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SURFACE CHEMISTRY

Crystal cuts on the nanoscale

A simple method has been developed to control the shape of nanoscale cuprous oxide crystals. Some shapes turn out to be much better than others as catalysts for a light-activated reaction.

PEIDONG YANG

The most popular diamond cut is the ‘modern round brilliant’, in which a gem is hewn to expose a specific set of crystal facets so as to produce exceptional brilliance. The arrangement of the facets is crucial for providing the maximum light return through the top of the diamond. It is becoming increasingly clear that crystal shape at the nanometre scale is similarly important for getting the best performance from solid catalysts. Writing in the *Journal of the American Chemical Society*, Huang *et al.*¹ report a beautiful example of how the specific crystal facets on nanoparticles of a material affect the catalytic properties of the particles in light-activated reactions.

Cuprous oxide (Cu_2O) has commonly been used as a pigment, a fungicide and an antifouling agent for marine paints. More recently, it has been reintroduced as a promising material for the cathode of photoelectrochemical cells, which use sunlight to split water into hydrogen and oxygen². Huang *et al.*¹ have discovered a simple process for controllably synthesizing cuprous oxide nanocrystals as cubes, rhombic dodecahedra (polyhedra with 12 rhombic faces) and a variety of geometries in between (Fig. 1). The rhombic dodecahedra expose only one kind of facet (known in crystallographic jargon as $\{110\}$ facets), and the authors observed that these nanocrystals are exceptionally good catalysts for the light-induced degradation of the organic compound methyl orange. This reaction serves as a model for reactions involved in clearing organic pollutants from the environment.

One of the tricks often used to control which shapes and facets form during the synthesis

of nanocrystals is to preferentially adsorb certain molecular species to specific planes of atoms exposed on crystal surfaces. This strategy generates direction-dependent nanocrystal growth by stabilizing a particular facet — growth is limited on crystal planes where

adsorption (and so stabilization) is strong, but is promoted on planes where adsorption is weak. A wide variety of chemical species can facilitate shape control in the growth of metal and oxide nanocrystals, including: surfactants, polymers and biomolecules; small molecules such as those in gases; and even atomic species, such as anions or metal ions.

It has previously been reported³ that the shape of cuprous oxide nanocrystals can be controlled by varying the ratio of chloride ions to sodium dodecyl sulphate ions in the solutions from which the crystals form; the chloride ions stabilize the $\{100\}$ planes of the crystals, whereas the dodecyl sulphate ions stabilize the $\{111\}$ planes. In this way, a range of nanoscale polyhedra has been produced.

To make their cuprous oxide nanocrystals, Huang *et al.*¹ used a different recipe from that previously reported³, and found that, by simply adjusting the amount of the reducing agent in the reaction mixture, they could control the shapes of the crystals. Their approach allowed them to make an alternative series of polyhedra (Fig. 1) to that produced in the earlier work. In addition, their shape-control method can be used at room temperature, unlike many previously reported strategies, which typically require higher temperatures.

Different nanocrystal shapes naturally display crystallographically distinct facets. In the absence of any major surface reconstruction processes, each facet type contains surface

