superior advantages to using defatted pollen as micromotors. For example, sporopollenin in the exine layer is tough and stable enough to ensure the structural and functional integrity of the encapsulated substances even in harsh environments (22). For defatted pollen–based micromotor applications, one of the biggest challenges during preparation is the response to external stimuli. One approach is to coat conductive materials on the surface of defatted pollens to achieve their electrical property. Another, more effective, approach is to modify the pollen surface with magnetic materials, so as to respond to magnetic actuation, which is more suitable than chemical fuels–driven gas actuation in biomedicine. Sun et al. (72) encapsulated doxorubicin and Fe_3O_4 particles into the hollow sacs of pine pollen via vacuum loading, transferred pollen precisely to specific regions by reconfiguring magnetic fields, and killed cancer cells by releasing the drug using a fluid field generated by the rotating magnetic block (**Figure 3*c***). Zhang et al. (74) used a similar method to produce magnetic spore-based micromotors for toxin detection. Mayorga-Martinez et al. (22) prepared a series of defatted sunflower pollen–based micromotors via asymmetric deposition of thin-film metal layers (Au, Co, and Au) on one side using electron beam evaporation (**Figure 3*d***), which endowed the pollen with both magnetic actuation and charge-induced attraction for cancer cells and drugs. The uniform micron-scale structure and comprehensive sources of defatted pollens suggest the possibility of large-scale preparation and application of micromotors.

4.2. Diverse Applications of Sporopollenin Exine Capsules

Sporopollenin is one component of pollen and spore walls that offers highly effective protection to genetic material against environmental stressors. It can be extracted as SECs via available processing methods. Sporopollenin is composed predominantly of phenolic, alkane, and alkene groups and contains large amounts of crosslinked structures with strong covalent bonds that contribute to chemical and physical stability (75). Although chemical components and specific configurations of sporopollenin remain unknown, SECs have attracted scientific attention since the 1980s due to their remarkable resistance, structural and microsize consistency, biocompatibility, and natural abundance (76). SECs exhibit exceptional rigidity to chemical and physical attacks, making them useful in peptide synthesis as stable solid-phase support (77). After chemical and physical treatments, SEC morphology remains intact and stable without swelling or collapsing, facilitating their surface functionalization for chromatography techniques (78, 79). Further, SECs present several advantages over other commercial products, in consistent particle size, quality, and rapid exchange rate, especially as ion- or ligand-exchange mediums (79).

Along with the above-mentioned fundamental benefits, SECs offer several other benefits in biomedical engineering, including the ability to adhere to mucus, compatibility with living organisms, resilience to high temperatures and extreme surroundings, protection against UV irradiation and oxidation, and even the ability to traverse the intestinal wall (61, 80, 81). These characteristics have been used widely for encapsulation and targeted delivery of various active components, including drugs (82, 83), contrast agents (84), proteins (18), and potentially enzymes and DNA. In addition, a recent study revealed that SECs from camellia, cattail, and dandelion pollen could be broken down by the enzymes in human plasma, thus leading to release of their contents (85). SECs can be loaded with magnetite nanoparticles or filled with calcium phosphate and insoluble organic salts by generating compounds inside, through either a chemical reaction or a precipitation process (86).

L. clavatum SECs have been shown to be effective for encapsulation and controlled release of ibuprofen, masking its bitter taste (82). They have also been reported to encapsulate and trigger release of substances such as 5-fluorouracil (83), β-galactosidase (87), and vitamin D (88) for oral delivery. Sunflower SECs were reported to load BSA as a model drug with a practical loading efficiency of 22.3 ± 1.5 wt% and a theoretical maximum loading efficiency of 46.4 ± 2.5 wt% (18) (**Figure 4*a***). Due to their efficient photothermal conversion capability, they were also tested to control melanoma ablation in vitro/in vivo under near-infrared light irradiation (89) (**Figure 4*b***).

SECs from *Betula pendula* pollen were used for effective encapsulation and controlled release of imatinib mesylate (**Figure 4*c***). The drug-loaded SECs exhibit antiproliferative effects against leukemia cells, enabling their use in treatment (90). Ragweed pollen SECs were highlighted as potential oral vaccine delivery vehicles due to their immunomodulatory properties. Ragweed pollen SECs induce immune responses by activating dendritic cells and phagocytosis by macrophages. This was deduced after observing an increase in the secretion of proinflammatory cytokines (IL-6) and chemokines (IL-8 and MCP-1) as well as dendritic cell maturation markers (CD40, CD80, CD86, and MHC class II molecules) by measuring Caco-2 monolayer transepithelial electrical resistance (91) (**Figure 4*d***). Uddin et al. (69) showed that intramuscular injection of SEC spikes with the model antigen ovalbumin in mice led to a more robust and longer-lasting antibody response than injection with antigen alone. They also demonstrated that the biocompatible pollen SEC spikes had a more significant impact on immune response than pollen size and shape (**Figure 4*e***). *Chrysanthemum* pollen proved the cancer cells' capture capability after it was integrated into a nanocage-featured film. Jiang et al. (92) investigated the interaction between this film and MCF-7 (breast cancer) cells using peripheral blood mononuclear cells as a control and confirmed the selective matching effects of nanocage on cancer cell filopodia. The pollen nanocage–featured film was efficient in capturing 92% of rare cancer cells across various cancer types. This was attributed to the synergistic effect of nanocage–circulating tumor cell filopodia matching, large contact area, and strong adhesion forces between the cancer cells and pollen nanocage (**Figure 4*f***).

