

## SINGLE-MOLECULE CHEMISTRY

### Caught on camera

ACS Nano <http://doi.org/b4m5> (2017)

An open challenge in chemistry is the ability to follow a reaction at a single-molecule level. Techniques such as non-contact atomic force microscopy and aberration-corrected transmission electron microscopy (TEM) have been used, but neither have both the required temporal and spatial resolution for the task. Now, Chamberlain *et al.* use a particular TEM setup that allows them to track chemical reactions at a single-molecule level in real time and capture intermediate steps of the transformation.

The main advance of this setup is the fact that an electron beam is used both to image and trigger a chemical reaction. The intensity of the beam can also be tuned to adjust the reaction rate so that intermediate species can be captured.

In one example, the researchers trap perchlorocoronene molecules inside a single-walled carbon nanotube. The TEM image shows the molecules orderly stacked inside the nanotube. They then irradiate the sample with an 80 keV electron beam. The energy is transferred ballistically to the coronene molecule, causing the expulsion of a chlorine atom. The absence of a chlorine atom is seen in the TEM as a bright spot, instead of a distinctive dark spot typical of high-atomic-number atoms. The dechlorinated coronene then undergoes a Diels–Alder condensation reaction with a neighbouring molecule through the formation of an arylene intermediate. This step is seen in the TEM images as a loss of the stacking order

of the coronene molecules. The adduct finally rearranges to yield an elongated molecule. As the irradiation continues, the researchers observe polycondensation and the formation of nanoribbons inside the nanotube. *AM*

## WATER OXIDATION CATALYST

### Hierarchy and wettability

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The non-precious non-porous metal NiFe hydroxide catalyst has been attracting considerable attention for the oxygen evolution reaction (OER) due to its low cost and high catalytic efficiency. Now Li and Zhao have successfully enhanced the wettability while maintaining the structural hierarchy in NiFe hydroxide nanosheets.

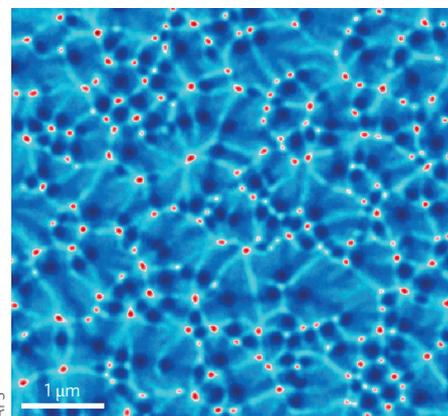
Firstly, nanoporous NiFe hydroxide was fabricated onto a carbon fibre paper substrate by electrodeposition. The hydroxide was then partially converted into phosphate by reacting with phosphine (PH<sub>3</sub>) and H<sub>2</sub>O vapour released by NaH<sub>2</sub>PO<sub>3</sub>·H<sub>2</sub>O decomposition. The formed NiFe and NiFe phosphate (P<sub>i</sub>) worked in synergy for the OER, exhibiting a current density of 10 mA cm<sup>-2</sup> at an overpotential of 290 mV, a high current density of 300 mA cm<sup>-2</sup> at a low overpotential of 340 mV and a much smaller Tafel slope compared to individual NiFe and Ni:P<sub>i</sub>. The improved OER activity of the synergistic NiFe/NiFe:P<sub>i</sub> catalyst has three possible explanations. One possibility is the easier water adsorption arising from the greatly improved surface wettability; another is the increased electrochemical surface area induced by phosphorylation; finally it could be due to the enhanced mass transport and charge transfer in the well-maintained 3D hierarchical

porous structure. Moreover, this electrocatalyst has been demonstrated to be stable for a long time, without any current density or surface morphology decay even after 1,000 cycles. *WS*

## MAGNETIC VORTICES

### Quenched pairs

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In condensed matter, structural inhomogeneities may favour the nucleation of topological defects within ordered phases. Fast thermal quenching can generate defect pairs with opposite topological character even in the absence of structural disorder, bearing intriguing similarities with the predictions of cosmological theories. However, although this latter scenario has been verified experimentally in several classes of materials, the observation of quench-induced defect pairs in magnets is still missing.

Now, Eggebrecht *et al.* report on the generation of metastable magnetic textures in Fe/Si<sub>3</sub>N<sub>4</sub> bilayers at room temperature. Using laser pulses with duration ~100 fs, the researchers heat the Fe layer locally, inducing a ferromagnet-to-paramagnet transition in μm<sup>2</sup>-sized areas. After the light pulse, the underlying Si<sub>3</sub>N<sub>4</sub> substrate induces thermal quenches with ultrahigh rates ~10<sup>12</sup> K s<sup>-1</sup>. The researchers then image the magnetic configuration of the iron layer by means of Lorentz electron microscopy before and after the laser pulse.

As long as the laser fluence is above a threshold value, a quench-induced generation of a dense, glass-like network of vortices and antivortices with fluid-like spatial pair correlations is observed (pictured). The observed nanoscale texture is stable over months, even though further sub-threshold laser pulses favour the annihilation of defect pairs. *GP*

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## GRAPHENE NANORIBBONS

### In the trenches

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In spite of graphene's exciting electronic and thermal properties, it is unsuitable as a transistor for future digital devices, due to the absence of a bandgap between the conduction and valence bands. This makes it impossible to switch between on and off states with respect to electron flow. Scaling things down, graphene nanoribbons of less than 10 nm in width do exhibit electronic bandgaps and are therefore potential candidates for digital devices. Precise control over their dimensions, and hence electronic properties, however, represents a challenging goal, and the ribbons typically possess rough edges that are detrimental to their performance.

Now, Chen *et al.* report on a strategy to grow graphene nanoribbons with controlled widths and smooth edges directly onto dielectric hexagonal boron nitride (h-BN) substrates. The team use nickel nanoparticles to etch monolayer-deep, nanometre-wide trenches into h-BN, and subsequently fill them with graphene using chemical vapour deposition. Modifying the etching parameters allows the width of the trench to be tuned to less than 10 nm, and the resulting sub-10-nm ribbons display bandgaps of almost 0.5 eV. Integrating these nanoribbons into field-effect transistor devices reveals on-off ratios of greater than 10<sup>4</sup> at room temperature, as well as high carrier mobilities of ~750 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. While gaining control over the length and specific placements of the ribbons will be the focus of future work, this method could offer a platform to access digital integrated circuitry based on ultra-narrow graphene nanoribbons. *VR*