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## On the use of bioprecursors for sustainable silicon-based anodes for Li-ion batteries

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The growing demand for sustainable and high performance Li-ion batteries has driven research into new bioprecursors for battery components. Among potential candidates for next-generation negative electrodes, silicon stands out due to its high theoretical capacity compared to conventional graphite. However, the challenges associated with silicon, including volume expansion and sustainability concerns, have limited its widespread adoption. In this context, bioprecursors have garnered significant attention as a green and renewable alternative for producing high performance silicon-based anodes. This perspective article explores the potential of bio-based precursors, specifically rice husks, diatom frustules, and other biomass-derived materials, for the development of sustainable silicon anodes for Li-ion batteries. While biowaste-derived silicon materials—such as rice husks—have been widely explored, this work contrasts them with the emerging potential of harnessing the morphological plasticity of diatom microalgae as a novel route to design biosilicas with tunable nanostructures, providing a controlled and sustainable pathway for high-performance Si-based anodes. We discuss the chemical processes, environmental benefits, and future directions for enhancing the performance of Si-based electrodes derived from these natural materials.

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## 1 Introduction

Lithium-ion batteries (LIBs) have revolutionized the portable electronics industry since their commercialization in the early 1990s, becoming the standard energy storage solution for devices ranging from mobile phones and laptops to electric vehicles (EVs).<sup>1</sup> Their widespread success stems from their high energy density, long cycle life, and relatively light weight, making them particularly well-suited for applications where size, weight, and power efficiency are critical.<sup>2</sup>

Commercial LIBs use a range of materials as positive electrodes, but graphite is predominant on the negative side due to its excellent electrical conductivity and long-term cycling stability. Operating within a voltage range of approximately 0.01–0.3 V vs. Li/Li<sup>+</sup>, graphite enables efficient lithium intercalation—theoretical capacity of 372 mA h g<sup>−1</sup>—while minimizing structural degradation, therefore offering a well-balanced combination of energy density and durability. Its affordability and well-established manufacturing processes further reinforce its dominance in the market. However, higher energy density anode materials are needed to meet the growing demands of next-generation LIBs, particularly for EVs and grid-scale energy storage.<sup>3</sup> This necessity has driven extensive research into alternative or composite materials capable of increasing energy density without compromising stability or conductivity.<sup>4</sup>

Silicon (Si) has emerged as a promising alternative—or supplement—to graphite at the negative electrode. Si presents a theoretical capacity of about 4200 mA h g<sup>−1</sup> (ref. 5)—over ten times that of graphite—and low operating voltage (about 0.1 V vs. Li/Li<sup>+</sup>). Hence, silicon's ability to store a higher quantity of lithium ions should *a priori* significantly improve the battery's overall energy capacity, increasing the range of EVs or extending the usage time for portable electronics. However, the practical application of Si as an anode material faces important challenges, mainly related to the significant volume expansion of up to 300% that silicon undergoes during lithiation reaction, which causes mechanical stress, cracking, and degradation of the material. This expansion not only reduces the cycle life of the battery but also hinders the development of durable, high-performance electrodes. To improve the performance of Si anodes, the synthesis of Si nanoarchitectures capable of providing strain relaxation to prevent electrode pulverization has been proposed.<sup>6</sup> In parallel, nanostructured silicon oxides (SiO<sub>x</sub>,  $x \leq 2$ ) have attracted significant attention due to their ability to deliver capacities close to that of pure silicon while offering more stable electrochemical performance.<sup>7</sup> SiO<sub>x</sub> provides a compromise between high capacity and structural stability by forming a mixed-phase composite of lithium oxide and lithium silicates during cycling. These phases act as mechanical buffers against silicon's volume expansion, thereby improving cycle life.

As research efforts advance, the broader landscape for silicon-based anodes is increasingly shaped by considerations

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of scalability, cost, and sustainability. Global demand for silicon is rising rapidly—driven largely by the growth of EVs—with production expected to increase from 3.45 million tons in 2025 to 4.49 million tons by 2030.<sup>8</sup> Yet, despite this expanding market, a major limitation to the adoption of Si-based anodes lies in the high manufacturing cost required to engineer particles capable of withstanding extreme volume fluctuations during cycling.<sup>9</sup> Going forward, success in commercial deployment will require manufacturers to strike a balance between cost competitiveness, product performance, and sustainability.<sup>8</sup>

### 1.1 Sustainable Si-based precursors

Silicon is the eighth most common element in the universe (by mass) and of the most abundant materials in the Earth's crust. As such, silicates have historically been widely used in a myriad of applications. In addition to those, pure silicon is also required in fields that are either critical or in expansion for our current society, such as electronics or photovoltaics. Since it seldom occurs in its pure form, inorganic resources, like quartz, are commonly used as raw materials. While one could obviously simply rely on them for the production of silicon based electrode materials for LIBs, the state-of-the art processing and purifying protocols used in semiconductor electronics and photovoltaic panels are very energy intensive<sup>10</sup> (e.g. the Siemens process achieving a purity of 99.9999%). Also, traditional carbothermal reduction requires temperatures close to 1900 °C and generates substantial CO<sub>2</sub> emissions.<sup>11,12</sup> Thus, alternative silicon resources that allow for lower-cost and more energy-efficient processing are required, especially when targeting energy-related applications. In this regard, bioprecursors are promising, as their variability could enable the controlled synthesis of (micro)nanostructured silicon, a key factor in anode performance.

Over the past decade, significant progress has been made in synthesizing porous Si-based structures from SiO<sub>2</sub>-rich bioprecursors and clays using energy-efficient, low-carbon footprint metallothermic processes.<sup>13,14</sup> Among these, magnesiothermic reduction reaction (MgTR) has emerged as the most widely adopted synthesis route.<sup>15</sup> Conventional and molten salt assisted-MgTR typically operate at temperatures between 250 °C and 650 °C, enabling the formation of Si-based porous structures with enhanced electrochemical properties.<sup>16,17</sup> Renewable bioprecursors—such as rice husks, bamboo, and microalgae exoskeletons—offer a sustainable and cost-effective alternative to traditional mineral sources, providing abundant SiO<sub>2</sub> and enabling high-purity silicon production *via* MgTR with a low environmental impact.

