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論文題目	Carbon Based Membranes for Molecular Separations (炭素素材を基調とする膜の合成及び分子分離特性の研究)		
<p>(論文内容の要旨)</p> <p>In the past few decades, membrane-based separation has become a promising technology for solving the enormous challenges in chemical and environmental industries. Compared with conventional separation methods, membrane separation is an easy-operation, energy-efficiency, and environmental friendliness technology, which occupies less space and can be operated in a continuous mode. An ideal membrane should provide higher permeate flux enhanced selectivity through controlled pores and channels, and reduced thickness in large-areas to maximize higher throughput and increase membrane performance.</p> <p>By far, membranes prepared using conventional polymeric materials have been made and exhibit good separation performance. Nevertheless, conventional polymeric nanofiltration membranes usually constrained by a trade-off between permeability and selectivity, chemical resistance and high fabrication cost. Recently, significant interest has been focused on well-defined materials, such as zeolites, metal organic frameworks and carbon-based materials, because of their large surface area and highly ordered pores with tunable porosity. Indeed, MOF formed by metal ions and organic ligands with diverse functionalities and a wide range of pore have very good permselectivity characteristics, which would represent an important class of crystalline molecular sieve for gas separation. However, the poor workability, weaker intrinsic mechanical strength and chemical stability make it difficult to fabricate an ideal ionic sieve membrane for industrial use. Therefore, develop new membrane materials and structures with superior chemical stability, thermal stability, water permeability, as well as high selectivity are challenges need to be addressed.</p> <p>In chapter 1, the author firstly describes the basic characters, advantages and the development of membranes. Following that, the most used preparation methods for carbon based membranes are described. Furthermore, the author summarizes the current ways to control the structure and property of membranes. Finally, in the end of the chapter, the position and purpose of this thesis are stated.</p> <p>In chapter 2, facilitated transport MMMs were fabricated by incorporating ionic liquid covalent functionalized graphene oxide (GO-IL) into poly(ether-block-amide) (Pebax 1657). The strong hydrogen bonding interactions between the ionic liquid and Pebax provide a homogeneous dispersion of GO-IL at high filler loading. The high-aspect ratio of GO-IL, as well as its high affinity with CO₂, enhances the selectivity of CO₂ over other light gases. Moreover,</p>			

the modification of GO fillers improves the filler-polymer interface compatibility. Thin film composite membranes (<100 nm) showed high CO₂ permeance up to 900 GPU and the CO₂/N₂ selectivity.

In chapter 3, graphene oxide (GO) ultra-permeable hydrogen membranes with high selectivity were prepared. However, GO is also highly hygroscopic, and swells in the presence of humidity, to catastrophically disturb this sieving capability. Positively charged nanodiamonds (NDs) were used to neutralize the negative charge of the stacked GO sheets and stabilize the resulting membrane against humidity. Whereas a native GO membrane lost all of its sieving capability under aggressive humidity cycling tests, an un-optimized GO/ND stack was found to retain ~90% of its ability. The ND addition is shown to also extend the permeance of the native membrane by a factor of 3 (to ~3700 GPU) without drastically affecting the overall hydrogen selectivity of the membrane (e.g. $\alpha_{H_2/CO_2} \sim 210$). As a control, similarly-sized but negatively charged polyhedral oligomeric silsesquioxanes (POSS) additives were found to bring no enhancement to the swelling resistance of the membranes.

In chapter 4, multilayer graphene sheets were mass-produced using a liquid exfoliation method. The homogeneous dispersion was carefully deposited to prepare ultra-thin graphene membrane (~20 nm) without any defects by a vacuum filtration. The selective nano-channels created by stacking of multilayer, mismatched, partially overlapping graphene grains that enable excellent sieving capabilities for small species, leading to high hydrogen permselectivities and nearly complete rejections for methanol and small ions in gas, solvent, and saline water separations. Furthermore, the resulting membranes showed high thermal, long-term and moist stability due to its stable structure and hydrophobic nature of graphene.

In chapter 5, the architecture of nanodiamond particles at the polymerization interface has a significant impact on the morphology and performance of the synthesized nanofiltration membrane. Through delicately regulating the extent of aggregation, nanodiamond clusters can preserve certain nanomaterial features and generate more contact surface in-between aqueous and organic phases. This stimulates the transformation of polypiperazineamide membrane structure from nodules to ridges at the nanoscale. Such structure transformation entails the substantial augmentation of effective surface area, which leads to 70% enhancement of water permeance without compromising salt rejection.

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(論文審査の結果の要旨)

本論文は、性能の高い炭素素材を基調とする膜の合成及び分子分離特性の制御についての研究をまとめたものである。

分離膜は物質分離を目的とした、イオン、気体などの選択的輸送に関する機能性材料であり、重要な特性である透過性と選択性を高めるにあたり、膜材料構造の多様性を活用した多孔質設計が可能である。本論文では、水素、二酸化炭素と水の回収能向上に着目し、系統的な炭素素材の合成と構築及び分離特性の制御を検討した。

主な成果は以下に示す通りである。

(1) 酸化グラフェンをイオン液体により修飾することではじめて、大規模に均質な複合薄膜の合成に成功した。また、従来のナノフィラーとポリマーでは両立が困難であった相互親和性とCO₂回収性の双方を改善した。

(2) ナノダイヤモンドの凝集状態を精密に調整して、界面重合でナノ濾過膜の合成を行い、構造が膜性能に及ぼす影響を明らかにした。

(3) 正電荷のナノダイヤモンドを用いて、酸化グラフェンの負電荷を中和して水素分離膜を作製した。さらに、(高)透過性を保ったまま、膜の膨潤脆弱性を克服した。

(4) 液体剥離法で得た均一な多層グラフェンシートを用いて、高い水素選択透過性と、メタノール・エタノール溶媒に関する Pervaporation 分離能、および塩水分離能を有する薄膜の作製に成功した。

本論文は、気体分離、浸透気化分離に関して、分離膜に従前から指摘されてきた、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、その実証を行っていることから、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2年12月14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。

なお、本論文は、京都大学学位規程第14条第2項に該当するものと判断し、公表に際しては、当該論文の全文に代えてその内容を要約したものとすることを認める。