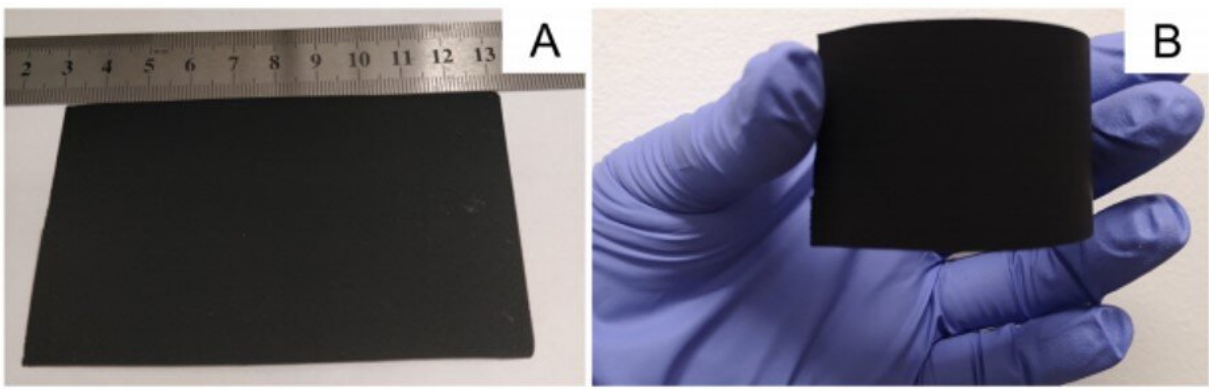
Designing hierarchical nanoporous membranes for highly efficient adsorption and storage applications

