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論文題目	Development of Carbon Capture Platforms using Membrane Technology and Enzyme-Mimicking Metal-Organic Complex Assemblies (分離膜技術と酵素模倣型有機金属錯体集合を用いた炭素回収プラットフォームの開発)		
(論文内容の要旨)			
<p>Sustainable energy supply and environmental protection are the major global scientific challenges in the 21<sup>st</sup> century. In this context, addressing the pivotal issue of CO<sub>2</sub> capture and storage stands out as a critical endeavor. Taking the motivation from this picture, this Ph.D. thesis is focused on the design and fabrication of highly-efficient nanotechnology-enabled systems to upgrade CO<sub>2</sub> capture and conversion with CA-mimicking supramolecular nanozymes.</p> <p>Membrane separation technology is a competitive approach for carbon capture, given its inherent advantages, such as energy efficiency and small device footprint. Nevertheless, the gas transport in conventional synthetic membranes, such as polymers, mainly follows passive diffusion and suffers a ubiquitous trade-off, <i>i.e.</i>, highly permeable membranes lack selectivity and vice versa. A practical approach involves mixing organic polymers with nanofillers to create mixed-matrix membranes (MMMs), which can help overcome the trade-off between permeability and selectivity seen in regular polymeric membranes. However, the limited compatibility between organic polymers and nanofillers typically creates non-selective voids at the interfaces between the material and the filler. To overcome this challenge, a promising strategy involves augmenting the interfacial interactions between the polymer and fillers using organic fillers that possess a high aspect ratio. The second chapter focuses on the integration of cellulose nanocrystals (CNCs) with a high aspect ratio of around 12 into polyethylene oxide based rubbery polymers to fabricate MMMs. Through improved interfacial interactions between the polymer matrix and CNC nanofillers, attributed to their surface functionality and high aspect ratio, the rapid and selective CO<sub>2</sub> transport is achieved, even at low filler concentrations. Notably, even at a filling ratio as low as 1 weight percent, the resulting membranes exhibit remarkable CO<sub>2</sub> permeability (&gt;90 Barrer) and CO<sub>2</sub>/N<sub>2</sub> selectivity (&gt;70). These findings highlight the potential of integrating CNCs into rubbery polymers as a promising strategy for the design and fabrication of highly efficient CO<sub>2</sub> capture membranes.</p> <p>The biological catalysts, enzymes, catalyze complex biochemical reactions, which might otherwise be impossible under mild conditions. Therefore, enzymes can be used to develop next-generation chemical processes that can address environmental challenges, such as anthropogenic climate change and industrial waste. However, the cost and operational stability considerations challenge direct enzyme utilization, in their native form, in industrial processes. Over the past decade, there has been significant growth in the number of fully synthetic enzyme-mimics, to harness the potency of enzymes for industrial and environmental purposes with great impact. Exploiting carbonic anhydrase (CAs), the fastest CO<sub>2</sub> hydrating enzymes, and their mimics in carbon capture,</p>			

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<p>utilization, and storage (CCSU) processes is one such application. In the third chapter, I demonstrate that the self assembly and metal coordination of histidine-based bolaamphiphiles (HisBola) form a robust supramolecular nanoarchitecture, exhibiting remarkable CA-like catalytic activity. I show that the resulting nanoparticles, catalyzes the conversion of CO<sub>2</sub> into bicarbonate (HCO<sub>3</sub><sup>-</sup>) in humid conditions. To capitalize on this principle for the facilitated transport of CO<sub>2</sub> through wet polymeric membranes, we first optimized the supramolecular assembly and zinc coordination conditions of a bolaamphiphile, achieving CA-mimicking nanozymes (His-NPs). I then combined these with a commercially available block copolymer of polyamide and polyethylene oxide. CA-mimicking nanozymes, with their inherent interfacial compatibility with the polymer matrix, arguably acted as a rate promoter for CO<sub>2</sub> absorption. As a result, the membranes presented in this work demonstrated exceptionally high CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity performances, well exceeding Robeson's upper bound.</p> <p>In the fourth chapter, I systematically controlled the catalytic activity of the nanozymes by varying the alkyl length of the HisBolas. The optimum structure (zinc-coordinated five-carbon-long HisBola) showed a significant esterase activity, considerably higher than that of most other previously reported CA-mimics developed with small biomolecules. The catalysis based CCSU technologies have the potency for realizing global decarbonization. Their viability, however, is impacted by their capacity to permanently and rapidly sequester CO<sub>2</sub>. The catalytic mineralization of CO<sub>2</sub> into solid inorganic carbonates requires scalable catalysts with rapid CO<sub>2</sub> hydration capability, which is not readily available at the moment. The developed nanozymes have been utilized as catalysts to enhance the CO<sub>2</sub> mineralization process. We have shown that the developed nanozymes could significantly enhance the rate of CO<sub>2</sub> hydration as well as the amount of CaCO<sub>3</sub> precipitated in the mineralization process. Notably, we exhibit controlled catalytic modulation of a supramolecular nanozyme via noncatalytic segments and elucidate the mechanism through molecular simulations.</p>			

