

1. Background and Impact

Petroleum sources are commonly used as feedstocks to meet the demand for aromatic compounds in numerous industries. Dehydrogenation and dehydrocyclization reactions enable the production of aromatics from alkanes. However, current methods of heterogeneous catalysis require prohibitively expensive metals to catalyze the reaction or suffer from coking or poisoning effects. Bimetallic catalysts allow the design of heterogeneous catalysts that avoid these issues, developing unique active sites. However, the successful implementation depends upon a fundamental understanding of these active sites. This is only possible with a technique that can yield chemical information with a high degree of spatial resolution. In this project, PI and his group use ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) and tip-enhanced Raman spectroscopy (TERS) to gain these necessary insights with the spatial resolution that allows the identification of site-specific chemical properties at the single active site and single molecule level.

In year 1 of the grant, the PI and his group have investigated two different chemical systems to serve as models to explore the effects of stereoselective reactions with sub-nanoscale spatial resolution. In addition, the group separately developed the fabrication of a unique bimetallic surface to consider for its activity in dehydrogenation reactions based off of calculated catalytic properties. One of the students has presented a part of the current work at 2019 Fall ACS meeting at Sand Diego.

2. Results

2.1. TERS Characterization of Adjacent Regioisomers

Many heterogeneous reactions, such as the dehydrogenation of alkyl species specifically, have the capability to result in regioisomeric products. In order to investigate the sensitivity of TERS to minute changes in the chemical structure of a molecule we selected two porphodilactone isomers where the only structural difference was the relative orientation of two lactone moieties. Prior to this work TERS had not been applied to study the regioisomeric effect of molecules.

Through sub-nanoscale spectroscopic characterization, adjacent regioisomers with ångström scale resolution was achieved. TERS mapping and line profile experiments identify the different regioisomers on the surface and confirm a self-recognition aspect to the self-assembly of molecules on the surface. Cis and trans isolate themselves forming pure islands even when co-deposited.

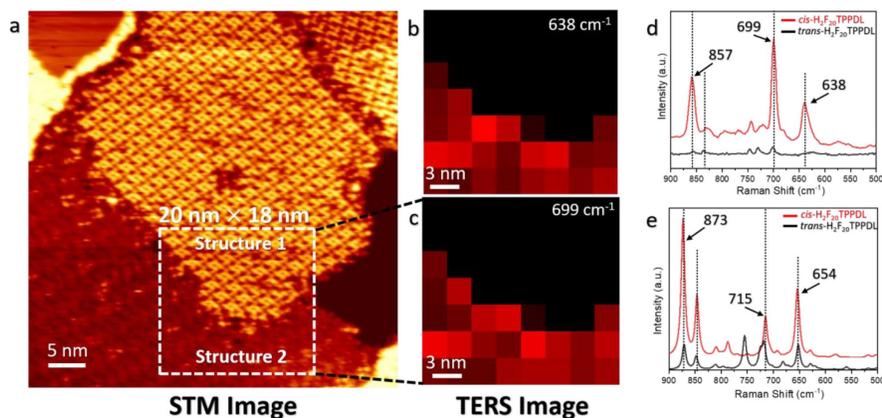


Figure 1. TERS 2D mapping of co-deposited regioisomeric molecules on Ag(100). (a) STM image of co-adsorbed trans- and cis-isomers. A white dotted rectangle area (20 nm × 18 nm) was selected to obtain the TERS images where Structure 1 and Structure 2 were identified. (b,c) TERS images by tracking 638 and 699 cm^{-1} peaks. (d) Comparison of experimental TERS spectra of cis- (red) and trans-isomers (black) in the 500–900 cm^{-1} region. (e) TDDFT-simulated spectra obtained from Raman (633 nm) calculations for cis- (red) and trans-isomers (black), 654, 715, and 873 cm^{-1} peaks were marked.

The expansion of TERS to spatially resolved studies of molecules with extremely similar structures holds promise to distinguish different species that may form during the course of a heterogeneous reaction on a bimetallic

surface, where there is a variety of active local chemical environments. This work was published earlier this year (*Nano Letters* **2019**, 19 (5), 3267-3272)

2.2. Stereoselective Adsorbates induced by modified surface structures

On-surface reactions can limit the dimensionality of reaction intermediates, resulting in stereoselective reactions that when carefully tuned can exhibit stereospecificity. To these ends, we investigated the thermally induced coupling reaction of 3,6-dibromo-phenanthrenequinone (DBPQ) on Au(100). The position of the leaving halogen atoms within the monomer's molecular structure determines where an aryl radical carbon is generated and subsequently where a C-C bond will form with an adjacent molecule. In this case, there is the potential for *cis* or *trans* dimers.

