

"Milk skin"-inspired ionogel membranes: From 3D colloids to repeatable 2D membranes through solvent-induced self-assembly

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Ionogel membrane (IGM) is an emerging gel system comprising ionic liquid and a solid polymer framework, characterized by several advantageous properties such as exceptionally low saturated vapor pressure, non-flammability, high thermal stability, and superior ionic conductivity. These properties make IGM highly desirable for use in flexible sensor and energy-related fields.¹ However, the conventional synthetic organic polymers employed as solid framework materials in IGM predominantly originate from petrochemical

sources, thereby giving rise to concerns regarding potential environmental pollution. In contrast, naturally derived polymer materials, like cellulose, exhibit remarkable mechanical properties, optical characteristics, and abundant porosity, rendering them appealing substitutes as IGM substrates. This substitution holds the prospect of mitigating the environmental impact associated with both the production and utilization of IGM.

In recent years, extensive research on the structure and functional modifi-

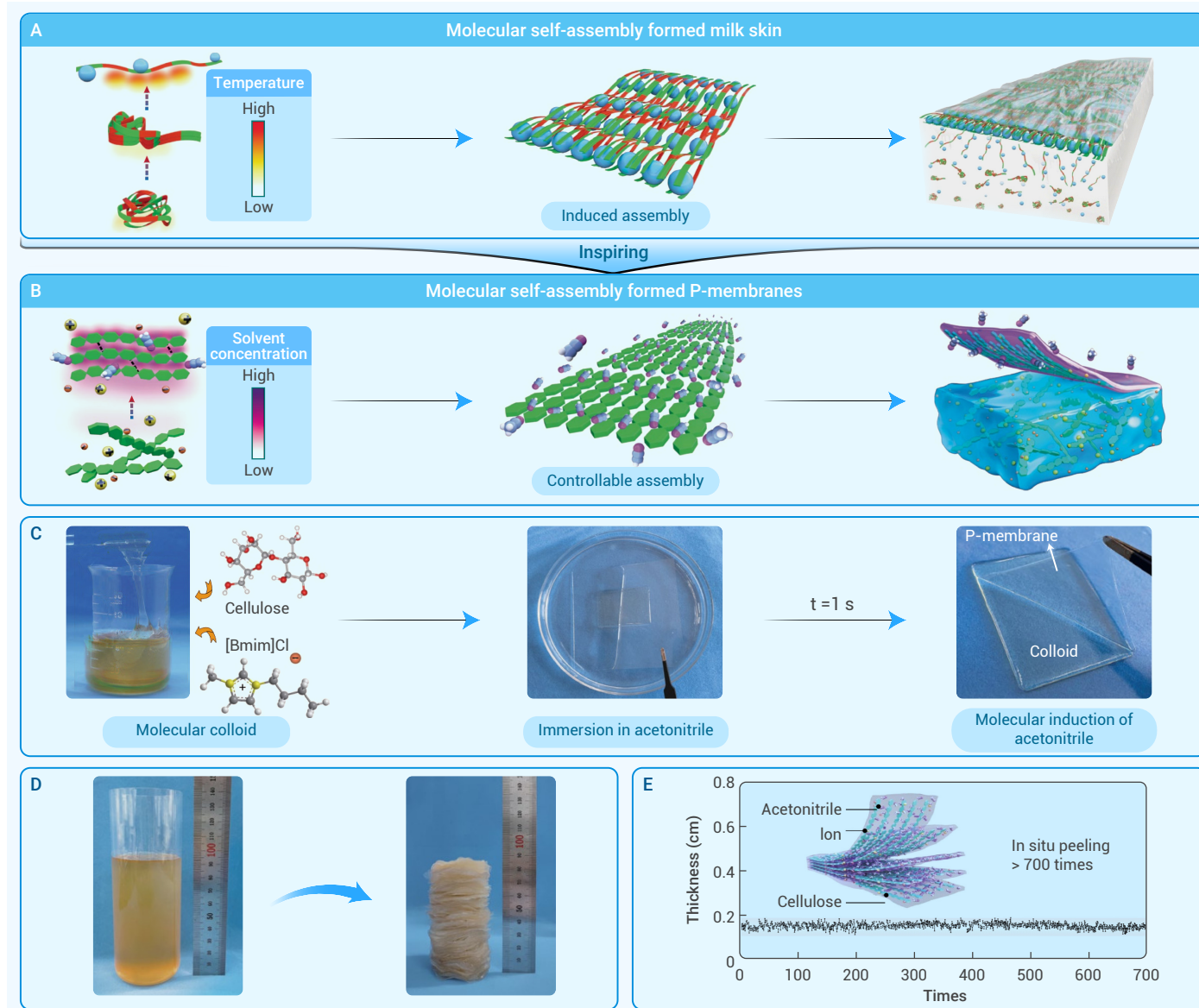


Figure 1. The fabrication process of 'Milk Skin'-inspired IGM via solvent-induced self-assembly (A) Temperature-induced molecular self-assembly leading to milk skin formation. (B) Solvent-induced molecular self-assembly leading to P-membranes formation. (C) 3D cellulose/[Bmim]Cl colloid peels off into 2D membrane in acetonitrile solvent. (D) A columnar cellulose/[Bmim]Cl colloid and its derived P-membranes. (E) Thickness distribution of the P-membranes. Reprinted with permission from Ref. [4].

cation of natural polymer materials has revealed that ionic gels derived from these sources demonstrate exceptional biocompatibility.² However, existing methods for preparing IGM either cannot control the membrane thickness or involve long preparation times, making them unstable, inefficient, and impractical for sustained operations. Furthermore, with regards to performance, current ion gels frequently face challenges in achieving a synergistic enhancement of both electrical conductivity and mechanical properties. Thus, the swift and dependable preparation of IGM with exceptional electrical conductivity, high tensile strength, and customizable specifications using bio-based materials remains pivotal in actualizing their commercial applications.