## (論文審査の結果の要旨)

持続可能なエネルギー供給と環境保護は、21世紀における地球規模の重要な科学的課題である。中でもCO<sub>2</sub>の回収と貯蔵という課題に取り組むことは、この文脈における中心的な取り組みである。この博士論文では、炭酸脱水酵素(carbonic anhydrase: CA)を模倣した超分子ナノザイムを用いて、CO<sub>2</sub>の回収と変換を改善する高効率ナノテクノロジーのシステムを創り出すことに焦点を当てている。

膜分離技術は、そのエネルギー効率と設置面積の小ささから、炭素回収のために有効なアプローチである。しかし、ポリマーのような従来の合成膜は、透過性と選択性のトレードオフに直面している。そこで、有機ポリマーとナノフィラーを混合して混合マトリックス膜(MMM)を作れば、このトレードオフを克服することができる。課題はポリマーとナノフィラーの相溶性に限界があることで、その界面に非選択的な空隙が生じる事である。これに対処するため、第2章では、高アスペクト比のセルロースナノ結晶(CNC)をポリエチレンオキシドベースのゴム状ポリマーに組み込んでMMMを作製した。表面機能性と高アスペクト比により、ポリマーマトリックスとCNCナノフィラー間の界面相互作用が改善された。低フィラー濃度でも迅速かつ選択的なCO<sub>2</sub>輸送が可能となり、効率的なCO<sub>2</sub>回収膜の設計におけるCNCの可能性を示した。

CAを模倣した合成酵素はコストや安定性の観点から、炭素回収・利用・貯蔵プロセスで注目されている。第3章では、ヒスチジン系両親媒性化合物(histidine-based bolaamphiphiles: HisBola)の自己組織化と金属配位により、CA様触媒活性を持つ強固な超分子ナノザイムが形成されることを示した。これらのナノザイムは、多湿条件下でCO<sub>2</sub>を重炭酸塩に変換するため、湿潤高分子膜を介したCO<sub>2</sub>輸送に適している。このナノザイムをポリアミド-ポリエチレンオキシドブロックコポリマーと組み合わせて、非常に高いCO<sub>2</sub>透過性と選択性を持つ膜が得られた。

第4章では、HisBolaのアルキル長を変えることにより、ナノザイムの触媒活性を制御した。最適な構造は、これまでに報告されたほとんどのCA模倣体を凌ぐ、顕著なエステラーゼ活性を示した。また、開発したナノザイムをCO<sub>2</sub>の無機化プロセスを促進する触媒として利用し、CO<sub>2</sub>の水和とCaCO<sub>3</sub>の沈殿を促進する能力を実証した。

本論文は、酵素模倣材料を用いたCO<sub>2</sub>回収・変換の基礎研究として新しい知見と応用手法を提供するものであり、分離膜が持つ耐久性、高透過能、高選択性に係る課題を多くの点で克服できる指針を示していることから、学術上、實際上寄与するところが少なくない。よって、本論文は博士(工学)の学位論文として価値あるものと認める。また、令和5年11月21日、論文内容とそれに関連した事項について試問を行って、申請者が博士後期課程学位取得基準を満たしていることを確認し、合格と認めた。