Furthermore, the 3D hierarchical structures of SECs are excellent inspirations for the biomimetic design of biosensors. Compared with traditional bulk materials, the hollow SECs provide high surface area and monodispersed size for available and facile surface functionalization. Moreover, SECs are uniform in morphology and biocompatible with an abundant supply from nature, rendering them desirable candidate materials for sensing platforms with high sensitivity. Wang et al. (24) first fabricated bioelectronic platforms combined with SECs (*L. clavatum* spores) as natural building blocks. The natural cellular materials, SECs, were surface functionalized with reduced graphene oxide (rGO) to obtain electronic conductivity via a facile fabrication method (**Figure 5*a*, subpanel *i***). This hierarchical platform was further involved in a field-effect transistor with an antibody-detection scheme to measure the concentration of targeted proteins with ultra-high accuracy. In contrast to traditional silicon-based devices, flexible and wearable biosensors have potential for more practical healthcare applications. Inspired by the rGO-coated SECs, Wang et al. (23) further extended the hybrid materials to flexible substrates with high selectivity and rigidity. Sunflower pollen–based SECs, functionalized with rGO, were deposited on a flexible polyethylene terephthalate substrate for prostate-specific antigen detection with outstanding sensing performance (**Figure 5*a*, subpanel *ii***). The feasibility of SECs as hierarchical building blocks in wearable biosensors has opened a new direction for wearable devices. That, combined with their great durability and elasticity, has also led to them being incorporated into wearable e-skin pressure sensors with high stability and high sensitivity (93) (**Figure 5*b***).

Besides the cellular microcapsules assembled into biosensors, the monodispersed sunflower SECs with unique spiky morphology also induced great interest in surface functionalization. The hollow SECs were coated with a platinum catalyst to generate oxygen bubbles via the catalytic

