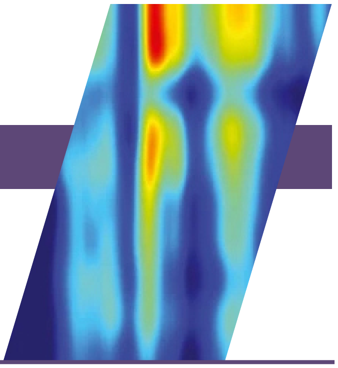
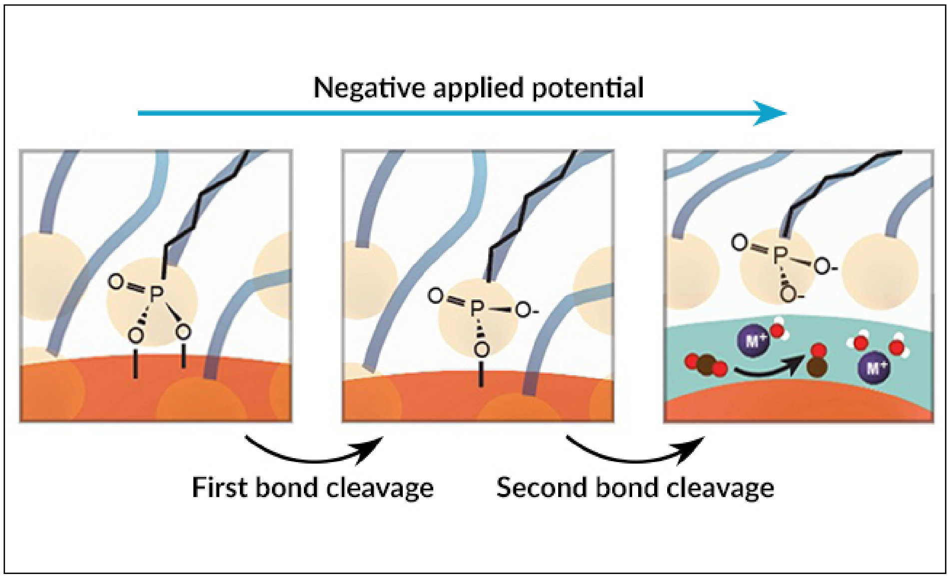
ADVANCED LIGHT SOURCE



CHEMICAL SCIENCES

Mechanics of a Floating Molecular Layer for CO_2 Reduction



Schematic illustration of organic molecules (beige heads with gray tails) attached to the surface of a nanoparticle (orange). As a negative potential is applied, oxygen–metal bonds at the surface sequentially break. At the highest negative potentials, the heads detach completely from the surface, creating an aqueous interlayer "pocket" that is highly active and selective for CO_2-to-CO conversion. Brown = C, red = O, white = H, purple = alkali cations.

Scientific Achievement

At the Advanced Light Source (ALS), researchers discovered how a layer of organic molecules on a nanoparticle surface detaches to create a highly catalytic pocket for reducing CO_2 to CO.

Significance and Impact

The ability to probe molecular-scale events under realistic conditions with nanometer resolution will help guide the design of responsive systems for a wide range of applications, from medicine to optoelectronics.

Enzyme-inspired catalysts

In living things, enzymes catalyze chemical reactions with exquisite efficiency and specificity. These enzymes are proteins with amino-acid side chains that optimize the active site for specific reactions. Inspired by nature, scientists have been working to improve electrocatalysts using a similar strategy.

