

NANOCATALYSIS

More than speed

The role of catalysts is greater than simply increasing the rate of a reaction. Modifying nanoparticles enhances two significant catalyst attributes: selectivity and thermal stability.

Andrew J. Gellman and Nisha Shukla

Most scientists understand that the activity of a catalyst represents its ability to accelerate the rate of a chemical reaction ($A \rightarrow B$) without the catalyst itself being consumed in the process. Fewer scientists appreciate that an important problem is that of designing a catalyst that will select between two reaction pathways ($A \rightarrow B$ or $A \rightarrow C$), perhaps to yield the product that is less energetically favoured. Moreover, it is the catalysis practitioner who truly values a catalyst with stability; long life under the most demanding chemical reaction conditions.

Two significant steps forward in catalyst design are reported on pages 126 and 132 of this issue by Somorjai *et al.*¹ and Lee *et al.*², respectively. The group lead by Gabor Somorjai use innovative methods of nanoparticle synthesis to prepare a core-shell Pt catalyst that is orders of magnitude more stable than bare Pt nanoparticles. Lee and co-workers (led by Francisco Zaera), meanwhile, exploit basic principles of surface chemistry to design and synthesize a Pt catalyst that selectively produces the less energetically favoured of two reaction products.

Many catalytic materials are nanometre-sized metal particles, usually supported on high-surface-area materials because small metal particles expose the greatest possible surface area per gram of metal. The activity and selectivity of these catalysts are determined by characteristics such as nanoparticle size and the atomic-level structure of the planes that they expose^{3,4}. The concept that catalytic activity is linked to the structure of catalyst surfaces is commonly attributed to Taylor⁵. Much of the earliest work to elucidate the details of this relationship was achieved by preparing catalysts with narrow particle-size distributions such that the set of crystal planes exposed was well controlled⁶. It therefore should be appreciated that catalysis research was a well-defined 'nanoscience' many decades before the term was popularized.

Nevertheless, it must also be noted that the progress made by Somorjai and Zaera, and their colleagues, would not have been

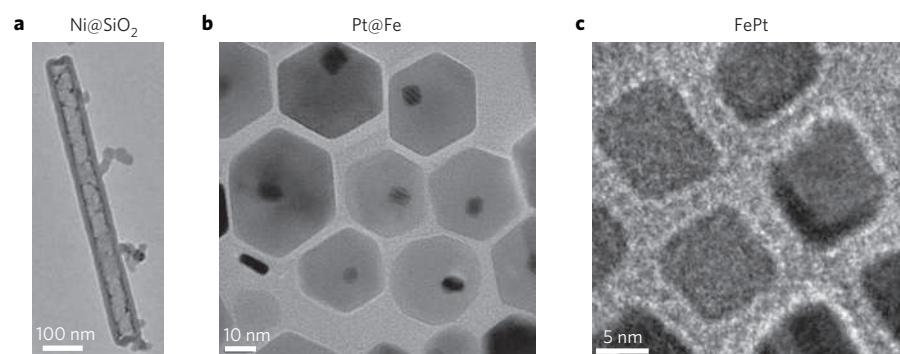


Figure 1 | Chemically synthesized nanoparticles with well-defined size, composition and shape. **a**, Size-controlled Ni nanorods coated with SiO_2 . **b**, Pt nanoparticles embedded in hexagonally shaped Fe nanoparticles. **c**, Self-assembled cubic FePt nanoparticles with their (100) planes parallel to the substrate.

achievable without the significant advance in nanoparticle synthesis that has been made over the past decade as a direct result of the popular interest in nanoscience. It is now possible to synthesize all manner of metal nanoparticles by controlling the particle size and, more impressive still, the particle shape. Figure 1 shows examples of composite, metal and alloy nanoparticles that have been synthesized with control of size, shape and morphology, respectively⁷. From a catalysis science perspective, the virtue of shape control is the ability to synthesize particles that only expose one atomic plane. Whereas a small spherical nanoparticle exposes a variety of atomic environments for a catalytic reaction, a cubic nanoparticle (Fig. 1c) exposes surfaces with just one atomic structure. Homogeneity of surface structure translates directly into high catalytic selectivity and perhaps maximal activity⁸.

Lee and colleagues² take advantage of the ability to prepare tetrahedral-shaped Pt nanoparticles of uniform size that expose only (111) facets on which the atoms are arranged in a hexagonal lattice. This catalyst facilitates the interconversion of *cis*- and *trans*-2-butene with selectivity that favours the formation of *cis*-2-butene, despite the fact that, in the gas phase, it is energetically less stable than *trans*-2-butene. The team demonstrate that this subtle level of

control over selectivity is possible because *cis*-2-butene is energetically more stable than *trans*-2-butene when adsorbed on the Pt(111) surface. What is most intellectually satisfying is that this achievement was made through a deep understanding of butene surface chemistry on Pt — temperature-programmed desorption experiments and density functional calculations indicated that Pt surface reconstruction is central to the adsorption of the isomers. The marriage of surface science methods and fundamental concepts of surface chemistry with nanoparticle synthesis has resulted in a catalyst that could not have been created a decade ago.