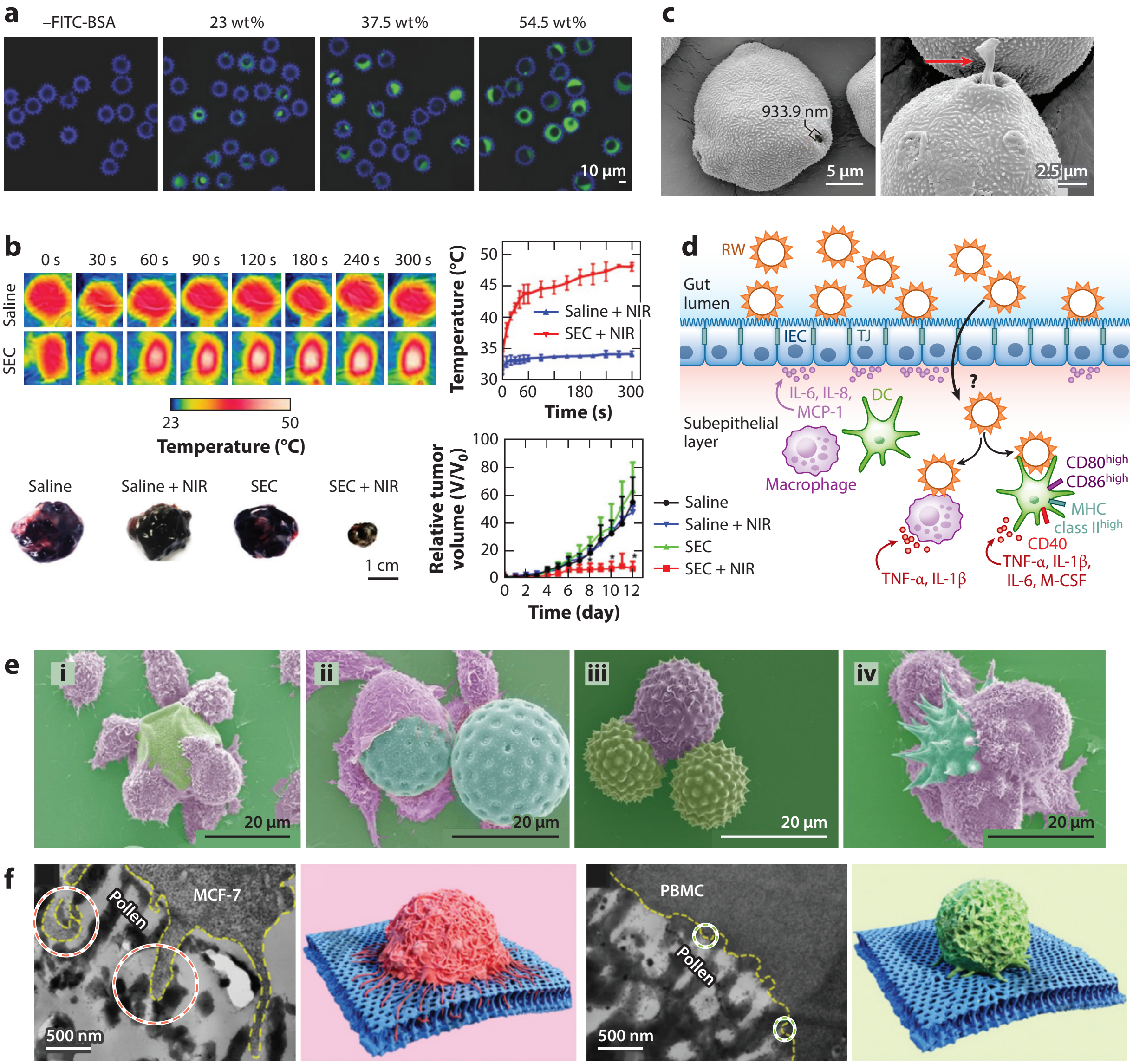

Figure 4

Representative biomedical engineering applications using SECs. (*a*) FITC-BSA-loaded sunflower SECs (reproduced with permission Reference 18; copyright 2017 John Wiley and Sons). (*b*) Photothermal effect of sunflower SECs applied in tumor inhibition (reproduced with permission from Reference 89; copyright 2021 Elsevier). (*c*) Imatinib mesylate crystal loaded *Betula pendula* pollen SECs (reproduced with permission from Reference 90; copyright 2017 Elsevier). (*d*) A proposed mechanism for ragweed pollen–based oral vaccination (reproduced with permission from Reference 91; copyright 2017 Elsevier). (*e*) Pseudo-colored SEM images of macrophage cells (*purple*) interacting with different pollen SECs (*i*, black alder; *ii*, lamb's quarters; *iii*, ragweed; *iv*, sunflower) (reproduced with permission from Reference 69; copyright 2020 John Wiley and Sons). (*f*) Preferential interactions of *Chrysanthemum* pollen–derived nanocage to MCF-7 cancer cell over PBMC (reproduced with permission from Reference 92; copyright 2020 John Wiley and Sons). Abbreviations: BSA, bovine serum albumin; FITC, fluorescein isothiocyanate; NIR, near-infrared; PBMC, peripheral blood mononuclear cell; RW, ragweed; SEC, sporopollenin exine capsule; SEM, scanning electron microscopy.

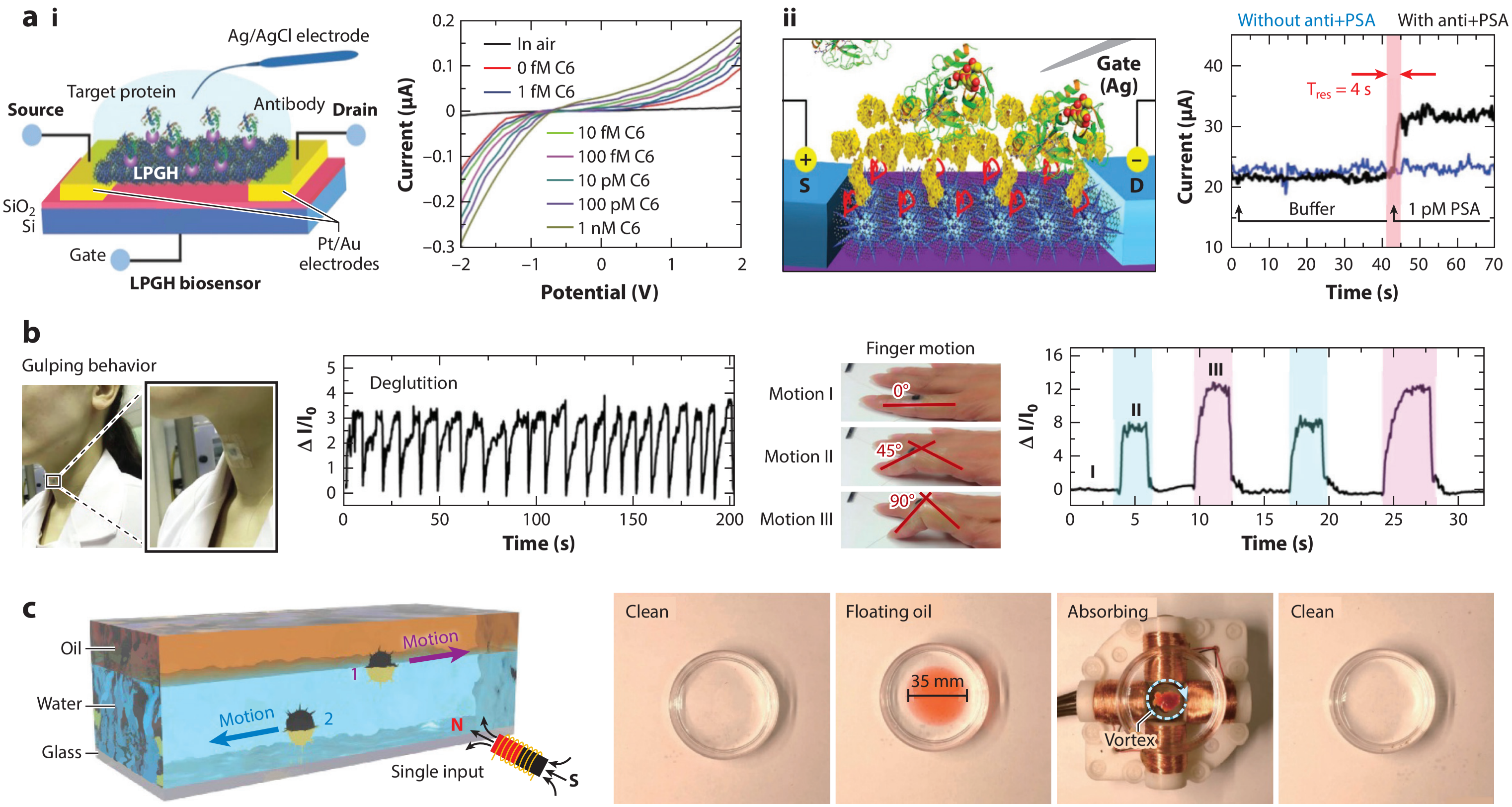

Figure 5

Biosensor-related applications of SEC particles. (*a*) SEC-based biosensors including the antibody detectors and flexible sensors for PSA detection (*i*, current–potential curves of the LPGH-based biosensor responding to different concentrations of C6 antigen; *ii*, response time of reduced graphene oxide–coated sunflower-based biosensor detection against 1×10^{-12} M target PSA) (reproduced with permission from References 23, 24; copyright 2016 John Wiley and Sons). (*b*) Signal detection of SEC-based electronic skin sensor (reproduced with permission from Reference 93; copyright 2017 Elsevier). (*c*) SEC-based magnetic microsubmarines for oil removal (reproduced with permission from Reference 94; copyright 2020 Elsevier). Abbreviations: LPGH, *Lycopodium clavatum* sporopollenin exine capsule–reduced graphene oxide hybrid; PSA, prostrate-specific antigen; SEC, sporopollenin exine capsule.