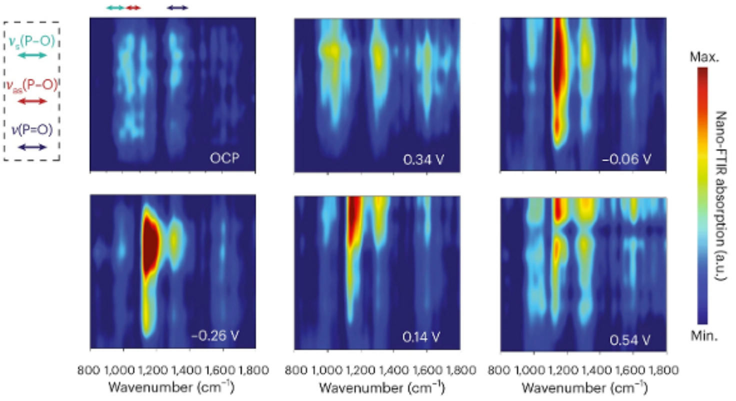
Several years ago, a group led by Peidong Yang at Berkeley Lab invented a system in which chains of organic molecules (ligands) are attached to the surface of a silver nanoparticle. Upon application of an external negative potential, the ligands reversibly dissociate from the nanoparticle. The resulting reaction pocket, called a Nanoparticle/Ordered-Ligand Interlayer (NOLI), supports the markedly efficient conversion of CO_2 to CO with 100% selectivity. However, understanding of the mechanism by which electrochemical bias modulates nanoparticle–ligand interactions has been elusive.

Spectroscopic fingerprints

To investigate how ligands on the nanoparticle surface respond to electrochemical conditions and how these responses enhance catalytic performance, the researchers turned to two forms of infrared spectroscopy: synchrotron-based Fourier-transform infrared nanospectroscopy (nano-FTIR) and laser-based surface-enhanced Raman spectroscopy (SERS). The work was also supported by electron microscopy at the Molecular Foundry and density functional theory (DFT) calculations performed at NERSC. The experiment samples consisted of silver (Ag) nanoparticles capped by tetradecylphosphonic acid (TDPA) ligands.

The nano-FTIR was performed at ALS Beamlines 2.4 and 5.4. Both beamlines provide a low-noise, broadband, high-coherence infrared beam, which can be used to detect the characteristic vibrational modes of the ligand while minimizing radiation damage. Furthermore, because of the high spatial resolution and surface sensitivity of nano-FTIR, ligand behavior that occurs only on the nanoparticle surface can be tracked, with a spatial resolution on the order of the nanoparticle size. In addition, the special polarization of this technique (z-polarized) can assist in determining the ligand binding configuration on the nanoparticle surface. Finally, both the beamlines can accommodate a customized liquid cell, which enables the detection of ligand behavior under electrochemical conditions.

SERS was used to follow the evolution of the molecular structure within the NOLI up to more negative bias compared to nano-FTIR. This enables tracking the changes in ligand species through the onset of full detachment. However, SERS is not polarized and hence there is no preferential orientation axis as in nano-FTIR.



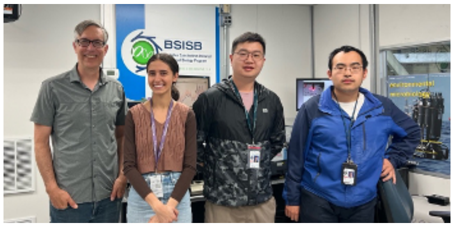
Nano-FTIR intensity maps, acquired along a linear scan direction (vertical axis) over nanoparticle–ligand assemblies under various (positive and negative) applied potentials (OCP = open-circuit potential). The frequency ranges for various stretching modes of the ligands' phosphonate head are indicated by colored double-headed arrows. At −0.06 V, the enhanced intensity is attributed to the partial dissociation of Ag–O bonds, indicating a transition from bidentate to monodentate binding of the ligand head group.

Step-by-step detachment

Analysis of the data revealed that the interlayer pocket forms through a consecutive bond-cleavage mechanism. Initially, the TDPA binds to the Ag surface through two Ag-O bonds (a bidentate binding configuration). Increasing the electrochemical bias triggers a transformation to a monodentate configuration. A second bond cleavage is observed by SERS at higher overpotentials.

The high spatial resolution of the experiments uniquely allows a direct comparison of spectra originating from nanoparticles of varying sizes and evolving statuses, which leads to the conclusion that the bidentate-to-monodentate transformation occurs universally across all nanoparticle surfaces, maintaining consistent ligand structural dynamics irrespective of nanoparticle sizes.

This methodology could be applied to investigate the dynamic response of various interfacial species to multiple external stimuli with nanometer spatial resolution, thus providing fundamental guiding principles for the rational design of responsive ligand–nanoparticle systems with precise dosage, spatial, and temporal control for energy, medical, and optoelectronics applications.



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