In their work, Somorjai and co-workers¹ prevail over one of the phenomena that plague the practical application of many nanoparticulate metal catalysts: nanoparticle sintering. At high temperatures, and thus in the reactive environments of many catalytic processes, metal atoms are mobile to the point that metal nanoparticles change shape and large particles grow at the expense of smaller particles. This limitation is clearly illustrated, for instance, in the work of Lee *et al.*, whose tetrahedral Pt nanoparticles do not survive heating to 575 K. Above this temperature the particles change shape, causing a reversal in the selectivity for *cis*-to-*trans* isomerization of 2-butene. To prevent catalyst nanoparticle agglomeration,

Somorjai *et al.* use a creative synthesis that coats Pt metal nanoparticles with a mesoporous silica shell. The shell allows the particles to be heated to temperatures approaching 1,000 K without evidence of sintering. Although the nanoparticles are buried, the catalytic activity is not inhibited — the silica is sufficiently porous to allow transport of catalytic reactants and products to and from the Pt nanoparticle surface. This is likely to be the case for similar mesoporous shells surrounding nanoparticulate catalysts for reactions that are not limited by transport to and from the catalyst surface. The stability imparted

on the Pt nanoparticles by the silica shell provides an additional benefit — thermal stability. Even after heating to almost 1,000 K, most of the Pt cores retain their surface morphology.

The field of catalysis science is often criticized as being *ad hoc* and empirical. The papers by Somorjai *et al.* and Lee *et al.* are testament to the fact that this need not be the case. Creative use of the modern methods of nanoparticle synthesis coupled with a deep understanding of fundamental surface chemistry has yielded significant progress in some of the most important and challenging problems in the field. □

Andrew J. Gellman and Nisha Shukla are in the Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA and the National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15236, USA.

e-mail: gellman@cmu.edu; nisha@andrew.cmu.edu

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MIXED CONDUCTORS

The bridge to redox switches

The chain-forming tendency of chalcogens like tellurium can be used as an efficient internal redox system capable of switching electronic conduction from n-type to p-type through small temperature changes.

Jürgen Janek

The switching of materials properties by external stimuli is highly interesting from both the fundamental point of view as well as for a number of advanced technologies^{1,2}. Because most of the technologically relevant physical properties of a material depend more or less directly on the electronic structure, any switching mechanism relies on the control of the electronic structure — either locally, for example by amorphization and crystallization in optical phase-change materials³ — or non-locally, such as by the insertion of mobile atoms as electron donors in electrochromic devices⁴. An interesting question is whether the electronic structure can also be controlled through internal atomic rearrangements of redox-active elements that act either as an electron sink or source depending on the redox switching direction. An intriguing glimpse into this possibility is now given by Tom Nilges and colleagues⁵, who on page 101 of this issue report on an unprecedented reversible and large change of the electronically determined properties such as p- and n-type conduction, thermopower and bandgap in $\text{Ag}_{10}\text{Te}_4\text{Br}_3$ on subtle structural changes in the anion sublattice.

For several reasons, the binary silver chalcogenides and their more complex relatives, ternary or quaternary solid solutions of halides such as $\text{Ag}_{10}\text{Te}_4\text{Br}_3$ or the pnictides, take on the role of prototype non-stoichiometric materials with ionic and electronic conductivity. They show a wide

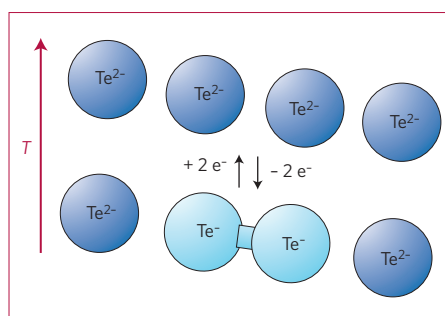


Figure 1 | Reversible redox switching in silver tellurides. As the temperature is increased, the Te_2^{2-} dumbbell pairs in the tellurium strands break up into two Te^{2-} ions.

range of interesting physical properties, often including high silver-ion mobility and a correspondingly high ionic conductivity (see ref. 6 for a review on Ag_2S).

Furthermore, the tendency of the chalcogen atoms to form chains with strong covalent character leads to a rich structural chemistry, especially in the case of compounds containing the heavier elements selenium and tellurium⁷. An attractive proposition is the possibility of controlling the exact metal to non-metal ratio of the notoriously non-stoichiometric chalcogenides by solid-state electrochemical techniques — mostly through so-called coulometric titration⁸. In essence, coulometric titration means to dope a compound with mobile ions via a solid

electrolyte phase in an electrochemical cell. Because electric currents can be measured very precisely, it is possible to control the metal content of a sample down to the sub-ppm range. Unfortunately this approach requires stable solid electrolytes for the dopant ions, which are only available with sufficient stability and performance for a limited range of ions. Among these, the silver ion is the most practical as stable silver electrolytes are easy to use.

Coulometric titration is one of the techniques that Nilges *et al.*⁵ use in order to understand the staggeringly large variation in electronic thermopower of $\text{Ag}_{10}\text{Te}_4\text{Br}_3$, which within a window of 30 K around temperatures of 390 K changes from about $+300 \mu\text{V K}^{-1}$ to $-900 \mu\text{V K}^{-1}$ and back to $+500 \mu\text{V K}^{-1}$. Combining detailed information from structural investigations with theoretical simulations of the electron structure as well as electronic transport measurements, the authors suggest that this variation in thermopower is indeed explained by the specific character of the chain-forming tellurium ions that act as an internal electron source and sink.

In an ionic picture, we may interpret $\text{Ag}_{10}\text{Te}_4\text{Br}_3$ as a solid solution containing a mixture of isolated Te^{2-} ions as well as Te_2^{2-} ‘dumbbell’ pairs. At low temperatures the tellurium dumbbells, together with two Te^{2-} ions and one silver ion, form $[\text{AgTe}_4]^{5-}$ strands within the crystal structure. With increasing temperature, this silver ion seems to increasingly leave the