October 14 2020, by Thamarasee Jeewandara

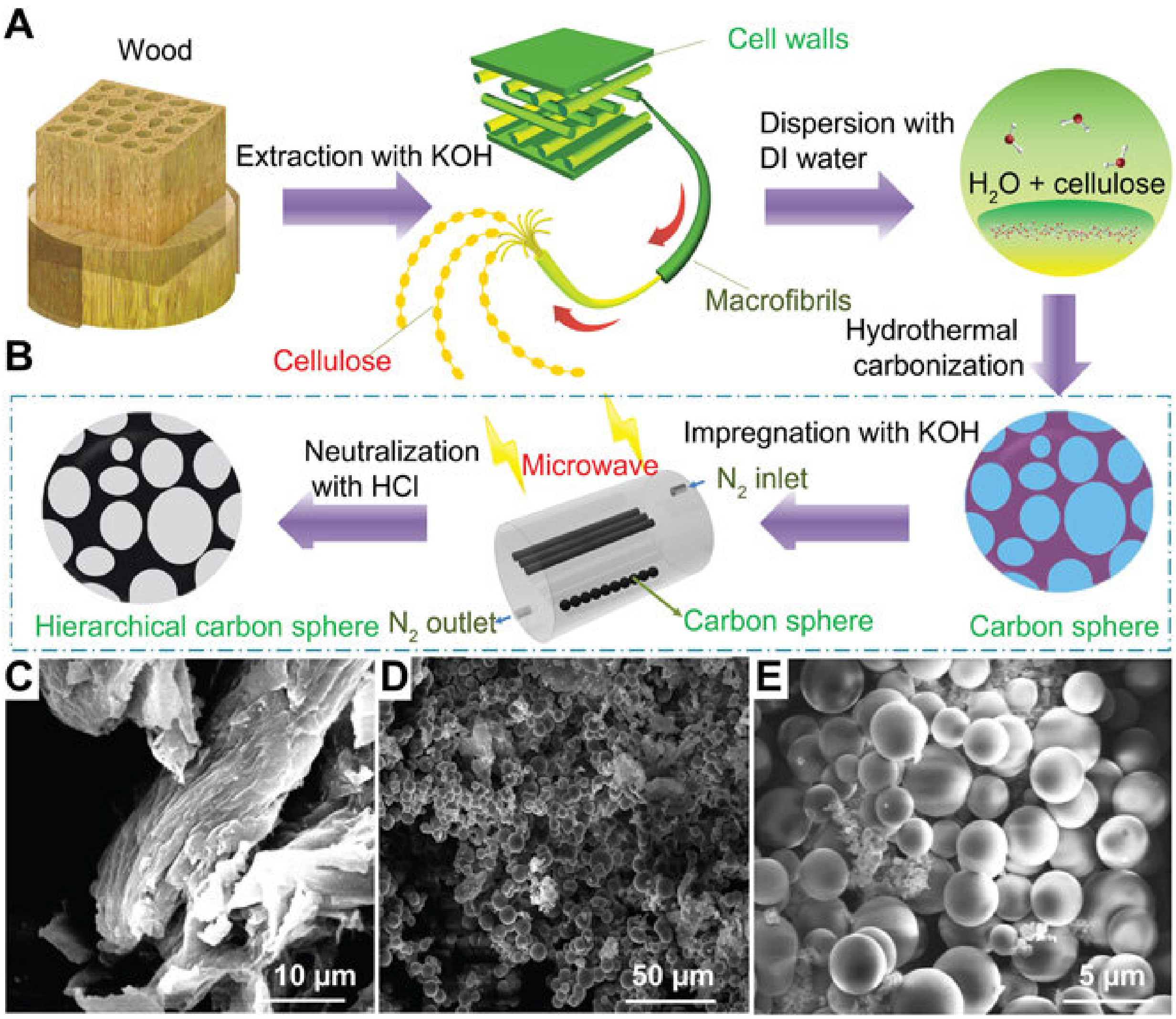


Photographs of the hierarchical nanoporous membranes created using a doctor blade coating method. A, Photograph of large-area HNM (10 × 10 cm2) fabricated by a doctor-blade method. B, Photograph of free-standing and flexible HNM without absence of cracks. Photo credit: J.T., Stanford University. Permission granted. Credit: Science Advances, doi: 10.1126/sciadv.abb0694

In the field of volatile organic compounds, graphene oxides have attracted attention as two-dimensional (2-D) materials with nanoporous membranes due to their molecular-sieve-like architectural properties and functional simplicity suited for hydrogen (H_2) adsorption. Nevertheless, the accumulation of graphene sheets can be challenging due to their low efficiency for long-term industrial applications. As a result, Haiyan Mao and a research team at the University of California Berkeley, Stanford University and the Lawrence Berkeley National Lab in the U.S. designed hierarchical nanoporous membranes (HNMs). They designed and developed the constructs by combining a class of nanocomposites with a carbon sphere and graphene oxide. The team followed Murray's law (an optimization principle) to prepare the hierarchical carbon spheres to act as spacers and adsorbents, using chemical activation alongside microwave heating. The HNMs contained micropores dominated by a combination of ultra-micropores and mesopores. The work can be expanded across environmental and energy fields.

Materials architecture for industrial gas separation and storage.

Designing materials for gas separation and storage can be challenging due to conflicting goals. For example, pores on the order of molecular dimensions are necessary to discriminate various gases on the basis of size, but they must also be chemically functionalized to facilitate chemical selectivity during adsorption. Capillary effects can also cause clogging in narrow pores due to impurities and gas condensation. Mao et al. therefore created hierarchical materials that combined elegant 2-D nanosheets with synthetic carbon spheres to create a "meatball sandwich" in an easily scaled production process. The materials successfully performed volatile organic adsorption and hydrogen gas storage. Industrial gas separation and storage have a long history where porous materials including activated carbon, zoolites and metal organic frameworks (MOFs) have facilitated the removal of volatile organic compounds and stored hydrogen, although their limited mechanical stability can restrict long-term applications. While some MOFs have shown high gas adsorption performance, their large-area production is associated with increased fragility.

