

Strong Ultralight Material Could Aid Energy Storage, Carbon Capture

2023-04-12

2D polymers are likely candidates for large-scale multifunctional applications. Scientists showed that fine-tuning interlayer interactions in a class of 2D polymers known as covalent organic frameworks (COFs) can determine the materials' loss or retention of desirable mechanical properties in multilayer or bulk form.

2D materials get their strength from their atom-thin, sheetlike structure. However, stacking multiple layers of a 2D material will sap it of the qualities that make it so useful.

[Rice University](#) materials scientist Jun Lou and collaborators at the [University of Maryland](#) showed that fine-tuning interlayer interactions in a class of 2D polymers known as covalent organic frameworks (COFs) can determine the materials' loss or retention of desirable mechanical properties in multilayer or bulk form. In the process, the researchers engineered a lightweight material with high stiffness and strength that preserves its 2D properties even as a multilayer stack, according to a study published in [Proceedings of National Academy of Sciences](#).

The finding is a first step toward enabling the use of 2D polymers in large-scale multifunctional applications where mechanical properties are important and could open the door to new high-performance filtration systems, carbon capture and energy storage technologies.

"This to us is a very exciting starting point," Lou said. "A really nice thing about COFs and other 2D polymers is that you have a lot of chemistry knobs you can tune. This means you can rationally engineer the interlayer interactions. Essentially, you can make very strong modular systems using interlayer interaction design."

Researchers looked at how two COFs with very similar structures behave when multiple layers were stacked together and found that a small difference in their structure led to completely different patterns of interlayer interaction.

“In order to successfully design COFs with desirable interlayer interactions you need scientific insight into the material structures of COFs,” said Teng Li, a professor of mechanical engineering at Maryland. “To this end, we rely on first-principles simulations of the COF materials at the molecular scale to offer crucial design guidelines.”

Qiyi Fang, a Rice alum and co-lead author on the study, said the Rice lab designed two types of COFs based on the scientific insight from the simulations developed by colleagues at Maryland.

“One of the COFs, like most 2D materials, does not have a very strong interlayer interaction, and the strength and elasticity of the material decreases with the number of layers added,” Fang said. “The other COF, however, exhibits strong interlayer interaction and retains its good mechanical properties even with the addition of multiple layers.”

Maryland researcher and co-lead author Zhenqian Pang said the simulations helped pinpoint why the two COFs behaved differently.

“We found that the strong interlayer interaction in the latter COF results from the significantly enhanced hydrogen bonding among its special functional groups,” Pang said.

The fact that strong interactions between the 2D-material layers correlate with the persistence of desirable mechanical properties in the material’s multilayer or bulk form gives researchers a clue about what it takes to make a bulk-layered material that retains the mechanical properties of its 2D counterpart.

“We believe this strong interlayer interaction is primarily due to the chemistry of the

hydrogen bond,” Lou said. “Hydrogen bonds are universal and occur in many systems. In our study, we show that those hydrogen bonds between layers are not only quite strong, but also dynamic in the sense that if they break under stress, they reform as the layers slide over one another.”

Facilitating stronger bonds between 2D-material layers can weaken the bonds connecting the atoms within a layer.

“Interlayer interaction-tuning is possible in other 2D materials, but what generally happens is you're going to sacrifice the strong in-plane bonding environment of those 2D materials in order to have those functional groups attached,” Lou said. “So it's actually a trade-off. With 2D polymers, you don't necessarily have to have that trade-off. That's one of the very important motivations for taking this direction in our research.”

A 2D polymer is made up of identical atom groupings with linking elements — the functional groups — along each of its edges.

“The 2D polymer is a sort of designer system, in the sense that it's very tunable,” Lou said.

In previous research on 2D materials, Lou and collaborators had shown hexagonal boron nitride (h-BN) was 10 times more resistant to fracture than graphene.

“Like in graphene or h-BN, you still have this hexagonal lattice structure — six atoms in a hexagon pattern that you repeat indefinitely,” Lou said. “But for the 2D polymer, you also have a linker or nodal unit, which makes that hexagon larger.”

A larger repeat element means the material is less dense.

“This COF is nearly 10 times less dense than graphene or h-BN,” Fang said. “As a result, the specific strength and specific stiffness of the COF are among the highest reported.”

“This is significant because if we can show that this 2D material is as fracture-resistant as h-BN, it is also significantly lighter,” Lou added. “When you want greater strength without increasing the weight of your structure, this can be useful.

“This finding relates to some of the more application-driven ideas,” he said. “COFs could make excellent filtration membranes, for instance. Now we have a way to design very strong, very fracture-resistant, multilayer 2D polymers that could be very good candidates for membrane filtration applications.”

Lou said another potential application is for upgrading energy storage.

“We’ve already explored COF functionality for optimizing lithium-ion battery performance, and this shows we’re on the right track,” he said. “For all these applications, 2D polymers’ mechanical properties — especially in terms of fracture resistance — are very important.”

According to Li, the study’s key insight is that “tuning secondary intermolecular bonding is an effective materials-design strategy that could enable the development of an array of new materials with enhanced properties.

“This is distinct from the conventional materials design methods that rely largely on primary bonding,” he said. “There are fertile opportunities to design materials with this new strategy.”

Read the [original article](#) on Rice University.