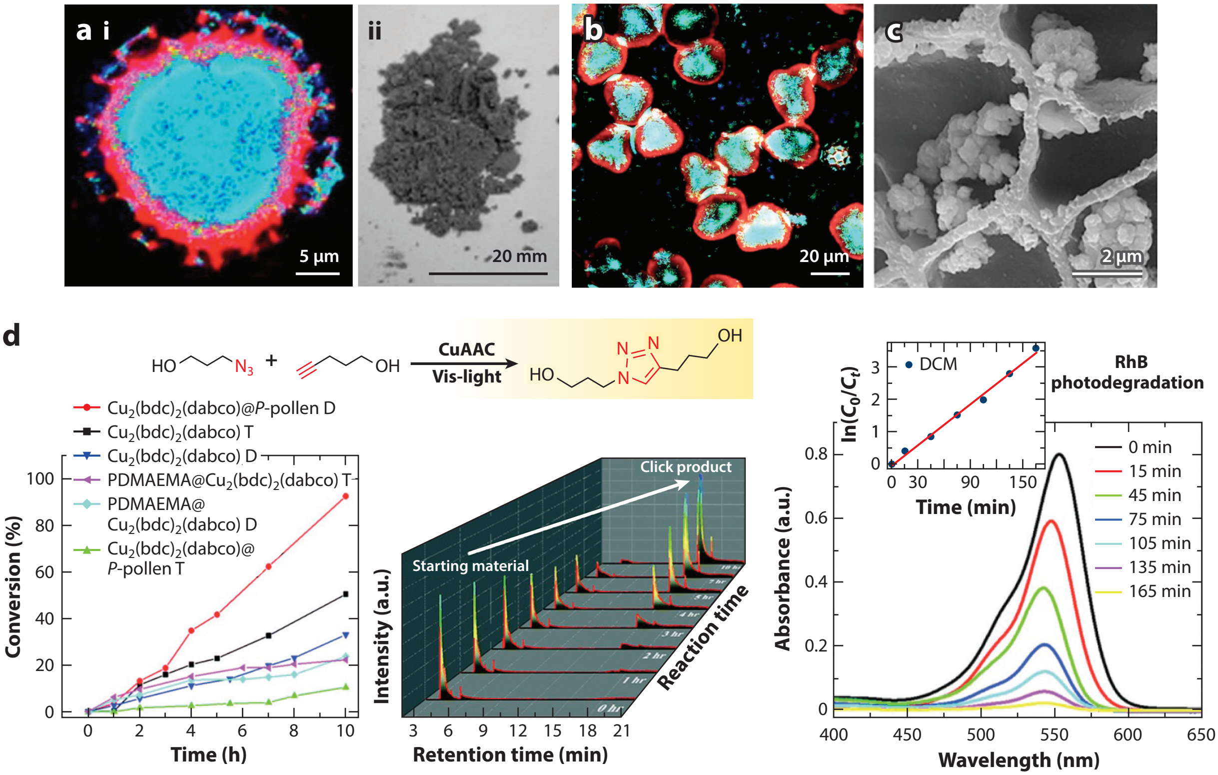

Figure 6

Pollen SEC applications in fields of food engineering and catalysis. (*a*) Cod liver oil–encapsulated *Lycopodium clavatum* SECs. (*i*) CLSM characterization (reproduced with permission from Reference 100; copyright 2010 Elsevier). (*ii*) SEC powder with 50 wt.% cod liver oil loaded (reproduced with permission from Reference 61; copyright 2011 Royal Society of Chemistry). (*b*) CLSM image of SEC containing oil–water mixture (reproduced with permission from Reference 97; copyright 2012 Royal Society of Chemistry). (*c*) Micrograph of the magnetic nanoparticles in SEC holes (reproduced with permission from Reference 98; copyright 2021 Elsevier). (*d*) Pollen SEC-based catalyst (reproduced with permission from Reference 99; copyright 2019 Royal Society of Chemistry). Abbreviations: CLSM, confocal laser scanning microscopy; CuAAC, copper(I)-catalyzed azide–alkyne cycloaddition; DCM, dichloromethane; RhB, rhodamine B; SEC, sporopollenin exine capsule.

decomposition of H_2O_2, which generated individual motion and improved heavy metal absorption and removal (17). Fe_3O_4 nanoparticles can also be coated on the SECs (*Ganoderma lucidum* spores) to form magnetic porous biohybrids to remove toxic heavy metals with remarkable efficiency (95). Sun et al. (94) also treated sunflower SECs with acidolysis and sequential sputtering as a noncontact method for environmental remediation to efficiently remove oil from water (**Figure 5*c***) and controlled removal of microplastics. As low-cost, abundant natural sources with environmentally friendly biodegradability, natural materials have gradually become vital functional materials. Given their unique properties, SECs in particular are expected to have great potential for ecological remediation, biosensor fabrication, and broader applications in the future of sustainable development.

The encapsulation capability of SECs has been further explored and applied in the field of food engineering. For example, *L. clavatum* SECs were studied to encapsulate fish oil (**Figure 6*a*, subpanel *i***), a commonly recognized healthy food containing omega-3 fatty acids eicosapentaenoic acid and docosahexaenoic acid. The mixture remained a dry powder even with a fish oil load as high as 50 wt% (**Figure 6*a***, **subpanel *ii***). Encapsulation greatly masked the unpleasant smell of the fish oil. It further enhanced the bioavailability of eicosapentaenoic acid (96). In addition, various unstable materials, such as easily oxidized polyunsaturated oils, the enzyme streptavidin-horseradish peroxidase, and alkaline phosphatase, were studied for encapsulation in SECs. Neither oil oxidation nor enzyme denaturation was observed following their full recovery (61), indicating that SECs possess great capabilities for food quality and freshness retention. SECs are also used to sequester and recover edible oils from the oil–water mixture (**Figure 6*b***). After their surfaces are acetylated, SECs become more efficient and can recover oil in almost quantitative yields. Aside from oil recovery, SECs can also release oil in stages through the repeated gentle pressure of a finger due to their robustness, elasticity, and porosity (97). Similarly, magnetic phosphonate-functionalized SECs (**Figure 6*c***) were used for stir bar sorptive dispersive microextraction of melamine in milk and milk-based food products (98). So far, all research regarding use of SECs in food applications has been based on *L. clavatum*. As more diverse SECs from different plant pollens are developed, it will be interesting and important to explore the performance of other kinds of pollen SECs in food applications.