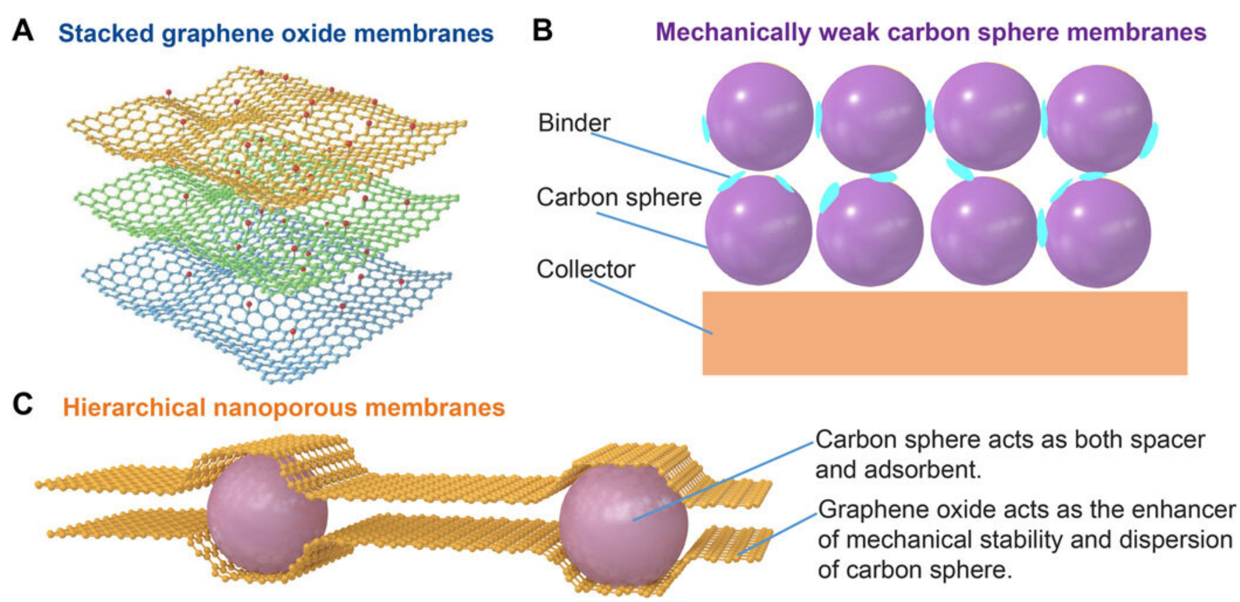


Wood-derived hierarchical carbon spheres (HCS). (A) Schematic diagram of the fabrication process of the carbon sphere. (B) Schematic diagram of the fabrication process of the HCS. (C to E) SEM images of cellulose and the carbon spheres. Credit: Science Advances, doi: 10.1126/sciadv.abb0694

Engineering carbon spheres

Scientists had therefore recently developed carbon spheres with hierarchical micro- and mesospheres for applications in the presence of volatile organic compounds (VOCs) and hydrogen (H2) adsorption due to their high sphericity, selectivity, and porosity. Mao et al. transformed these spheres into membranes using binders, but the constructs were susceptible to expensive manufacturing costs and mechanical instabilities. The team therefore assembled hierarchical nanoporous membrane (HNM) structures by assembling carbon spheres as effective nanoporous spacers to improve cross-plane mass transfer through expanded interlayer spacing. The team crafted hydrothermal carbonization of pinewood-based cellulose mixed with graphene oxide (GO) to create membranes based on an extremely simple doctor-blade method. Generally, the method is widely used to produce thin films in large surface areas, and the resulting porous HNMs contained micropores and mesopores.