The feasibility of converting bioprecursors into commercially viable materials is exemplified by coconut shell charcoal, which has been industrially processed into high-value activated carbon.<sup>18–20</sup> This material is used as an electrode in supercapacitors, demonstrating the practical potential of biomass-derived resources and their ability to bridge sustainable material sourcing with large-scale technological deployment. Building on the sustainable potential of bioprecursors for real applications, this perspective explores the use of specific

natural sources—such as siliceous plants and the exoskeletons of microalgae—for the production of silicon-based negative electrodes for LIBs. These materials, when processed *via* MgTR, offer an eco-friendly and cost-effective route to high-purity silicon. The paper reviews recent advancements in the development of bioprecursor-derived silicon electrodes and discusses key challenges related to controlling material quality, achieving high purity, and ensuring scalability. Finally, future research directions are proposed to establish bioprecursors as viable building blocks for high-performance, environmentally sustainable LIB electrodes.

### 1.2 Si bioprecursors: plants and protists

Silicon, primarily in the form of silicate minerals, constitutes more than 25% of the Earth's crust. Through chemical and physical weathering processes in soils, these minerals release *ortho*-silicic acid (H<sub>4</sub>SiO<sub>4</sub>) into solution. Once dissolved, silicon may form secondary clay minerals, be transported to aquatic systems such as rivers and oceans, or be absorbed by the vegetation.<sup>21,22</sup> It is estimated that terrestrial plants and diatom microalgae store between 60–200 Tmol per year and approximately 240 Tmol per year of silica,<sup>23</sup> respectively, underscoring their crucial role as major biological reservoirs in the global silicon cycle.<sup>24</sup>

At pH values typical of most soils, H<sub>4</sub>SiO<sub>4</sub> remains soluble up to concentrations of ~2 mM.<sup>25</sup> In plant shoots and leaves, the accumulated H<sub>4</sub>SiO<sub>4</sub> spontaneously polymerizes into amorphous silica (SiO<sub>2</sub>·*n*H<sub>2</sub>O) through a process known as biosilicification.<sup>26</sup> Many higher plants, especially those belonging to the Poaceae family, such as rice, sugarcane, reed and bamboo, are known for their ability to actively accumulate silicon. Their elevated silicon content enhances resistance to both biotic and abiotic stresses, improves light-interception and reduces transpiration losses.<sup>27</sup> Depending on the species, silicon can constitute between 0.1 and 10% of a plant's dry weight, with rice being among the most efficient silicon accumulators.<sup>28</sup>

Similar biosilicification processes also occur in aquatic organisms. Biosilicas are found in the spicules of marine sponges<sup>29–31</sup>—multicellular animals—as well as in the exoskeletons of radiolarians<sup>32</sup> and diatom microalgae.<sup>33–35</sup> Unlike sponges, radiolarians and diatoms are unicellular eukaryotes belonging to the kingdom Protista. These protists are capable of producing highly ordered silica architectures at the nano- and micro-scale, making them particularly interesting as renewable sources of nanostructured silica for technological applications.

After the removal of organic biomass through thermal or acid treatment, the remaining inorganic component of siliceous plants, radiolarians, and diatoms consists primarily of silica, along with various inorganic impurities. Table 1 provides a comparative overview of these inorganic fractions across a range of plant- and protist-derived sources. Key parameters such as SiO<sub>2</sub> content, major inorganic impurities, particle size, and surface area are highlighted as benchmarks for evaluating the suitability of each bioprecursor for use in LIB negative electrodes. The data indicate that most bioprecursors exhibit



**Table 1** Composition and properties of the inorganic fraction of various siliceous bioprecursors after removal of their organic content

| Bioprecursor | Inorganic derivate               | SiO <sub>2</sub> content (wt%) | Main impurities                                                                                                                                                      | Particle size (μm) | Surface area (m <sup>2</sup> g <sup>-1</sup> ) | Ref.      |
|--------------|----------------------------------|--------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|------------------------------------------------|-----------|
| Plants       | Reed leaves ash                  | 80.2–98                        | Na <sub>2</sub> O, MgO, Al <sub>2</sub> O <sub>3</sub> , P <sub>2</sub> O <sub>5</sub> , SO <sub>3</sub> , Cl, K <sub>2</sub> O, CaO, Fe <sub>2</sub> O <sub>3</sub> | —                  | —                                              | 37 and 38 |
|              | Sugarcane ash                    | 54.9–88.7                      | Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , (PO <sub>4</sub> ) <sup>3-</sup> , NiO, CaO, K, MgO, MnO, Na                    | 5–500              | 5.9                                            | 39 and 40 |
|              | Bamboo leaves ash                | 50.2–94.1                      | Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , CaO, MgO, K <sub>2</sub> O, Na <sub>2</sub> O, TiO <sub>2</sub> , SO <sub>3</sub> , Cl             |                    |                                                | 41–45     |
|              | Rice husk ash                    | 86–99                          | CaO, MgO, K <sub>2</sub> O, Na <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , MnO, P <sub>2</sub> O <sub>5</sub> , ZnO            | 0.03–100           | 7–352                                          | 46–54     |
| Protists     | Radiolarian                      | 90                             | Na, Mg, Al, Cl, K <sup>a</sup>                                                                                                                                       | N.A.               | N.A.                                           | 55        |
|              | Diatomaceous earth               | 80–93.5                        | Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , CaO, MnO, P <sub>2</sub> O <sub>5</sub> , K <sub>2</sub> O, Na <sub>2</sub> O   | 8–20               | 3.8                                            | 56–61     |
|              | Frustules from harvested diatoms | 94.8–97.9                      | Na, Mg, Al, P, K, Ca, Fe <sup>a</sup> , Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>                                                              | 36                 | 8.6                                            | 62 and 63 |
|              | Frustules from cultured diatoms  | 98–99.15                       | Na, Mg, Al, K, Ca, Fe <sup>a</sup>                                                                                                                                   | 4–5                | 16.9–214                                       | 64–66     |

<sup>a</sup> Results from elemental analysis.

high SiO<sub>2</sub> content, with rice husks and cultured diatoms showing the highest levels of purity. Surface area and particle size vary significantly, reflecting differences in biological origin and structural complexity.

## 2 Siliceous plants

Reed, sugarcane, bamboo and rice are among the most relevant siliceous plants with potential as bioprecursors for Si-based negative electrodes.