Given their unique structures, pollen SECs also have great potential for use in catalysis. For example, rape pollen were used as pivots surface coated with an environment-responsive polymer, poly(2-(dimethylamino)ethyl methacrylate), which efficiently traps nano metal-organic frameworks (MOFs) and enhances MOF dispersibility in liquid-phase reactions. As a result, MOF photocatalytic performance was improved (99) (**Figure 6*d***). This work developed MOF catalysts by taking advantage of the unique features of natural plant pollen SECs, including high specific surface area and hollow structure. This opens up new possibilities in pollen-based catalysis research.

4.3. Pollen Microgel Transformation and 3D Printing

Despite advantages such as large packing capacity and time-/cost-effective fabrication as a cargo carrier, shell mechanical stability and chemical inertness have hindered SEC capsule development, especially when myriad smart cargo delivery systems with on-demand release kinetics have been proposed in the current market (65). To transcend this dilemma, researchers have explored the use of SEC capsules in studying pollen germination processes. During this exploration, they noticed that a part of the remodeling process involves the biochemical conversion of pectin into carboxylic acid group–rich pectate that advances surface charge density (101) (**Figure 7*a***). This results in the hydrogel-like intine acting as an osmotic stress motor that regulates reversible deformation of the whole pollen grain throughout its germination process. Inspired by this enzymatic conversion, a strategy similar to soapmaking was developed to transform hard pollen material into a stimuli-responsive microgel-like system (60). While various experimental tests and fine element analysis (FEA) models have shown good alignment, they unraveled ionic-induced swelling/deswelling behavior of sunflower pollen microgel under different pH conditions. This can fundamentally be associated with the modulus ratio between exine and intine, as well as pollen classes. According to gelation screening of a series of plant pollen sources, eudicot-based pollens had superior pH-responsive capability (microgel conversion) compared with other clades like *Lycopodium* and pine. The underlying principle was validated by comparing structural and mechanical properties of the representative gelated and nongelated class, camellia grain and *Lycopodium* spore, respectively (102). Finite element method models were established with the help of experimentally acquired material parameters, and deformation under pH conditions was predicted (**Figure 7*b***). The study showed a fundamental relationship between capsule structure symmetry, location of apertures presented on the capsule, and degree of change in exine mechanical properties after alkaline treatment

