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Layered Biomimetic Composites from MXenes with Sequential Bridging

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Layer-by-layer (LBL) assembly is a widely used technique for assembling the layered nanocomposites from clay sheets, carbon nanotubes, graphene oxide, nanoparticles and other materials.[1–5] The classic LBL assembly is a cyclical dip-and-rinse process in which a macromolecules and nanocolloids are sequentially and conformally adsorbed onto the previous layer.[6] Nearly all the LBL nanocomposites from two dimensional (2D) materials display exceptional materials properties associated with the evolution-optimized repeating sequence of organic-inorganic multilayers similar to that found in nacre, bone and other biomineralized tissues. In particularly, their high mechanical performance originates from the tight binding of the polymer films filling nooks and crevices between the inorganic sheets. Other approaches for fabricating layered nanocomposites include vacuum-assisted filtration doctor blading and spin coating. These methods also take advantage of the self-assembly of 2D nanoplatelets into layered stacks but they are simpler and faster in implementation. However, molecular-scale organization of nanocomposites made by these materials can be optimized further compared to the structure of LBL multilayers and their prototypes from biology, because these methods introduced voids into layered structure. The voids reduce the tensile strength, stiffness, toughness and other properties of the assembled nanocomposites.

In a recent paper in *Science*,[7] Prof. Qunfeng Cheng's group found that dramatic reduction of voids is feasible for layered nanocomposites based on a new type of 2D materials, known as MXenes.[8] Building on their prior studies of nacre-like nanocomposites,[9] the authors used three-dimensional (3D) reconstructions obtained by the slice-and image tomography to evaluate the voids in the composites from $Ti_3C_2T_x$ MXene (**Fig. 1a**). They found that the relative volume of voids in composites MXene platelets made by the techniques based on accelerated self-assembly is as high as 15.4 ± 0.6%. They also found that the 2D nanocolloids from MXenes are difficult to assemble into compact nacre-like nanocomposites. Being related to local kinetic traps, the imperfect layering or packing represents a fundamental problem that can be traced in a variety of forms in many self-assembled nanostructures.

The team from Beihang University[7] successfully mitigated the void problem taking advantage of sequential bridging with sodium carboxymethyl cellulose interacting with $Ti_3C_2T_x$ nanoplatelets via hydrogen bonding. Borate ions were also added to further 'tighten' the material crosslinking it with covalent bonds. The percentage of the 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 ± 0.31% (**Fig. 1b**). The densified microstructure and improved interlayer interactions greatly enhance the mechanical properties of the SBM composite (**Fig. 1c**). The latter showed the tensile strength of 583 ± 16 MPa, Young's modulus of 27.8 ± 2.8 GPa and toughness of 15.9 ± 1.0 MJ/m^3, much higher than that of the MXene film with tensile strength of 87 ± 3 MPa, Young's modulus of 6.1 ± 0.6 GPa, and toughness of 1.3 ± 0.1 MJ/m^3. The SBM composites also displayed curled fracture edges, verifying the strong interface interactions induced by hydrogen and covalent bonding. The MXene nanocomposites without macromolecular bridging show flat fracture edges (**Fig. 1d**) indicating poor stress transfer and molecular-scale connectivity of the soft matrix with the platelets. The maximum stress obtained in the films exceeds the previous examples of biomimetic nanocomposites obtained by LBL technology, for instance from 2D platelets of clay[10] due to higher mechanical properties of individual inorganic platelets and chemical densification.

This work represents a milestone in layered nanocomposites because (1) it provides direct evidence of voids spontaneously formed during self-assembly processes typical for biomimetic materials; (2) the developed approach to mitigate the void problem is simple and effective; and (3) the high performance of nanocomposites based on MXenes opens a new path to layered materials needed in a variety of technologies.[11] One can also expect that the flexible chains of sodium carboxymethyl cellulose will also have high affinity to and can self-assemble in the pores observed in other bioinspired nanoscale components, such as nanofibrils cellulose and aramid nanofibers.

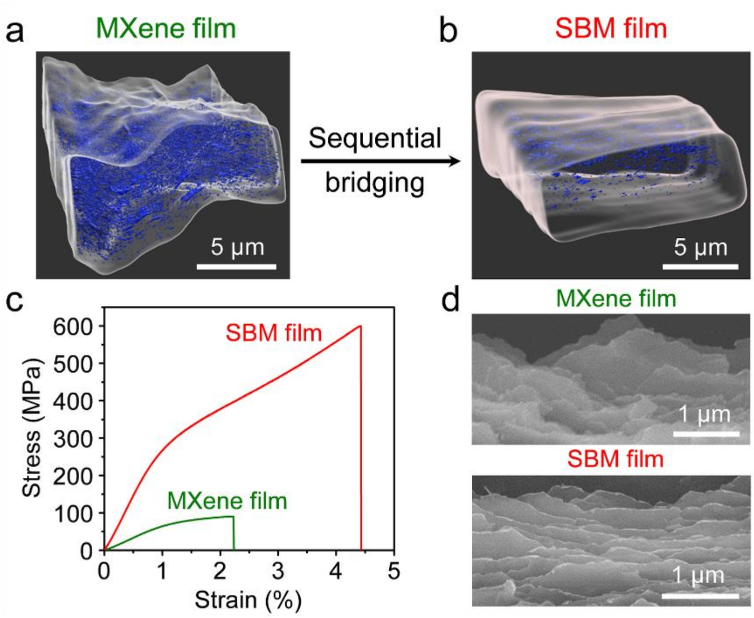

Figure 1. Three dimensional void microstructure of the MXene layered nanocomposites obtained by focused ion beam and scanning electron microscopy tomography (**a**) and SBM films (**b**). (**c**) Typical tensile stress-strain curves of the MXene and SBM films. (**d**) SEM images of the fracture surfaces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

SBM films.

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ABSTRACT

Biomimetic layered nanocomposites from clay sheets, carbon nanotubes, graphene oxide, nanoparticles and other materials reveal exceptional set of mechanical, electrical, optical and other properties much needed in many technologies. Methods for their fabrication are based on self-organization and include layer-by-layer assembly, spin deposition, vacuum-assisted filtration, and blade coating. While being simpler and faster than the traditional layer-by-layer assembly, the latter ones introduce voids into the architecture of layered materials, reducing their performance. The team from Beihang University thoroughly evaluated the voids structure in the $Ti_3C_2T_x$ MXene composites and found that the fundamental problem with voids successfully can be solved by sequential bridging of MXene platelets by sodium carboxymethyl cellulose combined with covalent bridging with borate ions, opening a new path to self-assemble two-dimensional platelets into high performance layered nanocomposites.

Keywords: nanocomposites, MXenes, biomimetic, layered, nacre

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