### 2.1 Reed

Reed plants, Fig. 1a, commonly found in temperate wetland regions, are used for making mats and as roofing material. When thermally processed, their leaves yield ash with a silica content ranging from 80% to 98%. Although the use of reed leaves as bioprecursors for Si-based electrode materials is relatively underexplored, initial studies have shown promising results. In 2015 Liu *et al.* pioneered a simple three-step synthesis of porous Si/C composite anodes from reed leaves, involving: (1) thermal decomposition of the organic matter, (2) SiO<sub>2</sub> MgTR to produce Si, and (3) carbon coating using glucose as the carbon source.<sup>36</sup> The resulting Si/C composite exhibited a high surface area of 224 m<sup>2</sup> g<sup>-1</sup> and 0.70 cm<sup>3</sup> g<sup>-1</sup> pore volume, delivering an initial lithiation capacity of 4000 mA h g<sup>-1</sup>, and 2435 mA h g<sup>-1</sup> after delithiation. Although capacity loss during the first 50 cycles was observed, the results achieved are promising as a discharge capacity of approximately 1050 mA h g<sup>-1</sup> was still maintained after 200 cycles, demonstrating its potential for application in LIB anodes.

A more recent study by Wang *et al.* demonstrated that SiO<sub>2</sub> derived from reed can be used in a modified MgTR process, assisted by CO<sub>2</sub> gas, to produce Si/C composites.<sup>67</sup> The resulting materials exhibited surface areas from 137 m<sup>2</sup> g<sup>-1</sup> to 343.9 m<sup>2</sup> g<sup>-1</sup> and pore volumes between 0.21 cm<sup>3</sup> g<sup>-1</sup> and 0.45 cm<sup>3</sup> g<sup>-1</sup>. Interestingly, the composite with the largest surface area delivered the best performance. However, the initial discharge

capacity of 1260 mA h g<sup>-1</sup> at 500 mA g<sup>-1</sup> decreased to 650 mA h g<sup>-1</sup> after 200 cycles, indicating that further optimization is needed to enhance cycling stability.

### 2.2 Sugarcane bagasse

Sugarcane, Fig. 1b, is one of the world's major sugar crops, generating approximately 10 dry tons of fibrous residue (bagasse) for every ton of cane sugar produced. Brazil, the largest sugarcane producer, processes around 657 million tons annually.<sup>68</sup> Bagasse is primarily burned as fuel in boilers for sugar and ethanol production. This combustion process generates about 3–12 million tons of ash per year, a low-cost byproduct that is underutilized and frequently discarded in landfills.

Sugarcane bagasse ash consists of up to 88.7% SiO<sub>2</sub>, along with minor quantities of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and other oxides, making it a promising silica source. Recently, Chen *et al.* demonstrated its viability as a precursor for electrode materials by using sugarcane leaves as both silica and carbon source to synthesize nano Si-SiO<sub>x</sub>@C composites *via* molten-salt-assisted aluminothermic reduction (ALTR) process.<sup>69</sup> The resulting electrode exhibited remarkable electrochemical performance, delivering a reversible capacity of 1562.8 mA h g<sup>-1</sup> after 400 cycles at a current density of 200 mA g<sup>-1</sup>, and 678.6 mA h g<sup>-1</sup> capacity after 3000 cycles at 2 A g<sup>-1</sup>, thus highlighting its potential as high-performance negative electrode material.

### 2.3 Bamboo leaves

Bamboo, Fig. 1c, widely distributed across Southeast Asia. As a fast-growing perennial, it covers over 14 million hectares worldwide, primarily in tropical and subtropical regions. While its culms and roots have established commercial uses, bamboo leaves are largely discarded as waste, with an estimated 107 million metric tons generated annually in China, India, and Japan alone.<sup>70</sup> Notably, bamboo leaves contain ~17.4–23.1 wt% silica, depending on species, climate, and growth conditions.<sup>71</sup>



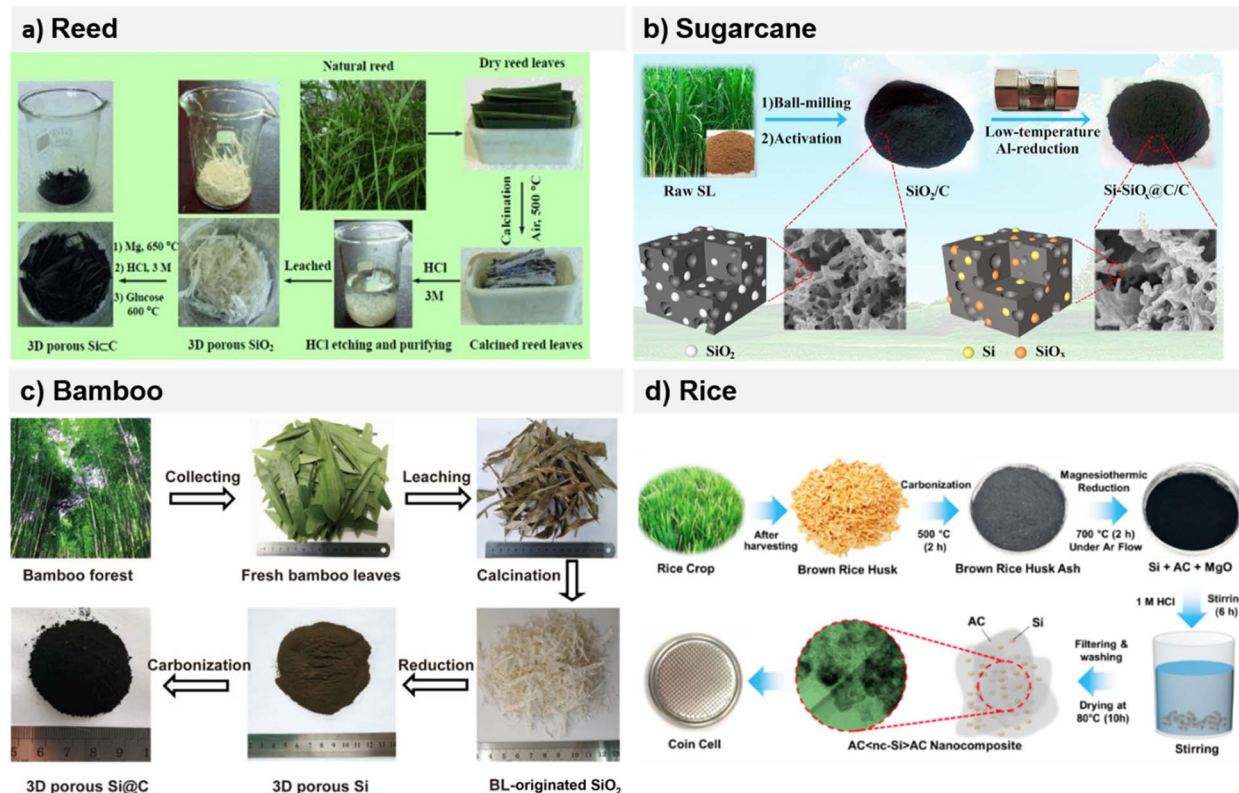


Fig. 1 Representative processes reported for the utilization of siliceous plants as bioprecursors for Si-based anodes: (a) reed plant, reproduced from ref. 36 with permission, copyright [2015], (b) sugarcane, reproduced from ref. 69, copyright © 2021, (c) bamboo, reproduced from ref. 75, copyright © 2022, and (d) rice, reproduced from ref. 80, copyright © 2019.