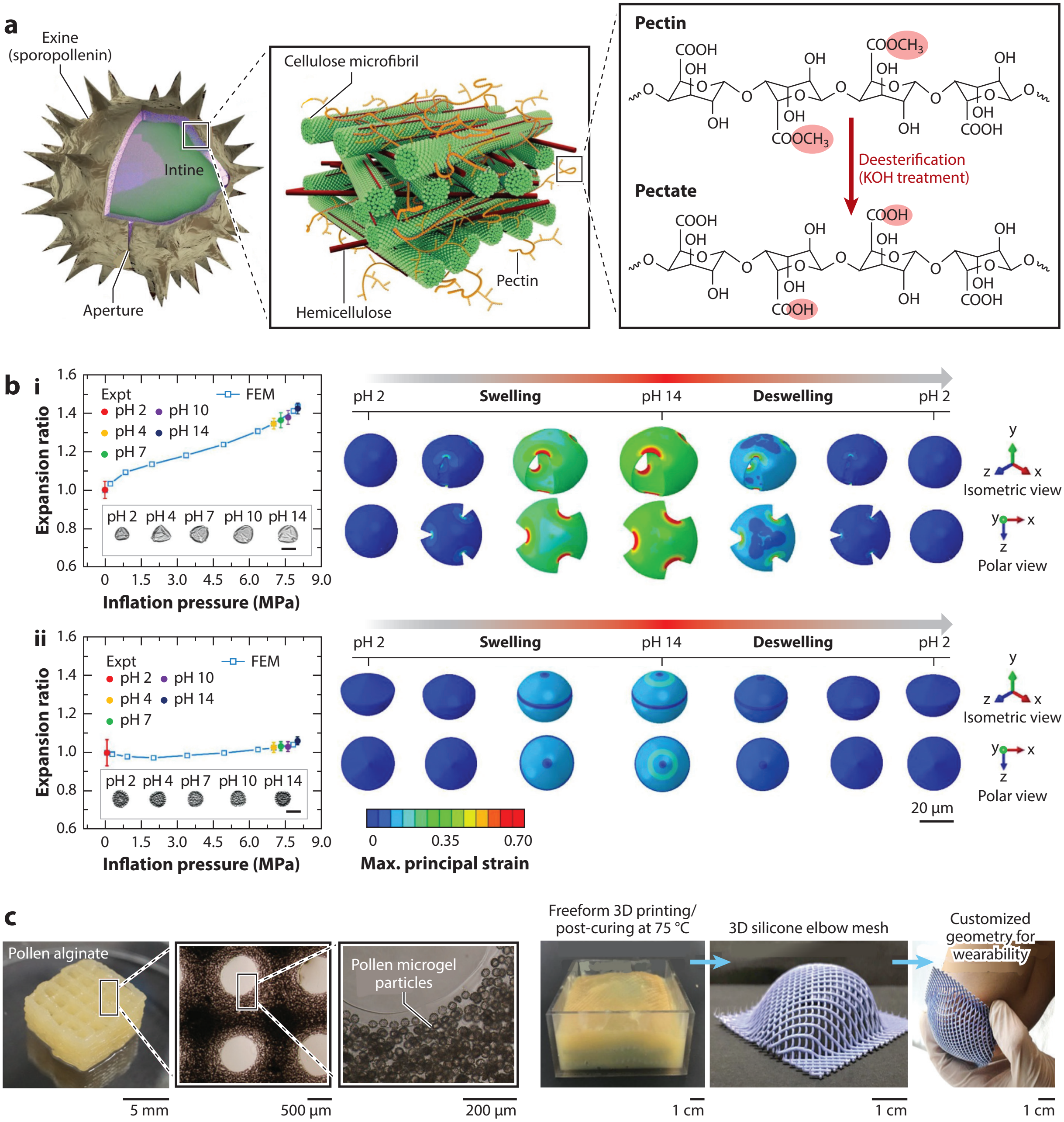

Figure 7

Physicochemical properties of pollen-derived microgel and associated studies. (*a*) Schematic illustration of stimuli-responsive pollen capsule behavior at multiple length scales (reproduced with permission from Reference 60; copyright 2020 Springer Nature). (*b*) Plot showing comparison of pH-induced expansion ratios in the experimental and finite element method–simulated results and strain contours for 6-h KOH-treated (*i*) *Camellia* pollen and (*ii*) *Lycopodium* spore (reproduced with permission from Reference 102; copyright 2022 Elsevier). (*c*) Multifunctional purposes of sunflower pollen–derived microgel in freeform 3D printing (reproduced with permission from Reference 44; copyright 2021 John Wiley and Sons).

in microgel formation of the material, providing guidance on material choice and use of underlying mechanics for different purposes.

An extended parametric study then investigated the effect of alkaline treatment on the physicochemical properties of sunflower pollen in terms of KOH concentrations used and duration of incubation. The sunflower microgel offered a maximum loading capacity approximately three times greater than that of the nongelated pollen capsule. The consistent and reversible swelling/deswelling behavior of the pollen microgel demonstrated its potential as a smart material in drug delivery and biosensor applications. Some proof-of-concept studies were also showcased. For instance, the pH-responsive capability of sunflower pollen–derived microgel was exploited in surface-based biosensor measurement (70). Through simple chemical functionalization, the study presented tethering of microgel on a glass slide with precise patterning and excellent functionality as a pH sensor. Considering the recyclability of bee pollen from waste and the reusability of microgel swelling properties, microgel-based biosensors are a sustainable candidate to reduce medical waste and environmental issues with high processibility.

Three-dimensional printing has driven revolutionary advancements in tissue engineering and regenerative medicine, owing in part to its ability to fabricate 3D constructs with customizable geometry and improved functionality for nutrient transport and construction of biomimetic microenvironments (103). Despite efforts to introduce copolymeric systems or additives to improve scaffold cell affinity while preserving good printing fidelity, development has been complicated and costly. Due to microgel shells' proven cell affinity and suspension capability (5), researchers proposed incorporating sunflower microgel into alginate-based ink for bio-scaffold printing (44). In the study, the microgel acted as a hydrogel ink reinforcement material with excellent printability and without nozzle clogging and particle aggregation issues commonly associated with ink suspension owing to its microscale size and spiky surface architecture. The microgel's excellent thixotropic behavior and cargo-carrying ability have also shown excellent potential in freeform 3D printing and pH-responsive hydrogel applications (**Figure 7*c***).

Structurally, the pollen microgel system resembles the core-shell architecture of traditional microgel systems, with distinct properties between the inner and outer layers, even though the internal layer consists mostly of environmental solvents. Exploration of more opportunities to fully exploit intra- and inter-particle interactions of pollen microgel may further advance the use of such sustainable biomaterials in further applications, such as cell encapsulation, surface modification, pollen microgel crosslinking, and heterogenic mixtures of pollen clades and physicochemical properties.

4.4. Humidity-Responsive Functional Pollen-Based Paper

Pollen papers are composed of dehydrated hollow pollen microgels that undergo structural collapse and flattening during the evaporation-induced papermaking process, which endows them with unique properties rarely seen in other polymer materials. Zhao et al. (25) found that pollen paper has an inherently laminated microstructure, an asymmetric surface micromorphology, and significant hydro-expansion capability (**Figure 8*a***). Synergetic coupling of these features brings powerful and anisotropic mechanical actuation in response to varying humidity levels, which can be adjusted easily by changing thickness and alkaline hydrolysis time to adapt to specific applications. As proofs of concept of the eco-friendly smart system, a bioinspired blooming flower and a walking robot based on pollen paper have been demonstrated successfully.

Pollen paper boasts high surface roughness, making it an excellent material due to its translucent optical properties and superior digital printability, similar to traditional wood-derived papers. To eliminate the issue of moisture damage, Zhao et al. (45) significantly improved the

