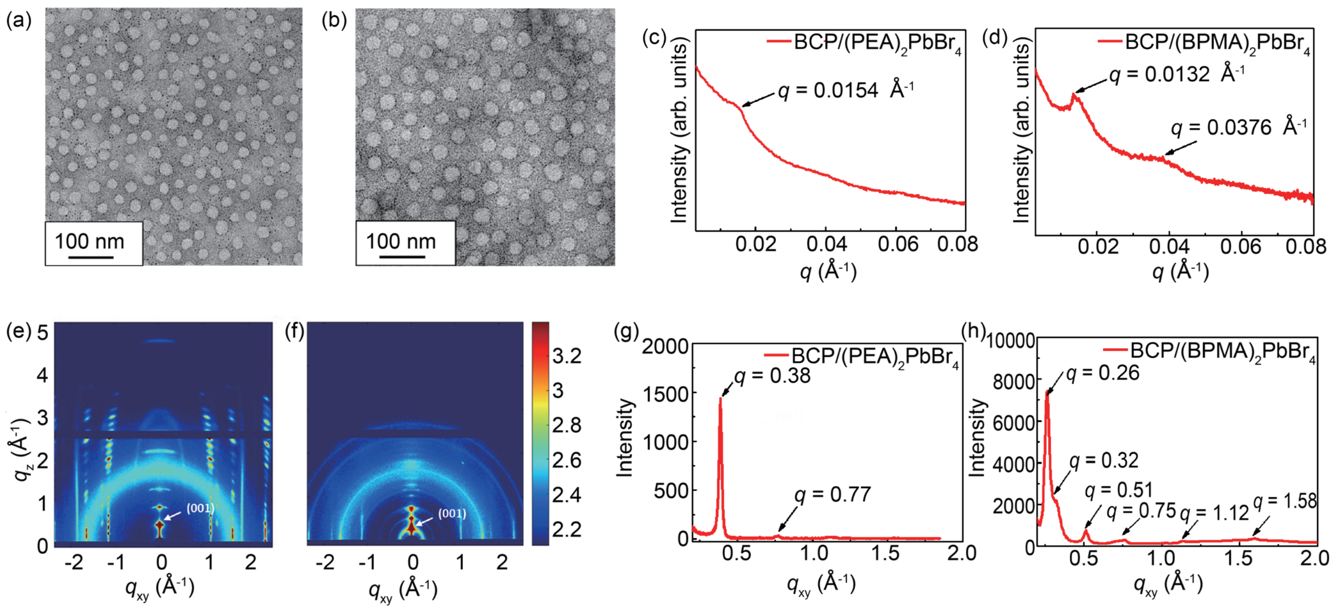

Fig. 1: TEM images of (a) PS-*b*-PEO/(PEA)$_2$PbBr$_4$ and (b) PS-*b*-PEO/(BPMA)$_2$PbBr$_4$ composite films. GISAXS 1D profile of (c) PS-*b*-PEO/(PEA)$_2$PbBr$_4$ and (d) PS-*b*-PEO/(BPMA)$_2$PbBr$_4$ composite films. 2D diffraction pattern of (e) PS-*b*-PEO/(PEA)$_2$PbBr$_4$ and (f) PS-*b*-PEO/(BPMA)$_2$PbBr$_4$ composite films. 1D profile of scattering vector in the out-of-plane direction of (g) PS-*b*-PEO/(PEA)$_2$PbBr$_4$ and (h) PS-*b*-PEO/(BPMA)$_2$PbBr$_4$ composite films. [Reproduced from Ref. 5]

This report features the work of Jian-Cheng Chen, Yu-Dao Lu, and Jung-Yao Chen published in Adv. Sci. ***10****, 2301028 (2023).*

TPS 25A Coherent X-ray Scattering
TLS 23A1 Small/Wide Angle X-ray Scattering

- GISAXS, GIWAXS
- Materials Science

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CO_2 Reuse Through Eco-Friendly Polymers

Recyclable gas separation membranes for CO_2 prepared from high-performance polyurethane (PU)/SiO_2 nanohybrids using recycled polycarbonate (PC) and CO_2-based compounds introduce the concept of circular economy into membrane materials.

In recent decades, the escalating levels of greenhouse gases, particularly carbon dioxide (CO_2), has become a worldwide concern. The surge in CO_2 emissions, driven by advancements in chemical industries and utilization of synthetic polymers derived from petroleum fossil fuels, has resulted in severe consequences including extreme weather events, glacier melting, rising sea levels, and the extinction of various species. Despite its negative impact to the environment, CO_2 is cost-effective, abundant, and non-toxic, making it a versatile industrial material. Researchers have extensively explored applications of CO_2 in areas such as oil extraction, drug solubility, and particle formation using supercritical fluid technology. CO_2 has also been utilized as a feedstock for polymers, significantly improving process design and polymer engineering. For example, cyclic ethers can be utilized as comonomers, combining them with CO_2 to form polycarbonate (PC) polymers such as aliphatic polycarbonate polyols which are used to prepare specialty polyurethanes (PUs). Although the use of CO_2 as a raw material is widespread, a crucial strategy for mitigating CO_2 gas emissions involves advancing selective gas capture and storage technologies based on separation membranes crafted from composite polymers.