The potential of bamboo leaves as a source for Si-based anode materials is gaining increasing attention. In 2015, Xu *et al.* synthesized  $\text{SiO}_2/\text{C}$  nanocomposites *via* a simple thermal decomposition process at 700 °C under a nitrogen atmosphere, achieving an initial discharge capacity of 586.2 mA h g<sup>-1</sup> at 200 mA g<sup>-1</sup>, which decreased to 294.7 mA h g<sup>-1</sup> after 200 cycles.<sup>72</sup> Wang *et al.* later developed Si nanoparticles from bamboo leaves through MgTR, yielding an initial discharge capacity of 2983 mA h g<sup>-1</sup> at 0.2C, which decreased to 1800 mA h g<sup>-1</sup> after 100 cycles.<sup>73</sup> Wei *et al.* further developed Si/ $\text{SiO}_x/\text{C}$  composites *via* AlTR,<sup>74</sup> reporting an initial discharge capacity of 1437 mA h g<sup>-1</sup>, and of 1075 mA h g<sup>-1</sup> after 350 cycles at 200 mA g<sup>-1</sup>. More recently, Wu *et al.* synthesized Si/C composites by drying and leaching bamboo leaves, followed by MgTR and carbon coating. The resulting anode exhibited an initial reversible capacity of 1633 mA h g<sup>-1</sup> at 500 mA g<sup>-1</sup>, with nearly 100% capacity retention after 50 cycles.<sup>75</sup>

Despite being at an early stage, research on bamboo-derived Si anodes has demonstrated significant potential and would require further systematic investigations.

## 2.4 Rice

Rice (*Oryza sativa*), Fig. 1d, is the second most cultivated crop species globally, with an annual production of approximately 700 million metric tons. A significant byproduct of rice processing is rice husks (RHs), which represent one of the largest

volumes of agricultural residues, with an estimated global output of 150 million tons per year.<sup>76</sup> RHs are predominantly organic, composed of cellulose (35%), hemicellulose (25%), lignin (20%), and crude protein (3%), alongside an inorganic fraction (17%). Upon combustion, RHs produce rice husk ash (RHA), which primarily consists of amorphous hydrated silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), accounting for 80–99% of the ash content.<sup>77,78</sup> The remaining composition consists of various metal oxides, including  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{Al}_2\text{O}_3$ ,<sup>79</sup> as indicated in Table 1.

Owing to the vast global availability of RHs, the literature on their use as silica source for Si-based anodes is significantly more developed compared to other siliceous plants, such as reed, bamboo, or sugarcane. As a result, a greater number of studies have investigated how processing parameters—particularly calcination temperature and MgTR conditions—affect the structure, silica content, and conversion efficiency of RH-derived silica into silicon.<sup>80</sup>

The silica content and quality within RHA are significantly influenced by the conditions of calcination. Studies have shown that silica content ranges from 25.81% in untreated RHs to 83.66% when calcined at 500 °C, and reaching up to 92.9% when calcined at 800 °C. This underscores the importance of carefully tuning processing parameters.<sup>51</sup> The combustion temperature of RHs plays also a crucial role in determining the phase composition of the resulting silica. In its natural state,



silica in RHs is amorphous; however, upon heat treatment, it can transform into various crystalline polymorphs. Amorphous  $\text{SiO}_2$  is typically retained when RHs are calcined between 550 and 750 °C, while crystalline  $\text{SiO}_2$  forms at higher temperatures, generally between 800 and 1000 °C.<sup>81</sup> While temperature is a key factor in maintaining the non-crystalline nature of Si-based materials derived from RHs, impurities and mineralogical constituents, are also known to influence the specific temperature range to avoid crystallization,<sup>82</sup> and should be therefore also considered.

Liu *et al.* in 2013 were among the first to introduce RHs as a viable bioprecursor for producing nano-sized silicon negative electrodes *via* MgTR. Their RH-derived silicon achieved a specific capacity of 2200 mA h g<sup>-1</sup> after 100 cycles, compared to 500 mA h g<sup>-1</sup> for metallurgical-grade Si.<sup>83</sup> These results demonstrate the suitability of RH-derived Si nanoparticles for LIB electrode materials. The unique attributes of RH-derived Si nanoparticles are their small size (10–40 nm) and porous structure, that allows them to effectively accommodate volumetric changes during lithium insertion and extraction, maintaining structural integrity upon prolonged cycling (86% of the capacity retained after 300 cycles).

More recent studies have focused on synthesizing advanced Si/C<sup>84</sup> and  $\text{SiO}_x/\text{C}^{85}$  composite electrodes using RHs as dual precursors, leveraging both their silica and organic content. These composites delivered capacities of 600 mA h g<sup>-1</sup> at 100 mA g<sup>-1</sup> and 1033 mA h g<sup>-1</sup> over 100 cycles at 1 A g<sup>-1</sup>, respectively. This approach highlights the potential to valorize the inherent carbon content of RHs—traditionally discarded or incinerated—thereby contributing to a more sustainable and integrated utilization of this biomass resource.

Hence, the exploration of RHs for the production of high-performance Si-based electrodes represents a significant area of research. This interest is driven by the potential to utilize an abundant agricultural waste and the inherent advantages of RH-derived silicon nanoparticles, such as their small size, porosity, and structural integrity, which contribute to improved battery performance and extended cycle life.

### 3 Protists

Protists are a diverse group of eukaryotic microorganisms that do not fall within the traditional classifications of plants, animals, or fungi. Among them, diatoms and radiolarians stand out for their remarkable ability to produce highly structured silica exoskeletons. In contrast to siliceous plants, the  $\text{SiO}_2$  purity of the inorganic fraction of protists, especially in naturally occurring and cultured diatom microalgae is significantly higher and presents less variability. Hence, these organisms offer particularly promising avenues for the development of Si-based electrode materials.