Molecular self-assembly, a phenomenon observed in both natural processes and materials manufacturing, involves the spontaneous formation of ordered structures and the assembly of specific shapes or functional structures between molecules. In recent years, researchers have increasingly utilized molecular self-assembly to design and fabricate materials or nanostructures with targeted functionalities.³ Hence, utilizing cellulose as a solid framework and capitalizing on the self-assembly of biomacromolecules to prepare IGM holds considerable promise. However, molecular self-assembly involves an extensive array of molecules, with interactions between them being complex, making it highly challenging to accurately predict and control the material structure and properties.

Throughout the extensive process of biological evolution, natural selection has bestowed organisms with remarkable adaptive abilities to thrive in their environments. Similarly, organic substances such as proteins and DNA, which constitute living organisms, possess distinct structures and functions. For instance, when milk is subjected to heat, a unique phenomenon occurs where a membrane forms on its surface.⁴ This process can be attributed to the external energy disrupting the non-covalent bonds within the protein molecules. As a consequence, the 3D protein curly structures transform into linear chains, then the molecular self-assembly is guided by the fat globules, leading to the formation of a membrane-like structure on the milk's surface (Figure 1A). The process of molecular self-assembly bears significant guiding implications for synthesizing, regulating the performance, and efficiently manufacturing membrane materials.

In a recent research publication in *Nature Synthesis*,⁴ Yu et al. introduced a novel and efficient approach for fabricating 2D peeling IGM (P-membranes) through a biomacromolecular self-assembly method (Figure 1B). This innovative strategy draws inspiration from the natural occurrence of 'milk-skin'. The authors employed acetonitrile as the solvent to induce cellulose molecular self-assembly (Figure 1C). By carefully adjusting the stimulation time or the quantity of acetonitrile, it becomes possible to precisely control the thickness, which can range from 20 μm to 166 μm , as well as the ionic conductivity and mechanical properties of the resulting P-membranes. These fabricated P-membranes exhibit not only tunable shapes and thicknesses but also demonstrate remarkably high ionic conductivity ($> 14.0 \text{ mS cm}^{-1}$), superior mechanical tensile strength ($> 3.0 \text{ MPa}$), high tensile strain ($> 130\%$), and excellent thermal stability (degradation temperatures $> 300 \text{ }^\circ\text{C}$). Furthermore, the entire solvent-induced process takes an impressively short time, requiring only about 1 s to form a membrane ($\sim 20 \mu\text{m}$). Within a mere 30 s, complete and uniformly thick P-membranes ($\sim 118 \mu\text{m}$) can be prepared. Notably, more than 700 pieces with even thickness of $\sim 118 \mu\text{m}$ can be repeatedly peeled off from the same gel block (Figure 1D and E). This showcases the high potential of this approach for large-scale production of P-membranes with consistent performance.