Experimental hierarchical carbon spheres

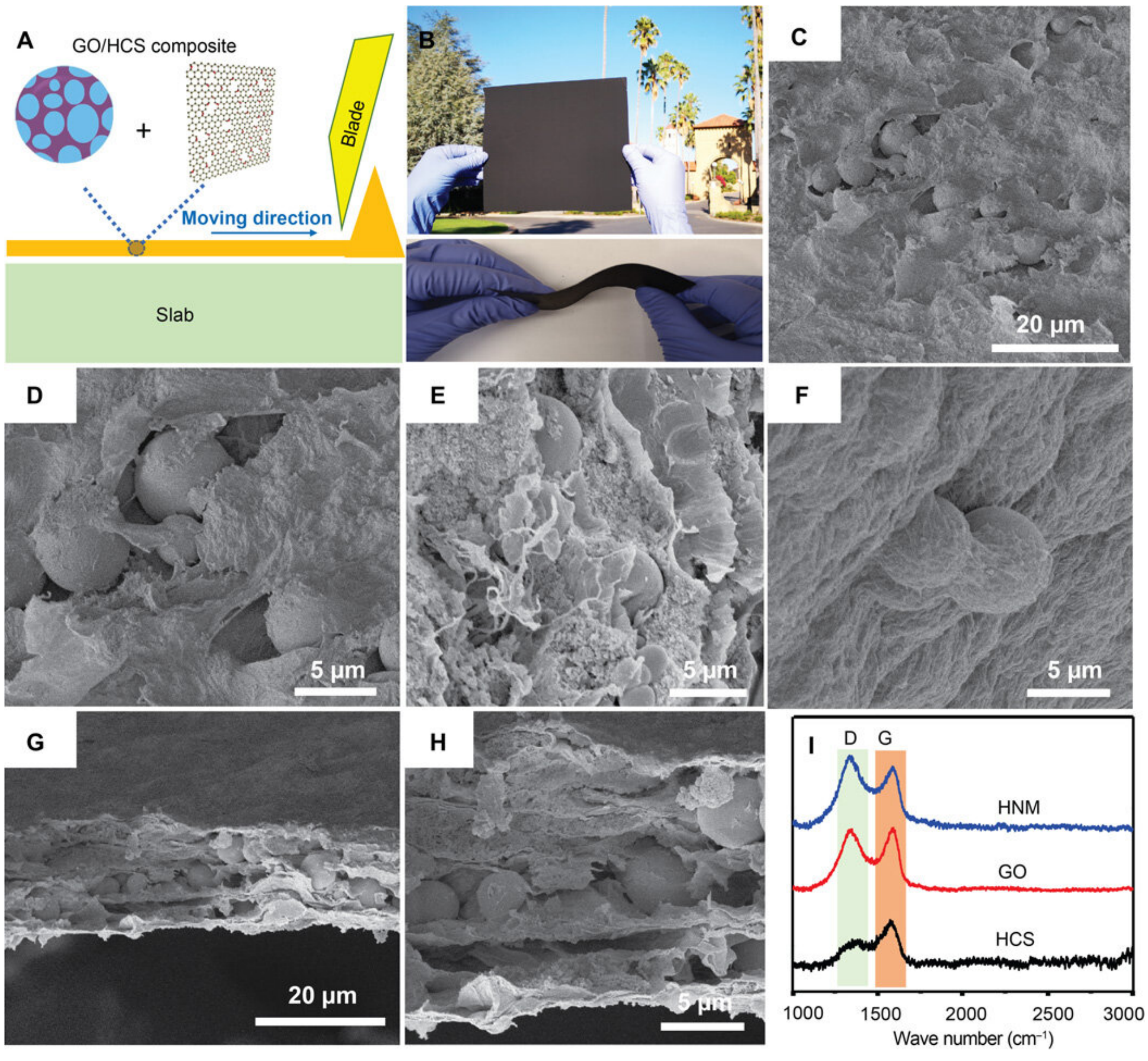


Comparison of a schematic illustration of GO membranes, carbon sphere membranes, and hierarchical nanoporous membranes (HNMs). (A) Designed structural model of stacked graphene membranes. (B) Model of mechanically weak layers of carbon sphere membranes by binders. (C) Model of the mechanical strength and high adsorption capacity of HNMs. As a comparison of GO membranes and carbon sphere membranes, our HNMs combined the merits of both GO and carbon sphere membranes: In this meatball sandwich structure, carbon spheres act as spacers and adsorbents, precluding the agglomeration of GO. GO sheets physically disperse carbon spheres, ensuring mechanical stability. Credit: Science Advances, doi: 10.1126/sciadv.abb0694