Ru-Jong Jeng (National Taiwan University) and his team recently developed a green process for preparing recyclable PU/silica (PU/SiO_2) nanohybrids as gas separation membranes for CO_2 capture and storage (**Fig. 1**). By using the heterofunctional reagent (3-aminopropyl)triethoxysilane (APTES) as an aminolysis agent, PC waste was selectively decomposed into key intermediates containing the versatile functional groups of active hydrogens and alkoxysilanes. One pot synthesis of PU/SiO_2 nanohybrids was achieved through click reactions with active hydrogens and subsequent sol–gel reactions of alkoxysilanes. Through the incorporation of key ingredients, such as poly(tetramethylene ether) glycol (PTMEG) or polycarbonate diols (PCDLs), PU/SiO_2 hybrids with robust elastomeric properties was obtained. In addition, the presence of various SiO_2 particle sizes and microphase separation in these PU/SiO_2-based membranes resulting in improved CO_2/N_2 selective gas permeation properties. Using recycled intermediates, their approach provided membranes with unique active sites (phenolic carbamate groups) that were recyclable even after consumption.

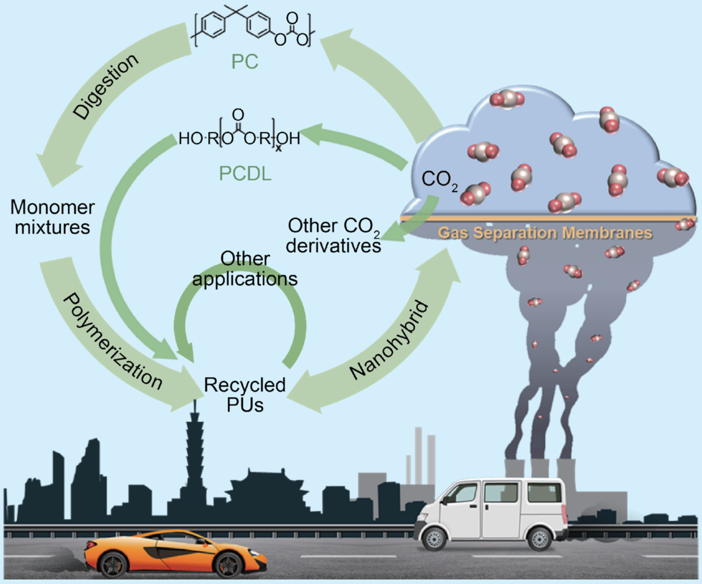

Fig. 1: Conceptual diagram of the CO_2 carbon cycle. PC: polycarbonate; PCDL: polycarbonate diol; PU: polyurethane. [Reproduced from Ref. 1]

PU/SiO_2 properties depend heavily on microphase separation morphology, which were analyzed using small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) at **TLS 23A1**. The scattering peaks at 0.02–0.06 $Å^{-1}$ (12–30 nm) signify long-range order between hard and soft segment domains in microphase separated structures with a large X-ray scattering contrast. For PU with poly(ethylene glycol) (PEG) diol samples, a well-mixed morphology without a significant domain size was observed in the SAXS measurement due to the partially soluble nature of PEG-based polyol in nanohybrids. In contrast, clear domain spacings were observed in the SAXS measurement for the nanohybrids composed of PTMEG or PCDL. These results suggest that the PTMEG-based and PCDL-based PU/SiO_2 nanohybrids exhibit morphologies with a larger extent of microphase separation, having more microcavities to facilitate diffusion of gas molecules, and thus leading to membranes with improved gas permeability. The microphase behavior of the PU/SiO_2 nanohybrids was also analyzed using WAXS. The characteristic scattering peaks of PEG (18.8° and 23.0°), PTMEG (19.5° and 24.0°), and PCDL (19.8° and 23.1°) crystallinity were observed before the sol–gel reaction. However, after the sol–gel reaction, all PU/SiO_2 nanohybrid samples only exhibited an amorphous phase signal because the sol–gel reactions hinder the crystallization of soft segments.

This new PU/SiO_2 nanohybrid gas separation membrane has a high P_{CO2} permeability of 24.02 Barrer and a selectivity of 32.85 ($\alpha_{CO2/N2}$), which approaches the upper bounds reported by Robeson.[2–3] Moreover, the joint presence of polycarbonate polyol and silica in the nanohybrids led to strong elastomeric properties, with tensile strengths of 35.5 MPa and over 700% elongation at the breaking point, exceeding those of previously reported PU-based gas separation membranes. The newly developed PC recycling process featured carbamate groups as the reaction sites, enabling the recycled PU/SiO_2 nanohybrids to be used as gas separation membranes for CO_2 capture and storage. In the traditional linear economy model, any membrane application can only be discarded as polymer waste after it has become ineffective. This study introduces the concept of a circular economy, and a wide range of advanced applications involving CO_2 reuse is within reach. (Reported by Orion Shih)

This report features the work of Ru-Jong Jeng and his collaborators published in J. Chem. Eng. ***452****, 139262 (2023).*

TLS 23A1 Small/Wide Angle X-ray Scattering
- SAXS and WAXS
- Chemistry, Materials Science, Green Sustainable Chemical Process

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