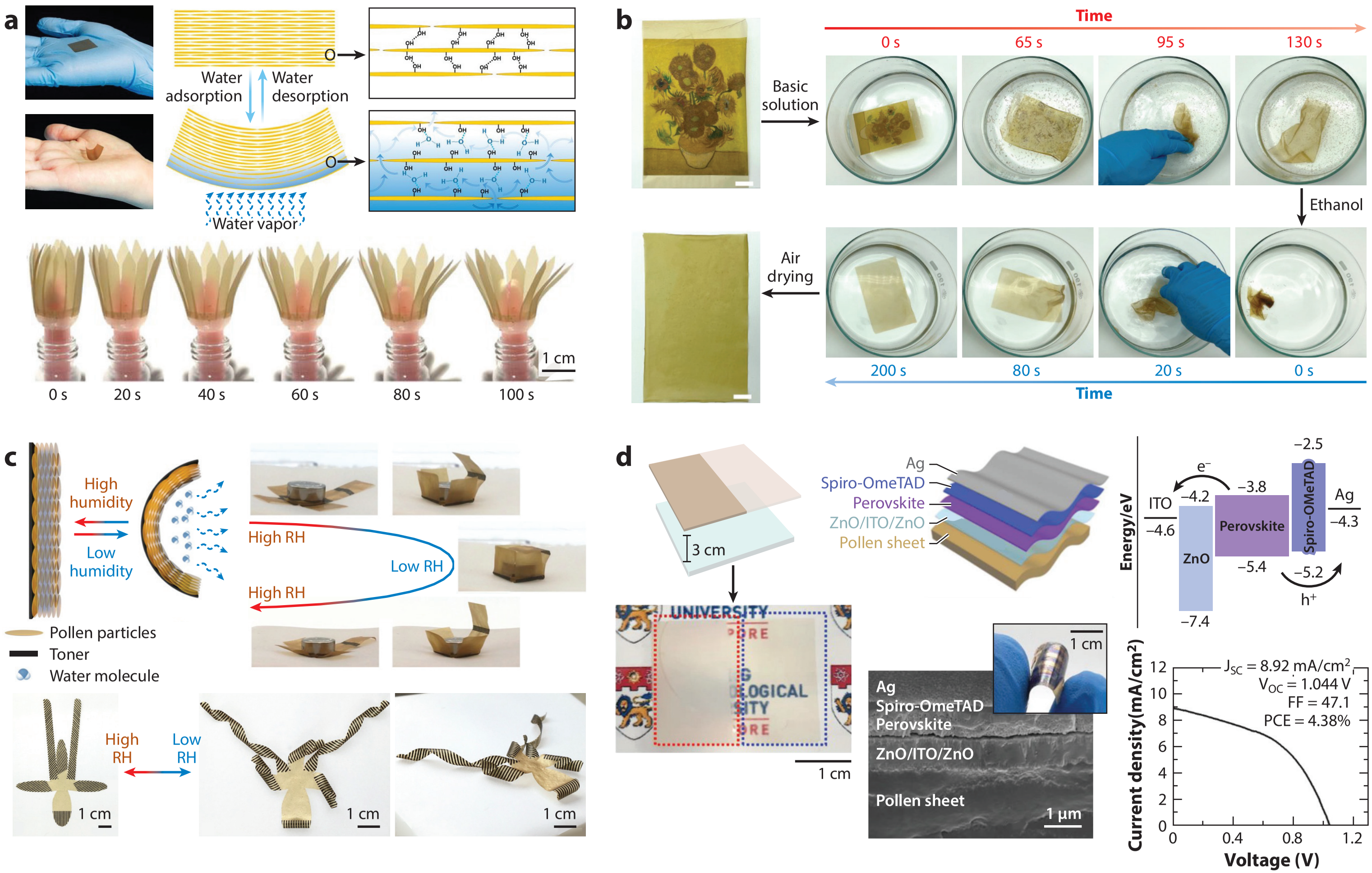

Figure 8

Pollen paper–based applications. (*a*) Powerful and anisotropic response of pollen paper to humidity and its biomimetic actuator application (reproduced with permission from Reference 25; copyright 2020 National Academy of Sciences). (*b*) Erasure of the pollen paper printed with toner during immersion in basic solution (reproduced with permission from Reference 45; copyright 2022 John Wiley and Sons). (*c*) Digital printing of pollen papers for an eco-friendly, programmable, and scalable shape-morphing natural system (reproduced with permission from Reference 104; copyright 2021 National Academy of Sciences). (*d*) Inherent optical properties of pollen papers for optoelectronic devices (reproduced with permission from Reference 105; copyright 2021 John Wiley and Sons).

hydrostability of the pollen paper through a one-step acid treatment, making it insensitive to various humidity conditions. Meanwhile, hydrostability could be switched easily by using acidic and basic solutions for on-demand erasure of printed toner and in situ recycling and reprinting, which cannot be achieved with conventional wood-derived paper (**Figure 8*b***). Taking advantage of the difference in hygroscopic properties between pollen paper and printed toner, they also developed an eco-friendly and scalable shape-morphing material with autonomous, on-demand deformation and programmable shape evolution, integrating easy-to-process pollen biomass with cost-effective digital printing technology (6). In this bilayer system, changes in humidity induce a strain mismatch between the moisture-active layer (pollen paper) and the moisture-inactive layer (toner), resulting in macroscopic deformation (**Figure 8*c***). Complemented by computational simulations, quantitative and mechanistic insights into the biomaterial's characteristics for creating complex deformation, including coiling, rolling, and folding, were gained. Moreover, the hygro-morphing shapes of the printed pollen paper can be "frozen" through postprocessing coatings.

Pollen grains possess species-specific architectural features, such as spiky appendages, nanoscale pores, and tripartite structures. These features give pollen self-assembled papers unique optical properties that differ from those of existing fiber-based materials, whose optical properties arise from entangled network architectures. Building on this, Hwang et al. (105) created a pollen paper substrate with high transparency (>92%) and high haze (>84%), enabled by the intrinsic micro- and nanoscale structural features of constituent pollen microgels that facilitate forward light scattering. This substrate could modulate light–matter interactions without extensive processing, making it a promising photonically active substrate for a perovskite solar cell, leading to a new class of sustainable optoelectronic devices (105) (**Figure 8*d***). Moreover, the flexible pollen-derived substrates are also feasible for other flexible and stretchable electronic devices that can be mounted on the skin for health monitoring (26).

The potential of pollen papers has been demonstrated in various applications, such as smart actuators, soft robots, optoelectronic substrates, and wearable devices. However, pollen paper must be explored further to optimize its properties, including relatively high environmental sensitivity, weak wet strength, and low transmittance compared to other biopolymer films or papers. Nonetheless, it holds substantial potential as a unique and innovative platform for a broad range of sustainable applications, particularly considering it offers a simple, low-cost, and scalable solution to synthetic polymers. Integrating other materials with pollen paper and using its characteristic physical, chemical, structural, morphological, and responsive features may lead to advanced functionality and performance, resulting in the development of pioneering composite materials.