#### 3.1 Radiolarians

Radiolarians are widely distributed across marine ecosystems, inhabiting all oceanic zones from surface waters to the deep sea. They produce intricate silica skeletons composed of

hydrated opal ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ),<sup>86</sup> featuring a diverse range of pore structures and morphologies.<sup>87,88</sup> These exoskeletons, Fig. 2a, are characterized by large, irregular pores that accommodate axopods—retractable pseudopodia used for prey capture and buoyancy, allowing the organisms to drift within ocean currents.

Radiolarians range in size from small species measuring less than 100 µm, with intricate siliceous skeletons, to larger non-colonial gelatinous forms reaching 1–2 mm in diameter. These larger species are less taxonomically diverse and predominantly found in surface waters. Noncolonial radiolarians can be broadly classified into two types: those lacking mineralized skeletons, instead enveloped in a gelatinous matrix, and those that form dispersed siliceous spicules within their cytoplasm. Upon death, the siliceous skeletons of radiolarians sink to the ocean floor, contributing to the sequestration of atmospheric carbon in deep-sea sediments. Over geological timescales, these silica remains undergo diagenesis, transforming into valuable paleoclimate indicators. As fossilized structures, they serve as archives of past oceanic conditions, offering insights into historical fluctuations in temperature and salinity.<sup>89</sup>

The use of radiolarian skeletons as bioprecursors presents an opportunity for material science, particularly if laboratory-scale cultivation becomes feasible. However, developing reliable culturing systems remains a challenge. Historically, continuous laboratory cultivation was unfeasible, as most specimens survived only a few days—likely due to the narrow and specialized environmental requirements of their early life stages.<sup>90,91</sup> While some progress has been made in maintaining radiolarians under controlled culturing conditions,<sup>92</sup> systematic studies remain limited.<sup>93–97</sup> Moreover, no reports to date have evaluated the purity or chemical composition of their siliceous skeletons in the context of materials science. Such information would be particularly relevant for assessing their suitability as precursors for Si electrodes in LIBs. Laboratory-scale cultivation could enable the growth of different skeletal morphologies under defined conditions, providing a platform to investigate their structural features, chemical purity, and performance as electrode materials.

#### 3.2 Diatoms

Diatoms are a major group of photosynthetic protists and dominant members of the phytoplankton community, known for producing intricate silica frustules with hierarchical micro- and nanoporous architectures. These structures serve multiple ecological functions, such as nutrient filtration and mechanical reinforcement against sediment pressure. The well-defined and highly porous morphology of diatom frustules offers a large surface area and facilitates ion diffusion, making them especially attractive for Si negative electrodes. Notably, their porous architecture can also accommodate the volume changes associated with Si volume variations upon cycling, enhancing the structural stability of the electrodes.

Diatoms exhibit either radial (centric) or bilateral (pennate) symmetry and display a wide range of regular shapes, according



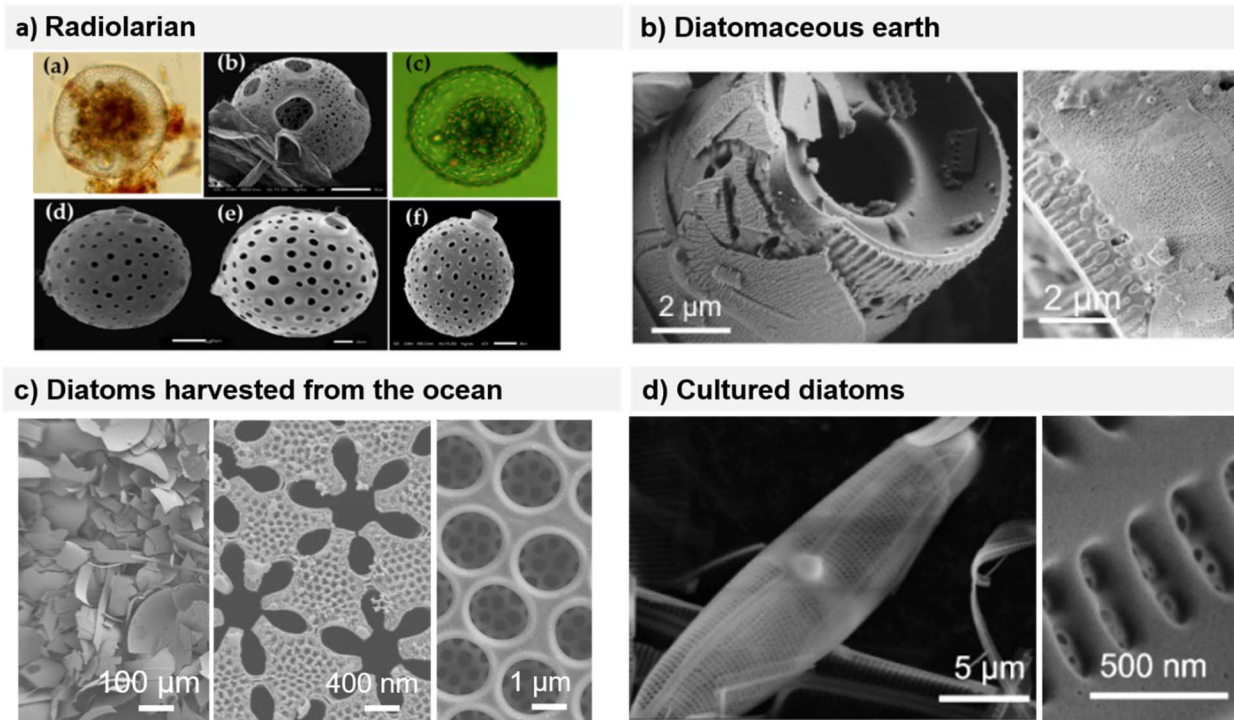


Fig. 2  $\text{SiO}_2$  exoskeletons from: (a) radiolarian, reproduced from ref. 32, (b) diatomaceous earth, reproduced from ref. 66, (c) diatoms harvested from the ocean, and (d) industrially cultured single-species diatom.<sup>66</sup>

to which they are classified as: ellipsoidal, spherical, triangular, rectangular, cylindrical, sigmoidal, fusiform, and complex. These morphologies, Fig. 2b, differ significantly in surface area, pore size, pore distribution, wall thickness, hardness, shape, and size. Naturally occurring frustules display properties with very distinctive values, along ranges covering multiple orders of magnitude. Reported values for relevant frustule's properties found in nature are: size  $2\text{ }\mu\text{m}$  to  $5\text{ mm}$ , wall thickness  $10\text{ nm}$  to  $5\text{ }\mu\text{m}$ ,<sup>98</sup> pore size  $1\text{ nm}$  to  $10\text{ }\mu\text{m}$ , area  $1\text{--}258\text{ m}^2\text{ g}^{-1}$ ,<sup>99</sup> and Young's modulus  $0.2\text{ MPa}$  to  $100\text{ GPa}$ .<sup>100</sup> During their reproduction cycle, new frustules with unchanged morphology are produced, and this mechanism ensures high reproducibility of shape, size, and nanostructure of the biosilica shells.

