Self-assembled nanostructures with atomically precise structure and tailored electronic properties

August 13 2018

On-surface 1D nanostructure based on a trinuclear metal-organic coordination motif: the local electronic configuration at the metal centre holds promise for novel functionalities in optoelectronics and catalysis. Credit: FLEET

Bio organisms are the most-complex machines we know, and are capable of achieving demanding functions with great efficiency.

A common theme in these bio-machines is that everything important happens at the level of single molecules – that is, at the nanoscale.

The functionality of these bio-systems relies on self-assembly – that is, molecules interacting precisely and selectively with each other to form well-defined structures. A well-known example of this phenomenon is
the double-helix structure of DNA.

Now, inspired by self-assembling bio-systems, an international group of scientists including FLEET physicists has created a new, carbon-based, self-assembled nanomaterial, which could be key to new photovoltaic and catalysis technologies.

Using self-assembly, the researchers were able to engineer, with atomic-scale precision, a new 1-D nanostructure composed of organic (carbon-based) molecules and iron atoms.

The findings are described in two studies published this month in *Nature Communications* and *ACS Nano*.

**Atomic-scale precision via self-assembly: a pathway to functionality**

"Fabricating nanomaterials by controlling the position of single atoms and molecules one at a time is very tedious, if not impossible," says lead scientist Dr. Agustin Schiffrin, senior lecturer at Monash University and FLEET chief investigator.

"Instead, we can create atomically-precise structures via self-assembly, by choosing the right molecules, atoms and preparation conditions."

"This has the benefit that no external intervention is required," explains Dr. Schiffrin.

Such self-assembly capability comes from using organic (that is, carbon-based) molecules as building nano-units.

The shape, size and interacting functional groups of these organic molecules can be tuned in an almost infinite number of ways using
organic synthetic chemistry.

s an alternative to programmed self-assembly of molecules, Monash researchers can actually place individual atoms. For example, this ‘microbranding’ project creates the FLEET logo from 42 individual iron atoms. Credit: FLEET

Control of interactions between molecules leads to creation of the desired, well-defined nanostructure, similarly to the way interactions between nucleic acids in DNA give rise to the double-helix.

"We can thus build materials with a very precise, engineered structure, which results in the material having the desired electronic properties," says co-author Marina Castelli, a Ph.D. student within Monash University's School of Physics and Astronomy.

"Just as the functions of bio-organisms depend on nano-scale interactions, the physical and electronic properties of these new materials come from their structure at a single-molecule level," explains Monash Research Fellow Dr. Cornelius Krull.

**Bottom-up beats top-down**

Conventional methods for material nanofabrication, such as lithography,
rely on 'top-down' approaches, with materials patterned by removal of matter. Such methods are limited to resolutions of the order of 1 nanometre at best.

Instead, 'bottom-up' methods can allow for sub-nanometre patterning resolution, with the potential for a higher level of control and efficiency of electronic properties.

Moreover, applying 'bottom-up' synthesis approaches with a surface as a substrate allows for nanostructures with properties that cannot be achieved via conventional synthetic methods.

Nanomaterials based on metal-organic molecular complexes allow for a vast range of useful functionalities, both technological and biological, from catalysis to photovoltaics to gas sensing and storage.

In these systems, the atomic-scale morphology and electronic configuration of the metal-organic coordination motif play a crucial role, dictating their overall electronic and chemical properties.

**The two studies**

The paper "Designing Optoelectronic Properties by On-Surface Synthesis: Formation and Electronic Structure of an Iron-Terpyridine Macromolecular Complex," published in *ACS Nano*, describes energy and spatial dependence of the electronic states (occupied and unoccupied) of the 1-D iron-based metal-organic nanostructure, in an energy range near the Fermi level, which can be useful for optoelectronic applications such as photovoltaics, photo-catalysis and light-emitting devices.

Studying structure and chemistry at the single-atom level The paper, "Iron-based trinuclear metal-organic nanostructures on a surface with
local charge accumulation," published in *Nature Communications*, describes at an atomic scale the intramolecular structure and charge distribution of the nontrivial iron-molecule coordination motif, useful for catalysis applications.


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