The design and preparation of the bio-based P-membranes exemplify an expansion and innovative progression stemming from the prior research endeavors of Hu et al.⁵ Early in this work, by disrupting the hydrogen bonding between cellulose molecular chains using the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), the authors obtained a homogeneous cellulose/[Bmim]Cl solution. In the preparation of P-membranes, the authors firstly employed the mentioned approach to generate a 3D cellulose/[Bmim]Cl ionic gel. Subsequently, molecular self-assembly was induced using acetonitrile as the solvent. The robust molecular interactions between acetonitrile and cellulose resulted in distinct self-assembly behavior, leading to the formation of P-membranes with microscale ripple patterns. From a molecular-scale perspective, the molecular dynamics simulations showed that cellulose chains exhibited stable stretched configurations in the

acetonitrile environment, favoring the formation of dense supramolecular hydrogen bonding networks and the oriented assembly of cellulose chains. The hydrogen bonding energy ($4.5 \text{ kcal mol}^{-1}$) between cellulose and acetonitrile was significantly higher than other hydrogen bonding types within the system, indicating the effective extraction of cellulose from the original ionic liquid by acetonitrile. Additionally, the $\text{C}\equiv\text{N}$ group further guided cellulose to form stronger hydrogen bonding networks, accelerating the self-assembly and detachment of P-membranes. This process rapidly achieved the preparation of 2D IGM from the 3D ionic gels.

To validate the remarkable performance of P-membranes, electronic circuit chips and electronic skin (e-skin) were successfully developed using direct inkjet printing. The outcomes showcased that the e-skin exhibited optimal signal feedback across diverse external stimuli. Furthermore, the authors extended the universal applicability of this strategy by employing other biomacromolecules (chitosan, silk fibroin, and guar gum) as raw materials and achieved successful preparation of the P-membranes. The choice of solvents is not restricted to acetonitrile; it also encompasses solvents with suitable dispersion force, polarity force, and hydrogen-bonding strength, such as acetic acid, dichloromethane, and others.

In summary, the exceptional performance and successful application instances of the 'milk skin'-inspired P-membranes collectively validate the efficacy of the solvent-induced molecular self-assembly strategy for IGM fabrication. This strategy effectively addresses multifaceted challenges encompassing production efficiency enhancement, precise control over thickness and geometry, and advancements in both mechanical and conductive properties. The versatility of this strategy has been substantiated across a range of biopolymer candidates, signifying its potential to supplant conventional methods for producing two-dimensional polymer membranes.

The proposed new strategy is not restricted to IGM but also holds promise for a broad spectrum of membrane materials. It's important to note that the external stimuli encompass not only solvent but also manipulation of factors like light, heat, electricity, pressure, and humidity. Leveraging these environmental parameters opens up possibilities for the development of self-assembled membrane preparation techniques. While the P-membrane approach offer the advantage of quick film formation, the need to take out these membranes from solvents presents a significant challenge in achieving automated mass production through optimized manufacturing processes. Moreover, uncertainties surrounding the biocompatibility of ionogels underscore the importance of conducting comprehensive investigations to assess their biocompatibility and potential biotoxicity. It is advisable to exercise caution when contemplating their use within human tissues until definitive conclusions are available.

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DECLARATION OF INTERESTS

The authors declare no competing interests.