The diatom- $\text{SiO}_2$  precursors used for LIB electrodes can be divided into three categories: (1) diatomaceous earth, (2) diatoms harvested from the ocean, and (3) artificially cultured diatoms.

**3.2.1 Diatomaceous earth.** Diatomaceous earth (DE), also known as diatomite, is a naturally occurring, soft, siliceous sedimentary rock primarily composed of fossilized diatom remains.<sup>101</sup> It is extensively utilized across various industries due to its unique properties, serving as a filtration agent, an insecticide component, a mild abrasive in products like toothpaste and metal polishes, and a soil conditioner in agriculture.

DE primarily consists of hydrated amorphous silica. Sediments rich in diatoms can be classified based on the weight percentage of biogenic  $\text{SiO}_2$  and burial depth.<sup>102</sup> For sediments containing over  $80\%$  biogenic  $\text{SiO}_2$ , the terms "diatomaceous ooze" and "diatomite" apply. The structural characteristics of

$\text{SiO}_2$  evolve with burial depth, transitioning from opal-A at depths below  $50\text{ }^\circ\text{C}$  and  $600\text{ m}$  to opal-CT and quartz at higher temperatures and depths. Despite this classification, the term "diatomaceous earth" is frequently employed in the literature without differentiation of biogenic  $\text{SiO}_2$  types.<sup>15</sup>

DE was first introduced as a bioprecursor for LIB electrode materials by Wang *et al.*<sup>103</sup> in 2012. They developed DE-derived Si/C composites, with DE- $\text{SiO}_2$  reduction conducted through the MgTR, and achieved a specific capacity of  $759\text{ mA h g}^{-1}$  after 30 cycles at  $50\text{ mA g}^{-1}$ . A later study by Campbell *et al.* enabled reaching  $1102\text{ mA h g}^{-1}$  after 50 cycles at  $700\text{ mA g}^{-1}$ .<sup>104</sup> While both studies pioneered the use of DE for silicon anodes, significant differences in the source of the DE precursor and the conditioning protocols employed for impurity removal and carbon coating resulted in distinct material properties. For instance, the surface areas of DE- $\text{SiO}_2$  were reported to be  $63.4\text{ m}^2\text{ g}^{-1}$  in Wang *et al.*'s study compared to  $7.3\text{ m}^2\text{ g}^{-1}$  in Campbell *et al.*'s research. Similarly, the DE-Si particles exhibited surface areas of  $46.9\text{ m}^2\text{ g}^{-1}$  and  $162.3\text{ m}^2\text{ g}^{-1}$ , respectively. Recent advancements further reveal that reducing DE- $\text{SiO}_2$  to  $\text{SiO}_x$  allows for the formation of  $10\text{--}30\text{ nm}$  crystalline Si domains embedded within an amorphous  $\text{SiO}_2$  matrix, yielding capacities of approximately  $1000\text{ mA h g}^{-1}$  after 200 cycles at a rate of  $0.2\text{C}$ . Hence, understanding the interplay between precursor sourcing, processing conditions, and resulting material properties is crucial for optimizing DE-derived anodes. A deeper exploration of these factors will be essential to harnessing the full potential of DE in the development of high-performance LIBs.



Importantly, non-reduced DE-SiO<sub>2</sub> has been also studied as a potential anode material. Nanostructured DE-SiO<sub>2</sub> has demonstrated promising electrochemical performance, achieving 575 mA h g<sup>-1</sup> after 100 cycles at 100 mA g<sup>-1</sup> when using pristine particles with an average size of 17 μm. Remarkably, this capacity increased to 840 mA h g<sup>-1</sup> when particle size was reduced to 400 nm through wet ball milling, followed by carbon coating and electrochemical activation.<sup>105</sup> Yet, these materials experienced significant capacity fading due to particle cracking after approximately 100 cycles,<sup>106</sup> which underscores the need for further research into mitigating degradation mechanisms.

**3.2.2 Diatoms harvested from the ocean.** In 2014, Lisowska-Oleksiak introduced the use of naturally occurring diatoms coated with carbon derived from red algae<sup>107</sup> to produce SiO<sub>2</sub>/C composite anodes. The diatom, harvested from the Baltic Sea and thermally treated, presented an average particle size of 30 μm and achieved a capacity of 500 mA h g<sup>-1</sup> after 80 cycles. In a later study, Renman *et al.* explored electrochemical activation procedures to enhance the performance of diatom-based SiO<sub>2</sub>/C composites, using naturally occurring *Coscinodiscus* diatoms and glucose as carbon precursor. The composites achieved capacities of 800 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>.<sup>108</sup> Subsequent research by Nowak *et al.* revealed significant variability in the crystalline phases—such as cristobalite, quartz, albite, and magnetite—found in thermally treated diatoms harvested from the ocean, highlighting the need for consistent sourcing and processing to optimize performance.<sup>109</sup>

**3.2.3 Cultured diatoms.** In contrast to radiolarians, diatoms are already cultivated at an industrial scale for applications including biodiesel production,<sup>110</sup> natural pest control, soil conditioning, and filtration technologies. These established commercial uses have driven the development of robust and reproducible cultivation protocols.<sup>111</sup> The battery research community is now leveraging these advances to grow diatoms under controlled laboratory and industrial conditions for use as Si sources in LIB electrodes.

One of the first studies to explore the use of frustules from laboratory cultured diatoms as negative electrode material was conducted by Nowak *et al.* in 2020.<sup>112</sup> In this work, the single species *Pseudotaurosira trainorii* was cultivated in Erlenmeyer flasks, and the resulting diatom biomass was used to synthesize SiO<sub>2</sub>/C composite electrodes, which delivered a specific capacity of 460 mA h g<sup>-1</sup> after 70 cycles at 40 mA g<sup>-1</sup>. Following this, investigations into various laboratory grown *Haetoceros*, *Navicula*, and *Nitzschia* mixed-species demonstrated higher capacities, approaching 1000 mA h g<sup>-1</sup> after 150 cycles at 200 mA g<sup>-1</sup>,<sup>113</sup> highlighting the influence of frustule properties and carbon content on electrochemical performance. More recently, laboratory-cultured *Navicula* sp. and a cobalt precursor were used to prepare SiO<sub>2</sub>/C-Co composites, which achieved capacities of 620 mA h g<sup>-1</sup> at 100 mA g<sup>-1</sup> after 270 cycles.<sup>114</sup> Although studies utilizing laboratory-cultured diatoms as a source of SiO<sub>2</sub> remain limited, they have contributed to the ongoing standardization of key cultivation parameters that influence algal growth, such as medium composition, temperature, light regime, and aeration. However, other critical

factors—such as culture volume and operational mode (batch, continuous, or semicontinuous)—should also be explicitly reported to ensure consistency and comparability across studies.

