

## Nanocomposites

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# Layered Biomimetic Composites from MXenes with Sequential Bridging

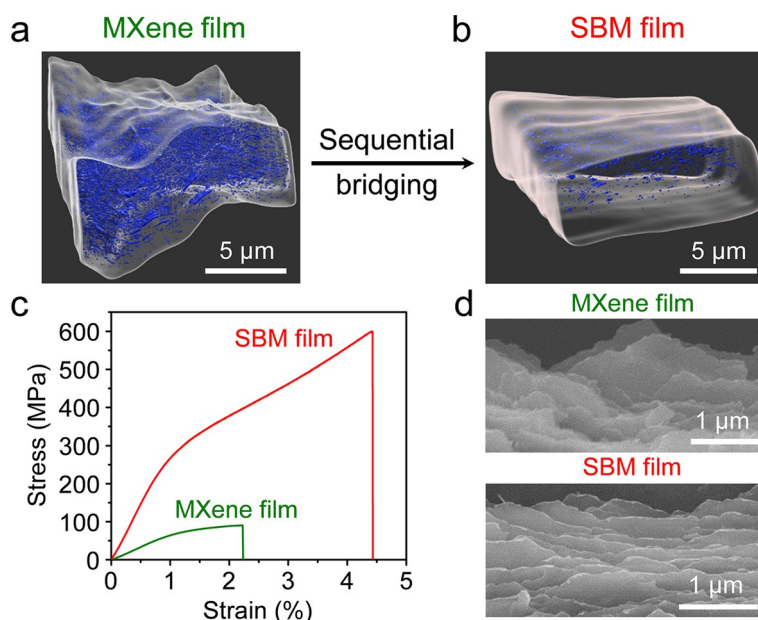
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**Abstract:** Layer-by-layer (LbL) assembly is a widely used technique for the self-assembly of layered nanocomposites from clay sheets, carbon nanotubes, graphene oxide, nanoparticles, and other materials. Other approaches for fabricating layered nanocomposites include vacuum-assisted filtration and blade coating. They are simpler than LbL assembly, but they all introduce voids into the layered structure, thereby reducing the performance of the resulting nanocomposites. A team from Beihang University evaluated the void structure in  $Ti_3C_2T_x$  MXene composites and found that the fundamental problem with voids can be solved by the sequential nanoscale bonding of MXene platelets with sodium carboxymethyl cellulose combined with covalent bridging with borate ions, thereby opening a new path to self-assemble two-dimensional platelets into continuous high-performance layered nanocomposites.

Layer-by-layer (LbL) assembly is a widely used technique for assembling layered nanocomposites from clay sheets, carbon nanotubes, graphene oxide, nanoparticles, and other materials.<sup>[1–5]</sup> Classic LbL assembly is a cyclic dip-and-rinse process in which a nanomaterial typically carrying a surface charge is adsorbed in a conformal manner onto the previous layer.<sup>[6]</sup> Nearly all the nanocomposites generated by the LbL assembly of 2D materials have exceptional materials properties (except on small scales) that originate from the organic-inorganic sequence of multilayers, similar to that found in nacre, bone, and other biomineralized tissues. Their high mechanical performance is also associated with the tight binding of the polymer films that fill all the nooks and crevices between the inorganic sheets. Other approaches for fabricating layered nanocomposites include vacuum-assisted filtration and doctor blading. These also take advantage of the self-assembly of 2D nanoplatelets into layered stacks but are simpler to implement. In contrast to natural nanocomposites and those formed by LbL

assembly, however, the other methods introduce voids into the layered structure, which reduces the performance of the resultant nanocomposites; however their molecular-scale organization can be optimized further to increase their mechanical performance.

In a new paper published in *Science*, Sijie Wan et al.<sup>[7]</sup> found that a dramatic reduction in the voids is feasible for layered nanocomposites based on a new type of 2D material, known as MXenes.<sup>[8]</sup> The team from Beihang University used three-dimensional (3D) reconstructions obtained from focused ion beam and scanning electron microscopy topography to evaluate the voids in the composites obtained from  $Ti_3C_2T_x$



**Figure 1.** 3D-reconstructed void microstructure of the a) MXene layered nanocomposites and b) SBM films obtained by focused ion beam and scanning electron microscopy tomography. c) Typical tensile stress–strain curves of the MXene and SBM films. d) SEM images of the fracture surfaces of the MXene and SBM films.

MXene (Figure 1 a). The Cheng group found that the relative volume of the voids in composites of MXene platelets made by the fast techniques is as high as  $15.4 \pm 0.6\%$ .<sup>[7]</sup> They also found that it is difficult to assemble these 2D materials into compact nacre-like nanocomposites.<sup>[9]</sup> The void problem was successfully mitigated by applying sequential bridging of the layered composites through the interaction of sodium carboxymethyl cellulose with  $Ti_3C_2T_x$  nanoplatelets through hydrogen bonding. Borate ions were also added to further “tighten” the material by cross-linking it with covalent bonds.

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The percentage of voids was greatly reduced due to the tendency of carboxymethyl cellulose to attach to the molecular segments present in the voids. The void volume in the sequentially bridged MXene (SBM) composites was reduced to  $5.35 \pm 0.31\%$  (Figure 1b).

The densified microstructure and improved interlayer interactions greatly enhance the mechanical properties of the SBM composite (Figure 1c). Its tensile strength of  $583 \pm 16$  MPa, Young's modulus of  $27.8 \pm 2.8$  GPa, and toughness of  $15.9 \pm 1.0$  MJ m<sup>-3</sup> are much higher than those of the MXene film with a tensile strength of  $87 \pm 3$  MPa, Young's modulus of  $6.1 \pm 0.6$  GPa, and toughness of  $1.3 \pm 0.1$  MJ m<sup>-3</sup>. The SBM composites displayed curled fracture edges, thus verifying the strong interface interactions involving hydrogen and covalent bonding. The MXene nanocomposites without bridging show flat fracture edges (Figure 1d). The maximum stress obtained in the films exceeds the previous examples of biomimetic nanocomposites obtained by LbL technology, for example, from 2D platelets of clay,<sup>[10]</sup> because of the enhanced mechanical properties of individual inorganic platelets and chemical densification.

This study represents a milestone in layered nanocomposites as it provides direct evidence of voids spontaneously formed during the self-assembly processes typical for biomimetic materials. Also, importantly, the Beihang team developed a simple and effective approach to mitigate the void problem and enhance the performance of nanocomposites based on MXenes, thus opening a new path to the mitigation of structural defects that leads to high-performance materials that are needed in a variety of technologies.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** biomimetics · layered materials · MXenes · nacre · nanocomposites

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