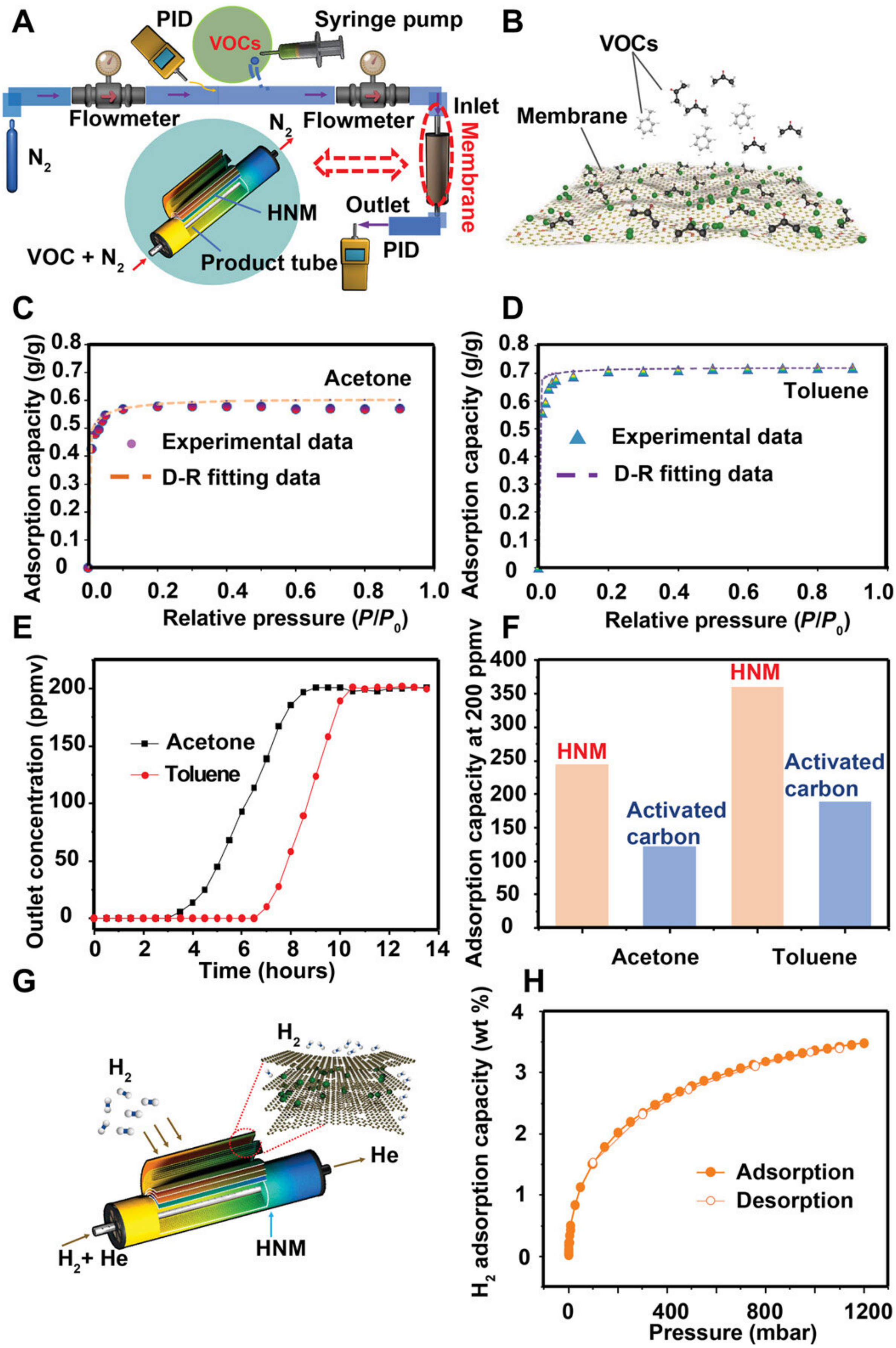
Mao et al. developed the hierarchical carbon spheres (HCSs) with high surface area, high sphericity and monodispersibility through several steps, which included hydrothermal carbonization synthesis and chemical-microwave activation methods. The team used scanning electron microscopy (SEM) to understand the effects of the reaction temperature, reaction time and cellulose concentration of the HCS. They noted rapid cellulose decomposition during hydrothermal temperature increase to generate hydrothermal carbons with a higher degree of aromatization. After optimal treatment, Mao et al. obtained optimized carbon spheres with spherical structure and a smooth surface without a hollow interior. Using infrared (IR) spectra, they showed how the cellulose and carbon spheres indicated the presence of many oxygen functional groups on the surface of the HCS. The cellulose underwent dehydration and aromatization during hydrothermal carbonization. Mao et al. used X-ray diffraction (XRD) analysis to understand the XRD patterns of cellulose and carbon spheres to show how the resulting carbon materials existed in an amorphous state.

