Atomic-scale imaging reveals secret to thin film strength

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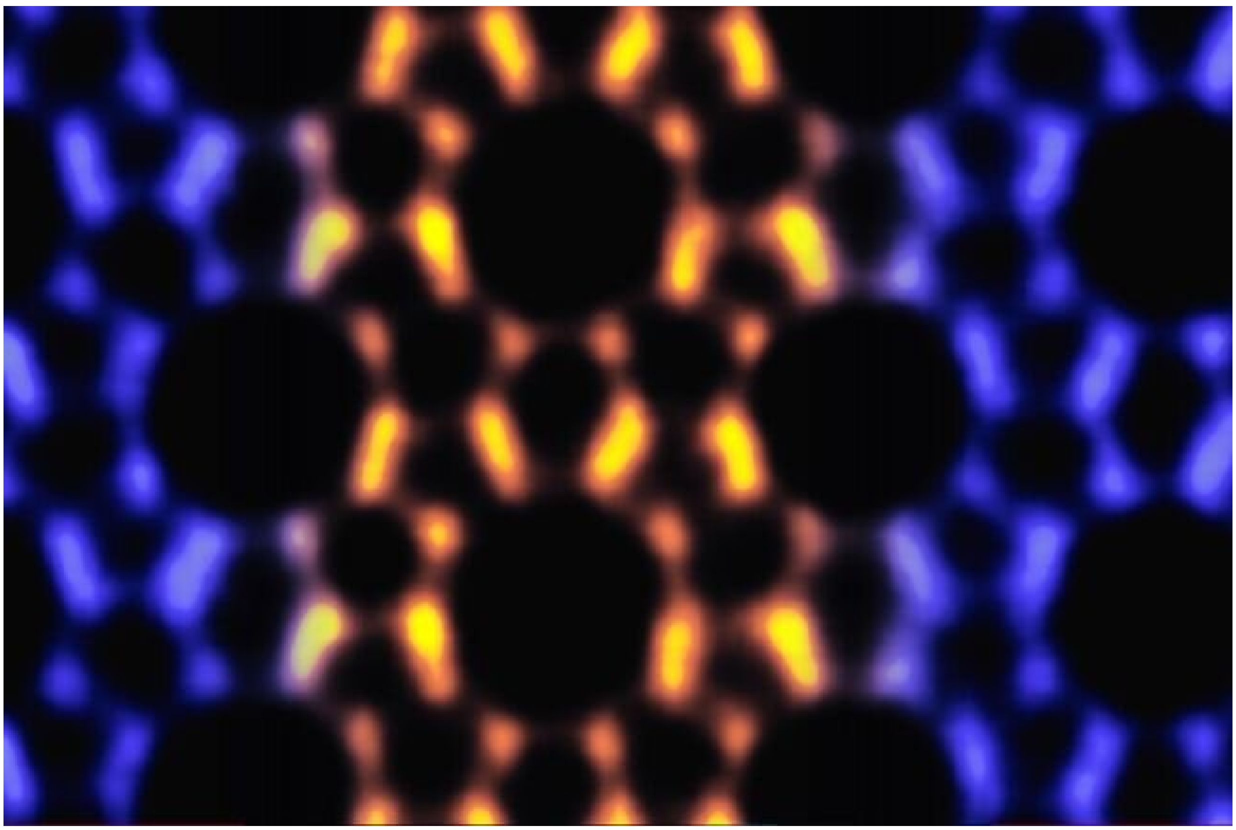

Atomic-scale details from transmission electron microscopy that reveals the porous structure of an MFI nanosheet, with MEL intergrown in it. Credit: Kumar et al., University of Minnesota

An international team of scientists and engineers, led by University of

Minnesota Associate Professor K. Andre Mkhoyan and Professor Emeritus Michael Tsapatsis (currently, a Bloomberg Distinguished Professor at Johns Hopkins University), have made a discovery that could further advance the use of ultra-thin zeolite nanosheets, which are used as specialized molecular filters. The discovery could improve efficiency in the production of gasoline, plastics, and biofuels.

