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News and opinions

Carbon nanotubes hold graphene membranes together

Cordelia Sealy

Researchers have taken a step towards realizing the ultimate filtration membrane that can remove salt and other undesirable chemicals from water to render it drinkable quickly, easily, and cheaply [Yang et al., *Science* **364** (2019) 1057, http://doi.org/10.1126/science.aau5321].

Theoretical predictions have earmarked atomically thin nanoporous two-dimensional materials as ideal membranes because they allow water to pass through rapidly while removing ions and other molecules highly effectively. Proof-of-concept demonstrations of graphene-based nanofiltration are tantalizing but have been restricted to small membranes with limited mechanical robustness. Graphene is highly brittle and even small cracks or tears in the material can render it useless as a membrane.

Now researchers from Wuhan University, Hunan University, Peking University, The Pennsylvania State University, University of California, Los Angeles, and National Institute for Materials Science in Japan, led by Quan Yuan and Xiangfeng Duan, have created large-area nanoporous two-dimensional membranes based on graphene flakes supported by a scaffold of single-walled carbon nanotubes (SWNTs) that are both strong and flexible.

“Scaling atomically thin membranes with sufficient mechanical strength and including high-density sub-nanometer pores in graphene to satisfy the practical nanofiltration applications seemed an insurmountable challenge,” says Yuan. “But we have designed a large-area, high mechanical strength graphene nanomesh/carbon nanotube hybrid membrane that maintains the merit of atomically thin two-dimensional materials for efficient ionic and molecular nanofiltration.”

The membrane consists of a graphene nanomesh (GNM) tightly bonded to an interwoven network of SWNTs, which form micro-sized islands reminiscent of insect wings or plant leaves. This reinforcing structure, which is known as a Voroni cell structure, curtails the spread of any cracks or tears in the delicate graphene sheets. The graphene/SWNT hybrid is coated with a mesoporous SiO_2 film and exposed to O_2 plasma to drill nanoscale holes into the membrane. The mesoporous SiO_2 film is subsequently removed leaving an ultrathin, flexible, but highly robust film. On average, the pores are less than a nanometer in diameter, but their dimensions can be tailored by adjusting the O_2 plasma etching time. The GNM/SWNT hybrid membrane can then be transferred onto a variety of different substrates and readily scaled up for large-area applications. The team built a reverse osmosis (RO) cross-flow filtration test device to investigate the capabilities of the hybrid material (Fig. 1).

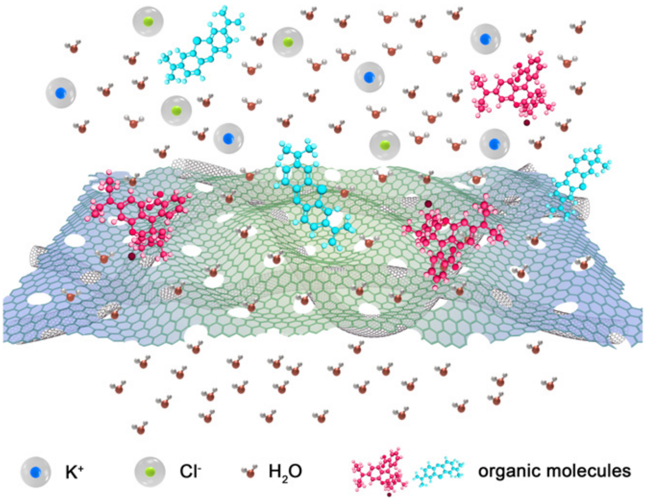

Fig. 1. Schematic of the GNM/SWNT hybrid membrane membrane for nanofiltration applications.

“The membranes show high water permeance, high rejection ratio for salt ions or organic molecules, and retain stable separation performance in tubular modules,” points out Yuan.

The membrane’s water transport properties and abilities to reject salt ions are ideal for desalination. Although the material’s 86% rejection of NaCl, for example, is lower than commercially available reverse osmosis membranes, it is significantly higher than most graphene- or graphene-oxide-based membranes reported so far. As well as typical salts, such as Na_2SO_4, $MgCl_2$, and KCl, the GNM/SWNT membrane can also filter out small charged or neutral organic molecules such as methylene blue, rhodamine B, and fluorescein isothiocyanate, which are not typically removed by commercial filtration membranes. The GNM/SWNT membrane is also resistant to bacteria over long periods, promising excellent antifouling properties. The researchers put this down to the smoothness of GNM, to which bacteria find it difficult to adhere, and the inherent antibacterial nature of graphene.

“The fine control of pore size and distribution is, we believe, one of the vital reasons for efficient permeation and separation,” explains Yuan. “The GNM/SWNT hybrid membrane, therefore, addresses the critical tradeoff between water permeance and solute rejection in conventional desalination membranes."