More recent studies have focused on the use of frustules derived from industrially cultivated diatoms, including both mixed-species cultures (*e.g.* *Chaetoceros*, *Navicula*, and *Stephanodiscus*)<sup>115</sup> and single species cultures (*e.g.*, *Nitzschia*).<sup>66,116</sup> These investigations have demonstrated promising electrochemical performance, with frustules from mixed-species diatoms, SiO<sub>2</sub>@C, achieving specific capacities of 930 mA h g<sup>-1</sup> after 200 cycles at 400 mA g<sup>-1</sup>, and frustules from single-species diatoms, SiO<sub>2</sub>, delivering 811 mA h g<sup>-1</sup> after 100 cycles at 100 mA g<sup>-1</sup>. Furthermore, SiO<sub>x</sub> and SiO<sub>x</sub>/C compounds synthesized *via* MgTR of single-species industrially cultivated diatoms were found to retain the intricate hierarchical nanostructure of the original frustules, while simultaneously allowing for the tuning of oxygen content to optimize electrochemical performance.<sup>117,118</sup> These findings highlight the potential of industrially cultured diatom frustules as a sustainable and scalable source of advanced electrode materials. In addition to enabling the development of high-performance anodes, this approach contributes to the establishment of practical methodologies for the extraction and processing of frustules from large-scale culturing systems—an essential step toward industrial implementation.

## 4 Scalability

Scaling up the production of high-performance Si-based anodes from bioprecursors requires the development of efficient industrial processes for biomass harvesting, processing, and conversion.

RH-derived SiO<sub>2</sub> offers significant scalability advantages due to its widespread availability and the large-scale infrastructure already established in the agricultural sector. Converting this agricultural waste into battery-grade electrode material would improve the sustainability of LIB production while addressing waste management issues. However, large-scale implementation must account for compositional variability in RHs. Although techno-economic assessments (TEAs) specific for RH-based silicon for battery applications are lacking, relevant insights can be drawn from related sectors. For instance, a recent TEA on RH-derived bioethanol demonstrated that biomass logistics, pretreatment requirements, and feedstock heterogeneous composition significantly affect process economics and scalability.<sup>119</sup> Similar factors are critical for evaluating RH use in energy materials, where precursor quality consistency is essential. Regulatory considerations—such as emissions from RH combustion and RHA disposal—also influence scalability and must be addressed.

When comparing RHs to other plant-based bioprecursors—such as bamboo leaves and sugarcane bagasse—both ash yield and silica content must be considered alongside global biomass availability. Bamboo leaves exhibit a high ash content of 25.86 wt% and silica content exceeding 90 wt%,<sup>120</sup> outperforming RHs, which typically contain around 16.1 wt% ash with ~90 wt% silica.<sup>121</sup> However, global RH annual production is



of ~150 million tons, whereas bamboo leaf waste is estimated at around 107 million tons per year across major producing countries. Thus, although bamboo leaves offer higher silica yield per unit mass, their overall biomass availability is currently lower than RHs. Sugarcane bagasse presents even lower ash productivity, with only 4.14 wt% ash and up to 88.7 wt% silica in the ash.<sup>122</sup> Despite the large volume of sugarcane processed annually—657 million tons in Brazil alone—the relatively low ash and silica yields limit its practical value as a primary SiO<sub>2</sub> source for anode production unless optimized pre-treatment strategies are applied. Overall, while bamboo leaves offer superior silica concentration, RHs remain the most scalable plant-derived bioprecursor due to their high global availability, well-established processing infrastructure, and competitive silica content.

Diatom cultures can also be scaled up at low cost, with estimated productivity reaching  $70 \times 10^6$  tons per ha per year in open ponds.<sup>123</sup> Their industrial-scale cultivation has been primarily driven by applications in food, feed, and biofuel sectors. Unlike siliceous plants, diatoms can be grown on non-arable land and in brackish or wastewater, avoiding competition with agricultural resources and enhancing sustainability. Moreover, large-scale diatom cultivation can contribute significantly to carbon capture efforts. As highly efficient solar energy converters, diatoms surpass forests in CO<sub>2</sub> uptake and are responsible for approximately 25% of the global oxygen supply, underscoring their dual role as a renewable resource and an agent of environmental remediation. Beyond LIB applications, large-scale diatom cultivation offers numerous environmental and economic benefits. The organic biomass fraction can be utilized for biofuel production, while the inorganic SiO<sub>2</sub> shells provide a high-purity feedstock for battery anodes. As the transition toward climate neutrality accelerates, early-stage investments in scalable production methods will be crucial for bridging fundamental research with commercial deployment.

## 5 Purity of bioprecursors

The use of siliceous plants as bioprecursors for Si-based anodes presents challenges related to compositional variability. The chemical composition of plant-derived silica can differ significantly depending on species, geographical origin, and environmental factors such as soil composition, irrigation practices and fertilizer use.<sup>124</sup> For example, the application of nitrogen-phosphorous-potassium (NPK) and iron-rich fertilizers significantly affects the uptake of trace metals like Cd, Zn, Pb, Fe, and Mn in rice plants, which accumulate in the husks.<sup>125,126</sup> These elements can act as impurities during silicon synthesis and may negatively impact battery performance. Therefore, impurity control strategies—such as acid leaching and standardized calcination—are essential for producing high-purity SiO<sub>2</sub> and minimizing batch-to-batch variability. Incorporating these agronomic and processing parameters into scalability assessments will be crucial for reliable RH valorization in LIB technology.

In addition to fertilizer-derived impurities, environmental contamination can introduce heavy metals that compromise battery efficiency and safety. Variations in silica content and impurity composition, depending on rice variety and cultivation conditions, make it difficult to ensure the consistency required for the reliable use of RHs and another plant-derived bioprecursors in commercial applications.

In addition to intrinsic sources of variation, post-treatment methods—such as thermal or chemical purification—have been shown to significantly influence both the purity and physicochemical characteristics of the resulting ash. This has been demonstrated for several systems, including rice husk ash<sup>127</sup> and bamboo leaf ash,<sup>128</sup> highlighting the need for further investigation to establish standardized protocols for impurity removal and material optimization.