The breakthrough discovery of one-dimensional defects in a two-dimensional structure of porous material (a zeolite called MFI) was achieved using a powerful high-resolution transmission electron microscopy (TEM) on the University of Minnesota Twin Cities campus. By imaging the atomic structure of the MFI nanosheets at unprecedented detail, the researchers found that these one-dimensional defects resulted in a unique reinforced nanosheet structure that changed the filtration properties of the nanosheet dramatically.

The findings are published in *Nature Materials*.

"TEM imaging of thin zeolite crystal at the atomic-scale has been a long-standing challenge as these crystals are readily damaged under the high-energy electrons, which are needed for atomic-scale imaging," said Mkhoyan, an expert in advanced TEM and the Ray D. and Mary T. Johnson/Mayon Plastics Chair in the Department of Chemical Engineering and Materials Science at the University of Minnesota's College of Science and Engineering. "It requires a deep understanding of the mechanisms of beam damage for zeolite crystals and the doses of electron beam that the zeolite can take. This work pushed the limits of our electron microscopes, where we can reliably produce atomic-resolution images of such extremely thin (just 3-nanometers-thick) zeolite nanosheets with identifiable one-dimensional intergrowths."

The minute differences between the two materials (see enclosed image) was detected by Prashant Kumar, a graduate in the University of

Minnesota Twin Cities College of Science and Engineering, after nearly five years of research.

"I have been fascinated by the beautiful symmetrical patterns in MFI crystal throughout my Ph.D. work," said Kumar, a lead author of the study. "After staring at noisy images in the TEM for countless hours, I finally saw the symmetry breaking in the TEM images of MFI nanosheets—I knew this was unusual."

Despite the subtle differences, this knitting of lines of one zeolite within another have pronounced consequences in the ability of nanosheets to recognize and selectively transport molecules enabling selective separations and catalysis. University of Minnesota Professors Traian Dumitrica (mechanical engineering) and Ilja Siepmann (chemistry) led the simulations to test this pattern and performance. Their findings revealed that the knitted materials are less responsive to stress and more selective in separating molecules based on size and shape.

Membranes made from these enhanced nanosheets for the lab simulations were fabricated by a research group led by Tsapatsis, and they were tested under industrial conditions as well by Benjamin McCool, head of separations and process chemistry at ExxonMobil. The latter resulted in record filtration performance—p-xylene and o-xylene separated at five times higher efficiency than the Tsapatsis' group has reported to date.

MFI zeolite is a porous structure of silicon and oxygen atoms and is previously known to grow with one-dimensional structures, or a zeolite called MEL, in bulk form. However, these defects have never been specifically fabricated or intergrown in two-dimensional nanosheets.

"Making ultra-selective thin film membranes and hierarchical catalysts by fine tuning the frequency and distribution of intergrowths of porous frameworks is a concept introduced by our research group a decade ago," said Tsapatsis. "The discovery by TEM of one-dimensional intergrowths in two-dimensional nanosheets and the practical implications suggested by modeling bring the potential of this concept to a new level and suggest new opportunities for targeted synthesis that we have not imagined possible."

His team now hopes to create heterostructures of MFI-MEL nanosheets that can maximize the MEL content and push the filtration performance of the thin films to even higher efficiency, as predicted by the lab simulations. For Mkhoyan—who runs the U's analytical electron microscopy lab, where research at the atomic scale is daily routine—the breakthrough finding is an opportunity to further improve the way microscopes are used to study nanomaterials in atomic-level detail.

More information: Prashant Kumar et al. One-dimensional intergrowths in two-dimensional zeolite nanosheets and their effect on ultra-selective transport, *Nature Materials* (2020). DOI: 10.1038/s41563-019-0581-3

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