The combination of high water permeance and salt rejection properties of the membrane could be ideal for transforming salty water sources into potable freshwater. The researchers believe that there are no fundamental limitations to producing large sheets of the material, even up to the meter-scale.

César Moreno of the Catalan Institute of Nanoscience and Nanotechnology (ICN2) believes the work of Yang et al. addresses the Achilles heel of graphene membranes, the porous support.

"The great interest in graphene as membrane stems from the capability to drill pores with exquisite precision, in addition to its atomic thickness," he explains. "The porous support should provide enough mechanical strength to enable one-atom-thick nanoporous graphene withstand the pressure required for filtration while avoiding the generation of cracks or defects. In Yang et al.'s work, this critical role is played by the carbon nanotube-based support, which provides a meritorious equilibrium between selectivity, permeability, and mechanical strength."

The future success of this approach will depend on improving the packing of the carbon nanotubes to enhance the permeance until it is one order of magnitude higher, he adds. This has been reported in atomically thin nanoporous graphene on flat silicon nitride supports but only at micrometer scales [Surwade et al., *Nature Nanotechnology* **10** (2015), 459–464].

Qilei Song of the Barrer Centre at Imperial College London points out that Yang et al. have applied the well-known oxygen plasma etching approach in an elegant new way to tune the porosity of graphene membranes on carbon nanotube membrane supports.

"The resulting hybrid membranes combine the size-exclusion function of nanoporous graphene and high mechanical strength of nanotubes," he says. "This will inspire further work on developing nanoporous graphene membranes or using the graphene membranes as building blocks for fabricating thin film composite membranes."

Song cautions, however, that there are many challenges to overcome before these supported graphene membranes can be used in practical seawater desalination or nanofiltration.

"The salt rejections are still low and need to be improved to a higher level (>99%)," he points out. "In practical nanofiltration applications, selectivity is more important rather than high water flux, so more precise control of pore size distribution and functional groups will be required, which is not an easy task. Furthermore, it remains challenging to scale up these membranes to the meter-square size for industrial applications."

While there is still a long way to go in making real membranes from graphene, Song believes that this study brings the possibility a step closer.

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Gold's atomic structure puts the brakes on carriers

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Gold atoms prefer to take up a particular spatial arrangement, face-centered cubic, in bulk material but can behave differently when limited to tiny nanoclusters. These collections of atoms less than 2 nm in diameter can adopt different packing arrangements including hexagonal close packed and body-centered cubic structures. Now researchers have found that these atomic structures have a profound effect on carrier lifetimes, which could have important implications for the application of metal nanoclusters in solar energy converters, photocatalysis, and optoelectronics [Zhou et al., *Science* **364** (2019) 279, DOI:10.1126/science.aaw8007].

Very small gold nanoclusters (Au NCs) protected by organic ligands have distinct energy levels and multiple absorption peaks in the ultraviolet-visible light spectrum. This presents an attractive option for light-harvesting devices converting absorbed solar light into electron-hole pairs. These electron-hole pairs either recombine unproductively or form free charge carriers. The lifetime of these charge carriers, which is vital to the usefulness of devices, depends upon various factors, such as the band gap and temperature, and can be tailored by varying the size, composition, and structure of the nanoclusters.

It is already well known that in larger nanoclusters reducing the energy gap leads to shorter carrier lifetimes, but in smaller nanoclusters structure-related factors can take over. Now Rongchao Jin of Carnegie Mellon University and De-en Jiang of the University of California, Riverside along with colleagues at Brookhaven National Laboratory have observed huge differences in carrier lifetimes in Au nanoclusters with different crystalline structures.

"We found that new structures of gold nanoclusters led to a difference in photoexcited states by more than three orders of magnitude," says Jin. "Such a drastic difference in carrier lifetime is unprecedented and fundamentally important."

When Au atoms take up a body-centered cubic structure, carriers show an exceptionally long lifetime (of 4.7 microseconds), which is comparable to that of Si. By contrast, the carrier lifetime in hexagonal close-packed Au nanoclusters is just 1 nanosecond (Fig. 1). The researchers believe that differences in the electronic structure of the various arrangements of Au_4 tetrahedral building blocks in the three crystal structures lead to the large variation in carrier lifetime.

"The achieved control over quantum states originates from the different overlap of molecular orbitals of the two nanoclusters," explains Jin.

In hexagonal close-packed Au NCs, the distance between neighboring Au_4 tetrahedral units is zero and the carrier lifetime is, as the researchers show, very short. By contrast, the distance between neighboring Au_4 tetrahedral units in body-centered cubic NCs is