Among biogenic silica sources, cultured diatoms represent a particularly compelling platform due to their high purity and precise compositional control, Table 2. Unlike siliceous plants, which incorporate soil-derived impurities and show variability across species and regions, cultured diatoms can be grown under controlled conditions that minimize contamination and ensure consistent silica quality. Parameters such as nutrient composition, light intensity, temperature, and growth duration can be carefully optimized, enabling the production of biosilica with minimal levels of trace elements and excellent chemical uniformity. Compared to natural diatomaceous earth or harvested diatoms—both of which may carry mineral impurities, crystalline inclusions, and environmental contaminants—cultured strains offer a more homogeneous and reliably pure silica. This high degree of purity is particularly advantageous for energy storage applications, where the presence of impurities can compromise the performance, stability, and scalability of silicon-based anode materials.

In summary, advancing the use of biogenic silica in energy storage applications requires addressing compositional purity. Both siliceous plants and diatoms present challenges related to impurity control—ranging from soil-derived contamination in plants to environmental variability in harvested diatoms. Tackling these challenges requires a systematic and standardized approach to material characterization and processing. Future research on diatoms, rice husk ash, and other biogenic SiO<sub>2</sub> sources should consistently report comprehensive geographical and biological metadata, detailed chemical compositional analyses, and well-documented post-treatment procedures such as thermal and acid purification protocols. Establishing standardized reporting practices will not only enhance reproducibility but also enable meaningful cross-study comparisons and accelerate the optimization of these materials for silicon anodes. Furthermore, understanding the influence of cultivation or growth parameters—whether in agricultural systems or controlled bioreactors—on impurity profiles will be key to tailoring biogenic silica sources toward commercial-grade purity. This will facilitate the transition from exploratory studies to scalable, high-performance energy storage technologies based on sustainable silicon sources.



**Table 2** Qualitative comparison of various biogenic silica sources in terms of SiO<sub>2</sub> scalability, purity and structural control for application in silicon-based anodes for LIBs

| Bioprecursor                    | Scalability | Purity        | Structural control |
|---------------------------------|-------------|---------------|--------------------|
| Reed                            | Moderate    | Moderate      | Moderate           |
| Sugarcane                       | High        | Moderate      | Moderate           |
| Bamboo                          | Moderate    | Moderate      | Moderate           |
| Rice                            | High        | Moderate/high | Moderate           |
| Radiolarian                     | Low         | Not known     | Not known          |
| Diatomaceous earth              | High        | Moderate/high | Low                |
| Frustules from the ocean        | Moderate    | High          | Low                |
| Frustules from cultured diatoms | High        | High          | High               |

## 6 Future perspectives

The development of Si-based electrode from bioprecursors would represent a significant step towards not only better performing but also more sustainable LIBs. However, several key challenges remain, requiring future research to overcome them.

One critical issue is that, although the environmental benefits of bioprecursors for Si-based anodes are widely assumed, they remain largely unquantified. For example, a recent life cycle assessment (LCA) examined the environmental impact of different chemical extraction methods for producing nanosilica from rice husk ash, showing that reagent choice and energy source significantly influence sustainability outcomes.<sup>129</sup> However, its scope was limited to silica extraction and did not encompass the subsequent conversion to silicon or its integration into battery anodes. Hence, to support the advancement and broader adoption of bioprecursor-derived silicon anodes, future research should prioritize the development of standardized LCA methodologies that address the full production pathway. Establishing robust, quantitative sustainability metrics is essential to substantiate environmental claims and to enable meaningful engagement with regulatory bodies and industrial stakeholders.

Also, to enable a rational comparison between different bio-derived silicon-based anode materials, future studies should prioritize the standardization of electrochemical testing protocols. Establishing common benchmarks—such as specific current densities, cycle numbers, electrode composition, and areal loading—would facilitate a more meaningful evaluation of performance across different bioprecursors and accelerate progress toward practical applications.

Another pressing challenge lies in the compositional variability of minor and trace elements present in siliceous plants, which may have a substantial impact on the electrochemical performance of silicon-based anodes—including parameters such as capacity, rate capability, and cycle life. For instance, correlating soil chemistry with electrode performance could enable more targeted strategies for optimizing biogenic Si-based materials. Systematic studies of impurity profiles and their effects are thus needed to guide the informed selection of bioprecursors for battery applications. Such approaches may not only enhance material quality and device performance but also enable region-specific, sustainable production pathways,

ultimately contributing to a broader understanding of how environmental factors influence the development of next-generation energy storage technologies.

Beyond the advantageous SiO<sub>2</sub> purity of cultured diatom frustules, diatoms exhibit remarkable morphological plasticity,<sup>130</sup> an attribute that remains largely untapped in materials science applications. Morphological plasticity allows diatoms to dynamically alter the shape, size, and structural organization of their silica frustules in response to environmental conditions such as nutrient availability, temperature, and salinity. By harnessing this adaptability, researchers could fine-tune the nanostructure of diatom-derived SiO<sub>2</sub>, optimizing properties such as porosity, surface area, and crystallinity. This ability to bioengineer frustule architecture presents a unique opportunity to design advanced silicon-based anodes with tailored nanostructures, enhancing charge capacity, cycling stability, and rate capability.

Advancing the application of diatom frustules as precursors for silicon-based electrode materials necessitates an interdisciplinary research framework. Close collaboration with experts in biology and biotechnology will be essential to foster synergies that effectively integrate biological insights into materials science and engineering. In particular, harnessing the morphological plasticity of diatoms through targeted bioengineering strategies offers a promising route to tailor the structural and compositional features of biosilica for energy storage applications. Such cross-disciplinary efforts hold significant potential for the rational design of biogenic materials with optimized properties for next-generation lithium-ion batteries.

Looking ahead, advancements in microalgae cultivation, agricultural practices, and waste management could accelerate the commercialization of bioprecursor-derived Si-based materials. Moreover, combining sustainable raw materials with next-generation battery architectures, such as all-solid-state batteries, may set new performance benchmarks while minimizing environmental impact. Ultimately, interdisciplinary research and strategic investment will be key to unlocking the full potential of biogenic silicon for high-performance, eco-friendly energy storage solutions.

## Data availability

This Perspectives article does not report any new data. All data presented in the article are available in the cited literature.



## Author contributions

MVB: conceptualization, writing – original draft, MRP: conceptualization, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

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