This work used the Ullmann-like coupling reaction to generate aryl carbon radicals on a surface. Ultimately, the bromine that remains adsorbed on the surface was found to exhibit stereospecificity towards *trans* dimers. Modifying the surface chemically was found to change the reaction products that are formed. This work was submitted this year and is currently under review.

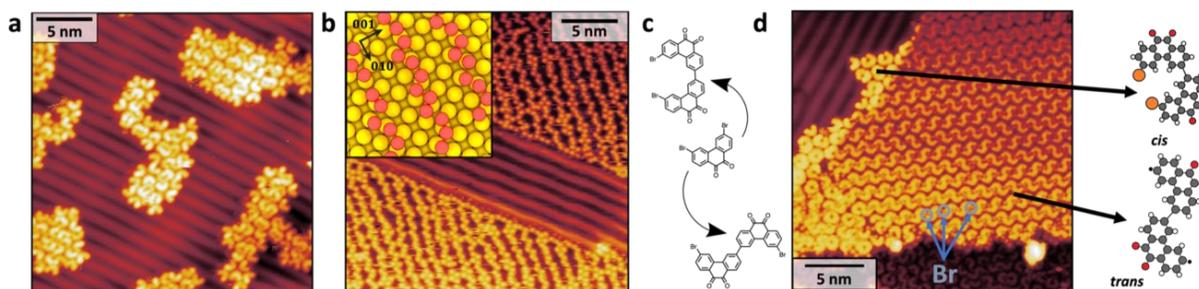


Figure 2. (a) STM image of DBPQ on Au(100). Molecules show intact terminal bromines. Inset shows a model of the DBPQ molecules on the Au surface (b) Following an anneal to 300 °C, the bromine atoms were found to form a semi-ordered structure on the Au surface. Inset image represents a model of the orientation of the Br adlayer relative to the Au(100) close-packed direction. (c) Anticipated isomer products. (d) STM image and reaction scheme highlighting the reaction selectivity for the Au(100) reconstruction and the Br adlayer respectively.

2.3. Preparation of a Bimetallic Pd/Cu Surface

In pursuit of fabricating a bimetallic surface, PI and his group developed methods to reliably deposit palladium atoms onto a Cu(100) surface with control that is important to vary the coverage from single isolated atoms of Pd all the way to a full monolayer. This process can be used to investigate the effects of the numerous local chemical environments of a bimetallic catalyst on a reaction process.

Preliminary work to establish a suitable probe molecule that undergoes a dehydrogenation reaction and is stable on the surface for subsequent imaging has been accomplished and future work will investigate the effects of single Pd atoms as well as the Pd surface on the reaction process with the spatial resolution of TERS to focus on the local chemical effects of the different active sites.

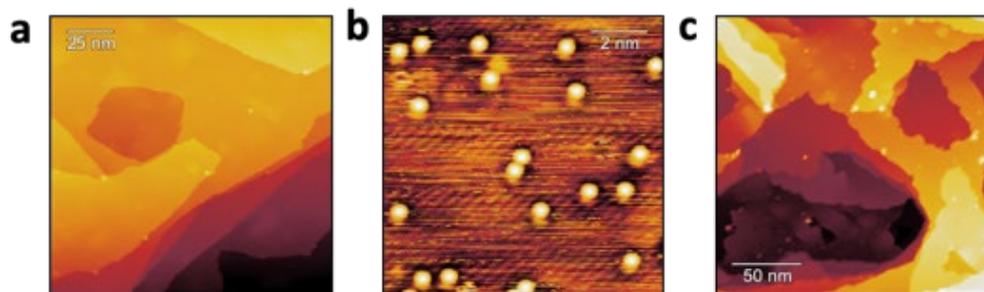


Figure 3. (a) STM image of the clean Cu(100) substrate (b) STM image of single isolated Pd atoms on the Cu(100) surface. (c) STM image of the surface following the deposition of a full monolayer of Pd. The step edges have new features confirming full coverage of Pd.