When Atoms mine for Gold

Novel nanochemistry techniques control the stereochemistry of self-assembled monolayers (SAMs) of small molecules. This is good news for basic research in the field, and also for future development of catalysts for renewable energy and other applications.

Not only humans are keen to dig for gold, sometimes atoms are as well. Exploiting a phenomenon known as "atomic gold mining" an international effort led by the NanoChemistry group at DTU Chemistry has solved a tricky problem.

Self-assembled monolayers (SAMs) promise great advantages in a number of fields such as catalysis, sensing and other nanoscale device function. Composed of small molecules, the SAMs are ultra-thin, meaning they change the behavior of the surface without altering the electronic carrier structure underneath. Further, the required amount of the material is extremely small, and as the layers are self-assembling they are highly uniform, since errors created by the processing are reduced to a minimum.

Some of the molecules of interest are chiral, meaning they have two forms which – like the human left and right hand - are mirror images of each other but cannot be superimposed onto each other. The two forms are described by the same chemical formula while in fact being differently structured and potentially with different properties.

It is very desirable to have only one of two such chiral forms in a given SAM. This will guarantee uniform surface properties and offer unique selectivity in SAM applications.

Danish-Chinese-Australian effort
A novel set of methods for controlling this so-called stereochemistry in a relevant chiral molecule SAM has been developed in a joint effort by the NanoChemistry Group and Organic Chemistry at DTU Chemistry, Xiamen University, The University of Sydney, University of Technology of Sydney, and Shanghai University. The results have been published in Journal of the American Chemical Society (JACS) 2014.

"Our cooperation with the groups in Australia and China go back 15 years, and we have had several joint publications in prestigious journals. Still, it is always a great pleasure to learn that this article has been accepted," says Associate Professor Jingdong Zhang, DTU Chemistry.

The project was focused on alkanethiols, R-SH. These are molecules with a thiol group (-SH) in one end of a carbon chain and different functional groups in the other end. Alkanethiols adsorb strongly on metals enabling the formation of SAMs. Among several possible metal supports, gold (Au(111)) was chosen since it is highly stable and can be processed into well-defined atomically planar surfaces.

"Alkanthiol SAMs on gold surfaces have come to offer more detailed understanding of the adsorption process than any other surface system. This is due to facile SAM handling and a unique combination of experimental technologies and theoretical computations," Jingdong Zhang explains. "Further, we can use electrochemistry and scanning probe microscopies directly in the chemical media, combined with large-scale electronic structure and molecular dynamics calculations offering structural SAM resolution to the unprecedented level of the single molecule or even atom."

Atomic gold mining
The target molecules of the project were the five butanethiols, each with one thiol group and four carbon atoms. Of these R- and S-2-butanethiol are chiral molecules. They are each other's mirror images, but in fact different molecules.

"The butanethiols display an amazing variety of SAM patterns determined by very subtle surface chemistry and by interactions between the R-groups," Jingdong Zhang remarks.

Adsorption converts thiol (-SH) to a thiyl group (-S·) bound to a gold surface site, Au-S·, which can be a single gold atom or a hollow site between several atoms. This is where the phenomenon "atomic gold mining" comes in. With the exception of one butanethiol, the bulky tertiary butanethiol, which is able to bind directly on a flat surface, the molecules adsorb by digging out surface gold atoms. Hereafter, they bind sideways to the mined gold atom, R-S-Au-S-R.

"The chiral butanethiols open new perspectives. They are the first case for thiol-binding at the same time to mined gold atoms and on the planar surfaces," Jingdong Zhang comments with enthusiasm. "Binding also induces new chiral centres in both the gold surface and the binding sulfur atoms, in addition to the molecular 2-C chiral centre. As a result a "collective" chirality in whole SAM domains arises, leading to the amazing outcome that chiral domains can arise from achiral molecules, and achiral domains from chiral molecules."

The results offer a new level of understanding of the molecular adsorption process.

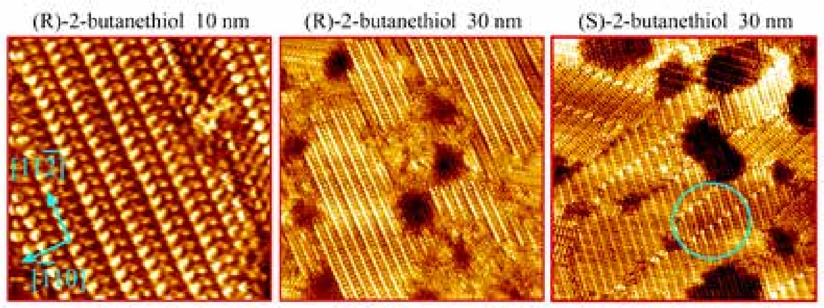
"They will help to understand a wide range of chemical, electrochemical, and spectroscopic phenomena," according to Jingdong Zhang.

Looking for biofuel catalysis applications
A possible field of application is heterogeneous catalysis in relation to renewable energy, for instance from bio-fuels. Recently, Jingdong Zhang received funding for a project on chemical production of 3D graphene biocatalysts for enzymatic biofuel cells. While the grant is not directly related to the SAM-study published in JACS, Jingdong Zhang hopes to find ways to apply the new nanochemistry findings:

"It is very important for us, as for DTU in general, that fundamental and applied research go hand in hand. Fundamental research is essential to push things to the next level, and applied research is the way we can bring value back to the society which has supported our research. Doing this through applications in clean energy which is highly desirable for society would be really beautiful."

The project on graphene biocatalysts for enzymatic biofuel cells has been granted 0.9 million EUR by the YDUN-program (Younger women Devoted to a University carreer) of the Danish Council for Independent Research.

Besides catalysis, the group's research on SAMs has potential applications for a number of new synthesis strategies for metallic nanostructures and chemical graphene in chemical and pharmaceutical production and research.



In situ STM images of SAMs of chemisorbed (R)-2-butanethiol and (S)-2-butanethiol in 25 mM KH_2PO_4.

Published article

The text is based on the scientific article published in *JACS* (Journal of the American Chemical Society).

You can download it as a pdf by scanning the QR-code below

Next step ...

The NanoChemistry Group's research on SAMs (Self-assembled monolayers) has also potential applications for a number of new synthesis strategies in chemical and pharmaceutical production and research.

CONTACT

Associate Professor
Jingdong Zhang
Inorganic Chemistry
jz@kemi.dtu.dk