The team subsequently synthesized the graphene oxide (GO)/hierarchical carbon spheres (HCS), followed by scanning electron microscopy investigations to distinctly identify the graphene nanosheets, which were in good agreement with previous work. The HCSs retained a spherical architecture without obvious damage or wrinkled textures; the method prevented the aggregation of graphene to successfully fabricate the new GO/HCS (graphene oxide/hierarchical carbon sphere) composites.

Developing hierarchical nanoporous membranes (HNMs) and proof-of-concept:



Doctor-blade coating technique to fabricate HNM. (A) Schematic illustration of the blade-coating method for forming HNM. (B) Photographs of a large-area HNM (10 cm by 10 cm) fabricated by the doctor-blade method. (C to F) SEM images of HNM. (G and H) SEM images of cross-sectional edge of HNM. (I) Raman spectra of HCS, GO, and HNM. The D band corresponds to the defects and disorder within the wood-derived carbon, while the G band is due to the in-plane stretching of sp2-bonded carbon. Photo credit: J.T., Stanford University. Permission granted. Credit: Science Advances, doi: 10.1126/sciadv.abb0694


A
PID
VOCs
Syringe pump
Flowmeter
Flowmeter
Inlet
Membrane
N_2
N_2
HNM
Outlet
PID
VOC + N_2
Product tube
B
VOCs
Membrane
C
Acetone
Experimental data
D-R fitting data
Adsorption capacity (g/g)
Relative pressure (P/P_0)
D
Toluene
Experimental data
D-R fitting data
Adsorption capacity (g/g)
Relative pressure (P/P_0)
E
Acetone
Toluene
Outlet concentration (ppmv)
Time (hours)
F
HNM
Activated carbon
HNM
Activated carbon
Adsorption capacity at 200 ppmv
Acetone
Toluene
G
H_2
H_2
He
H_2+ He
HNM
H
Adsorption
Desorption
H_2 adsorption capacity (wt %)
Pressure (mbar)

The volatile organic compound (VOC) and H2 adsorption performance of HNM. (A) Schematic diagram of experimental setup for measuring VOC adsorption. (B) Structural model for toluene and acetone adsorption. (C and D) Acetone and toluene adsorption isotherms and D-R fitting. (E) Breakthrough curves for acetone and toluene at 200 ppmv. (F) Adsorption capacities of HNM and activated carbons at the outlet concentration of 200 ppmv. (G) Schematic diagram of H2 adsorption. (H) Equilibrium H2 adsorption isotherms at 77 K. Credit: Science Advances, doi: 10.1126/sciadv.abb0694

Mao et al. used the doctor-blade deposition method to produce hierarchical nanoporous membranes (HNMs) with highly versatile, uniform and free-standing membranes with precisely controlled thickness. The structures showed a higher degree of corrugation in comparison to pure graphene oxide; beneficial for volatile organic compound (VOC) diffusion and adsorption. All experimental outcomes confirmed the facile fabrication procedure, large surface area and low cost of the starting materials used to develop HNMs as promising candidates for VOC and hydrogen storage. As proof of concept, Mao et al recorded the adsorption performance of VOCs to understand the contribution of hierarchical structures and the mechanical stability of hierarchical nanopore membranes. As an example, with volatile compounds such as toluene and acetone, the adsorption capacities were comparable to other porous materials. At high concentrations, the adsorption capacity increased gradually. In this way, the extremely well-developed micropores efficiently and rapidly adsorbed the toluene/acetone molecules. The outcomes indicated promising adsorption performance in low-concentration, volatile organic compound (VOC) environments.

Mao et al additionally tested the hydrogen storage capacity of HNM due to their exceptionally high surface areas and hierarchical micropore-dominated structures. The work showed advantages for hydrogen adsorption including low cost, good reversibility and safety. The team tested the cost-effectiveness and durability of HNMs through multiple adsorption/desorption cycles to confirm the cost-effective applications of the membranes.

More information: Haiyan Mao et al. Designing hierarchical nanoporous membranes for highly efficient gas adsorption and storage, *Science Advances* (2020). DOI: 10.1126/sciadv.abb0694

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