Nano Focus

IR vibrational crystallography visualizes molecular orientation on the nanoscale

The orientation of molecules is of central importance in determining the photophysical properties of organic materials, such as mobility of charge carriers and ions. These orientation-dependent properties of materials further control their functionalities in biological systems and electronic devices, including organic light-emitting diodes and solar cells.

Until now, optical crystallography has failed to yield high-resolution images of molecular arrangement, due to the diffraction-limited response, weak photon–material interaction between x-rays and organic materials, or sample damage. A group of researchers from the University of Colorado Boulder and Lawrence Berkeley National Laboratory has developed a new mapping technique called infrared scattering-type scanning near-field optical microscopy (IR *s*-SNOM), which can identify the molecular arrangement of subdomains smaller than hundreds of nanometers.

"In IR *s*-SNOM, we combined the nanometer spatial resolution capability of *s*-SNOM with infrared vibrational spectroscopy, and the orientation bond symmetry selectivity of vibrational dichroism," says Markus Raschke, the leader of the research team in the Department of Physics and Department of Chemistry at the University of Colorado Boulder.

"Apart from the nanometer resolution, IR *s*-SNOM also shows enhanced sensitivity to a sample volume containing only a few hundred molecules. This sensitivity is many orders of magnitude larger than conventional far-field IR spectroscopy, with the added feature of a spatial resolution 1000 times higher than the diffraction limit," he adds.

As reported in a recent issue of *Science Advances* (doi:10.1126/sciadv.1601006), Eric Muller and his colleagues focused polarized IR light onto a metallized atomic force microscope (AFM) tip, using a scanning probe microscope. By detecting the scattered light when the tip is in near contact with the surface of the sample, local spectroscopic information can be obtained.

The researchers implemented the IR *s*-SNOM measurement on thin-film perylenetetracarboxylic dianhydride (PTCDA), an organic material used in high-performance transistors. The colored three-dimensional (3D) map obtained shows the orientation of each domain within the thin-film crystal (see Figure). The orientations of the molecules vary from parallel to the substrate (blue region) to perpendicular to the substrate (red region). Using the high-resolution AFM mode, the orientation and defects inside the subdomain, within hundreds of a nanometer size, could further be resolved.

"The optical nanocrystallography technique developed by Muller et al. is an important extension of scanning near-field optical microscopy to tip-selective infrared vibrational spectroscopy, and represents another great example of the versatility of scanning probe microscopy-based techniques," says Tobin Filleter, a professor of mechanical and industrial engineering at the University of Toronto. With research interests in nanomechanics, Filleter points out that this simultaneous subdomain spatial resolution and local mapping of molecular order and heterogeneities enabled by the technique has great potential to unveil new discoveries and aid in the engineering of novel molecular devices.

"The next stage of our research is to investigate how the intermolecular interactions affect the optical and electronic properties of the film, such as carrier and ion conductivity," Raschke says. "We also plan to apply this powerful tool to study bio/microbial interfaces via the *in situ* imaging technique."

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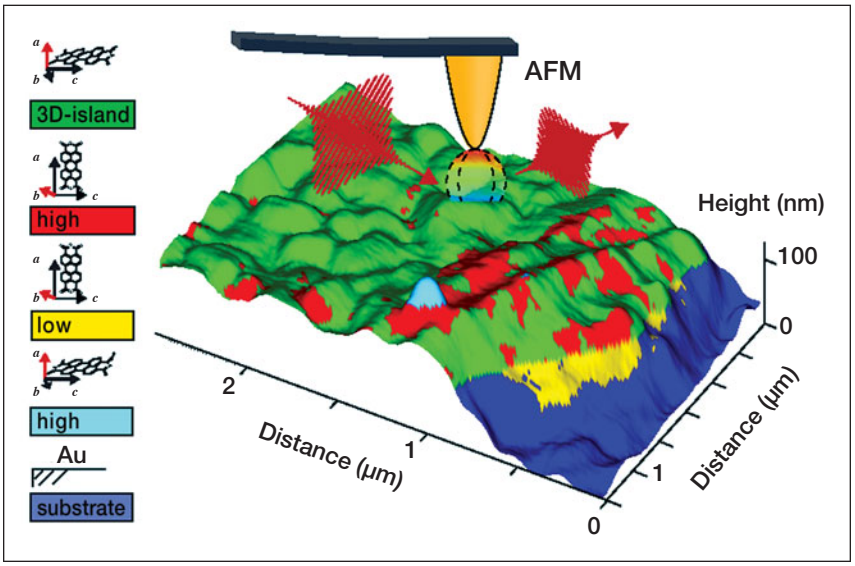

Three-dimensional molecular orientation mapping of perylenetetracarboxylic dianhydride (PTCDA) crystalline film, measured by infrared scattering-type scanning near-field optical microscopy. AFM is atomic force microscope. Credit: *Science Advances*.

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