research highlights
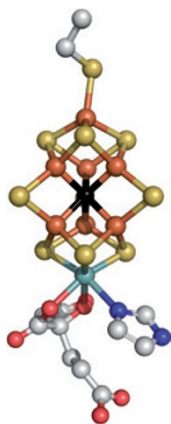
Carbon in the middle

Science **334,** 974–977 (2011);
Science **334,** 940 (2011)

© 2011 AAAS

Breaking dinitrogen's triple bond, one of the strongest known chemical bonds, is extremely difficult. Industrially, it is only done by the energy-intensive and high-pressure Haber–Bosch process. In nature, the only enzyme that performs the reaction is nitrogenase, through the use of the most complex biological metal centre known. This iron–molybdenum cofactor contains seven iron atoms, one molybdenum atom and nine sulfur atoms. Its structure was elucidated in 1992, but in 2002 a light atom was found to be present at the centre of the cluster. This was suggested to be nitrogen, although the resolution was not good enough to confirm this and rule out oxygen and carbon. Now, two teams of researchers have independently confirmed, using different experimental techniques, that this interstitial atom in the iron–molybdenum cofactor is in fact carbon.

Kyle Lancaster and colleagues used iron Kβ X-ray emission spectroscopy to examine the isolated cofactor as well as a protein that does not contain it, but which does have a structure similar to nitrogenase's 'P cluster'. This allowed them to isolate the contribution of the mysterious interstitial atom to the spectrum. This contribution was discovered to be lower in energy than would be expected for oxygen or nitrogen, suggesting it is carbon, which was supported by extensive calculations.

Taking a different approach, Oliver Einsle and colleagues obtained a higher-resolution crystallography dataset. The improved resolution meant that they could compare the measured electron density of the unknown atom at an improved probe radius. Together with improved thermal factors, Einsle and colleagues found that the evidence pointed towards carbon. They also used improved ^{13}C- and ^{15}N-enriched resonance spectroscopy to further confirm their findings.   *NW*

A promising pyrolysis

Energ. Environ. Sci. **5,** 5414–5424 (2012)

Converting biomass into biofuels first involves breaking down solid biopolymers — in particular cellulose, which are long chains of glucose moieties that constitute up to 60% of biomass — into small fragments. These are typically light oxygenated species or furans that can subsequently be transformed into biofuels. Unfortunately, various experimental and theoretical limitations have hindered a good understanding of cellulose pyrolysis, and in turn the development of efficient large-scale processes. The problems include: the starting material is a heterogeneous condensed phase which slows heat transfer; the large number of reactions that occur in the solid, liquid and gas phases further complicates the reaction environment and thus analysis; and the size of cellulose molecules themselves makes molecular dynamics simulations too difficult.

Paul Dauenhauer and co-workers have now circumvented these issues by using a thin-film technique, where cellulose is processed into thin layers, which enables rapid heat transfers and rapid diffusion of volatile products. Under these conditions, cellulose conversion is limited by chemical kinetics rather than heat transfer. On

---

An atomic search party

Nano Lett. **11,** 5553–5557 (2011)

Doping semiconductors with impurities has long been used to control their electronic properties, with materials scientists tuning them by using the appropriate dopant in the correct amount. In bulk materials, knowing precisely how many dopant atoms are present is not so critical, but this is certainly not the case when the materials to be doped are nanocrystals and the number of dopant atoms could be as low as one. The position of the dopant within the nanocrystal can also affect its properties, therefore being able to visualize dopant atoms within such nanomaterials is critical to a better understanding and control of their behaviour.

Now a team led by David Norris from ETH in Zurich and Andre Mkhoyan from the University of Minnesota have shown
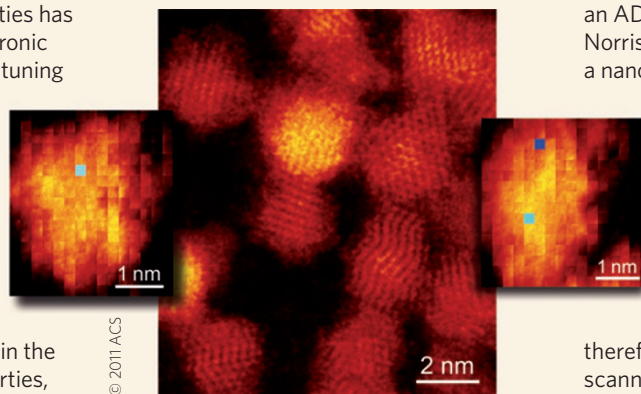
© 2011 ACS

that a combination of electron energy-loss spectroscopy (EELS) and annular dark-field scanning transmission electron microscopy (ADF-STEM) can be used to image manganese dopant atoms buried within zinc selenide nanocrystals. First, using an ADF-STEM image (pictured centre), Norris, Mkhoyan and colleagues selected a nanocrystal for further study. They then simultaneously measured the EELS map and the STEM image of the chosen nanocrystal.

In EELS, a sample is bombarded with electrons of known energy and the energy lost as a result of their interaction is measured. Different elements display distinct EELS spectra, therefore Norris, Mkhoyan and colleagues scanned across the nanocrystal, measuring the EELS spectrum at equally spaced points along the way. Areas with EELS features that matched a reference spectrum of a known manganese material therefore identified the position of manganese dopant atoms (pictured left and right).   *GA*