4.5. Ecofriendly Sponge from Plant Pollen

Porous 3D scaffolds have gained increasing attention, with multiple functions for various applications. Based on soft pollen microgel particles with a micro/nano hierarchical structure, further exploration of pollen-derived scaffolds has been motivated by the self-actuating pollen papers (25). Inspired by the traditional cryogel fabrication process, soft and hydrophilic pollen microgel particles were self-assembled to form porous scaffolds via freeze-drying (**Figure 9*a***). Large amounts of hydroxyl and carboxyl groups are exposed on the surface of pollen microgel particles, which form numerous hydrogen bonds in pollen-derived sponges during the ice growth and vacuum freeze-drying process. The freezing induces pollen wall lamination owing to ice crystal nucleation. Following lyophilization, the sublimation of ice crystals under vacuum resulted in 3D porous architectures. The freezing temperature strongly influences the fabrication quality of pollen-derived sponges, and more homogeneous sponge structures with few defects and smooth walls were obtained at –20°C. Pollen microgel particles act as colloidal building blocks to form porous structures

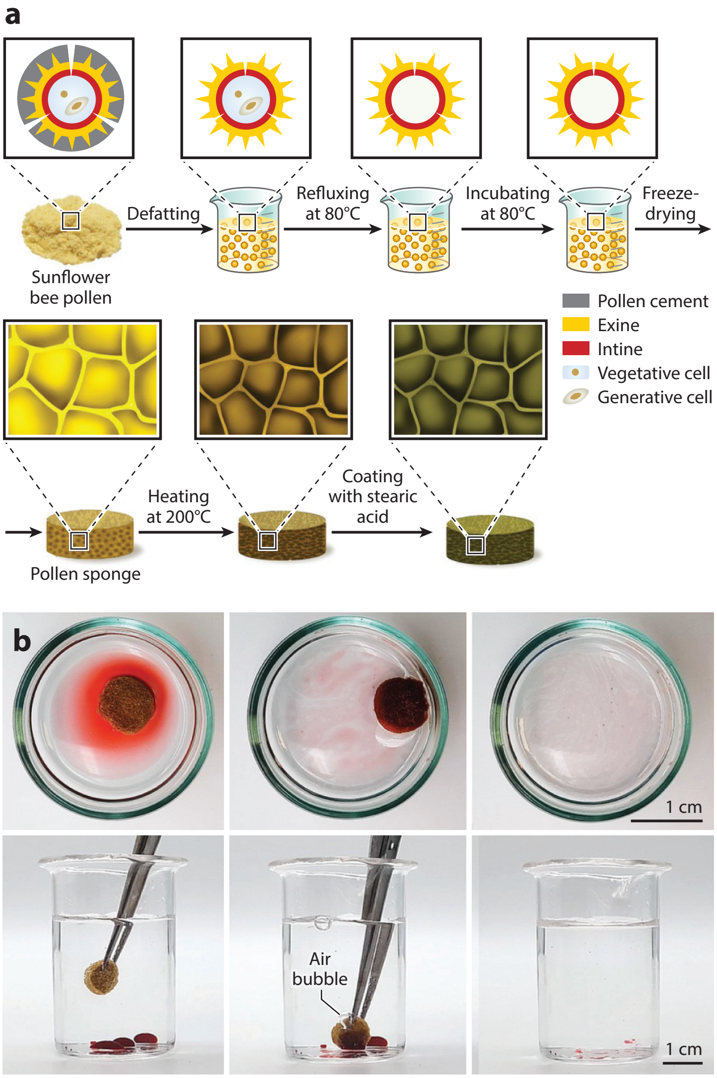

Figure 9

Fabrication process and application of pollen sponges. (*a*) The fabrication process of pollen sponges sourced from raw bee pollen grains. (*b*) Pollen sponges were applied to absorb oil in the water for environmental remediation. Reproduced with permission from Reference 27; copyright 2021 John Wiley and Sons.

with tunable properties, whose mechanical properties can be enhanced via thermal annealing. The hydrophobic functional groups can be involved in oil-absorbing applications for environmental remediation (**Figure 9*b***). However, the high dependence on freeze-drying hinders industrial fabrication of pollen-derived sponges due to size limitations of freeze-driers. Moreover, the pollen-derived sponges obtained by Hwang et al. (27) possessed worse hydration mechanical properties, requiring further heat treatment. Although pollen-derived sponges possess great biodegradability and abundant source supply, fabrication remains time consuming and energy intensive. With growing concern about the energy crisis worldwide and more attention on sustainable development, a more facile and energy-saving process is needed to develop pollen-derived scaffolds with more stable structures, as versatile materials for a broader range of environmental science and biomedical applications.

5. CONCLUSION AND OUTLOOK

Using materials science and chemical engineering processes, ordinary plant pollen can be converted into versatile building components, providing potential alternatives to various existing materials, such as paper, sponges, and even plastics, currently derived from unsustainable sources. The recent emphasis on a comprehensive and interdisciplinary approach to monitoring total environmental pollen diversity paves the way for investigating pollen characteristics for industrial uses (UN Sustainable Development Goal 9: Industry, Innovation, Infrastructure). This multifaceted approach could address critical global challenges, including the UN Sustainable Development Goals, while also raising social and political consciousness about these small but significant and intriguing particles.

The materials-focused perspective of these functions exemplifies the emerging notion of the cross-economy, which aims to achieve more than just sustainability. This concept entails transforming basic materials, like pollen, into various building elements that can encourage substitution of current industries and generate high-value industrial applications through eco-friendly processes, ultimately leading to a future that surpasses sustainability.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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