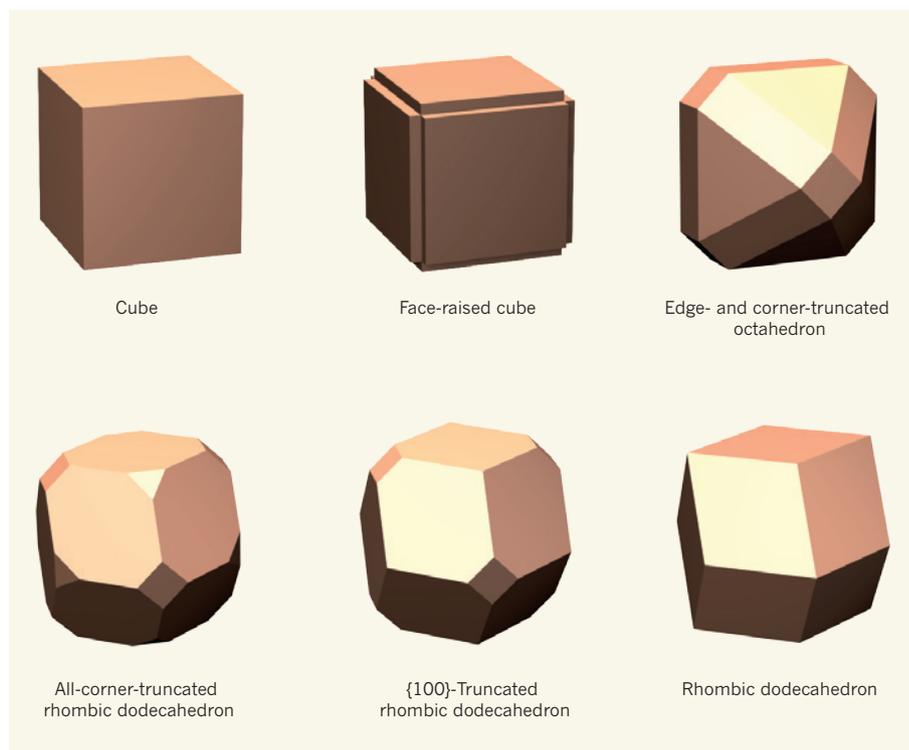


Figure 1 | Nanocrystal shapes. Huang *et al.*¹ report a simple process for controlling the shape of cuprous oxide nanocrystals during synthesis; the shapes made are depicted. The authors observed that the catalytic properties of the nanocrystals in a light-activated reaction — the degradation of methyl orange — largely depend on the kind of facets that the crystals have. Cubic crystals are essentially inactive, octahedra are moderately active, and rhombic dodecahedra are exceptionally active.

atoms that reside in particular environments (arrangements of nearby atoms). This in turn causes the surface atoms in different facets to have distinct catalytic activities. This fundamental insight dates back to the classic discovery that {111} surfaces on single crystals of platinum are typically much more catalytically active than {100} surfaces in reactions that form aromatic compounds.

Indeed, Huang and colleagues' cuprous oxide nanocrystals clearly exhibit very different catalytic properties depending on the facets displayed. The authors found that cubic nanocrystals that are bound exclusively by {100} faces are essentially inactive in the photodegradation reaction of methyl orange, whereas octahedra bound by {111} surfaces are moderately active catalysts. Rhombic dodecahedra bound by {110} surfaces, however, caused much faster photodegradation of methyl orange than the other nanocrystal shapes. The authors speculate that the observed catalytic activities correlate with the surface density of copper sites on the different facets, although they report no direct evidence for this. It is also unclear whether many of the atoms on nanocrystal surfaces undergo rearrangements during the reactions, or how ligand molecules that are bound to the different surfaces — either during crystal formation or in the photodegradation reactions — affect catalytic activity.

The new findings¹ form part of a growing body of literature documenting surface-dependent catalytic activities, perhaps most notably for metals. For example, key studies performed on the surfaces of samples of macroscopic single crystals under ultra-high-vacuum conditions have shown that some reactions are sensitive to surface structure⁴. A quintessential case is the platinum-catalysed reaction of benzene with hydrogen: the {100} platinum surface yields only cyclohexane (a saturated hydrocarbon) as a product, whereas the {111} surface also yields cyclohexene (an unsaturated analogue of cyclohexane)⁴.

This dependence of catalytic activity on surface structure extends to metal nanocrystals, particularly in the case of platinum, palladium and rhodium. For instance, in the hydrogenation of benzene, platinum nanocrystals that expose well-defined {100} and {111} surfaces behave⁵ in much the same way as larger crystals. In another example, faceted palladium nanocrystals that have high-index surfaces — {730} and {221} surfaces, which contain a high density of atomic steps and ledges — were found⁶ to be much more active catalysts in 'Suzuki' carbon-carbon bond-formation reactions than nanoparticles that have typical {100} surfaces. Such high-index faceted nanoparticles are also better catalysts for some electrochemical reactions^{7,8}. And returning to cuprous oxide, highly faceted polyhedral microcrystals that display high-index {311} surfaces are especially good catalysts for the oxidation of carbon monoxide⁹.

Although it is clear that the reactivity and selectivity of nanoparticle catalysts depend on the shape (and hence the exposed surfaces) of the particles, in many cases it is unclear whether these effects are truly surface-dependent. This is especially true for reactions in solution or in the gas phase, where there is evidence that changes to particle surfaces and shapes may occur during the reactions¹⁰. Methods for the direct *in situ* surface analysis of molecules adsorbed to nanocrystals in solution, analogous to the techniques commonly used to study larger single crystals, need to be developed to address this issue. Nevertheless, as Huang *et al.*¹ have shown, sculpting the shape of nanocrystals is a promising approach for developing catalysts that produce only one desired reaction product out of many other possible products at high reaction rates — an essential requirement for a wide variety of industrially important reactions. ■

PLANT BIOLOGY

Equal-parenting policy

During early embryo development in animals, maternal genes are expressed in preference to those of the zygote — the newly fertilized egg. But in plants it seems that zygote genomes switch on within hours of fertilization. [SEE LETTER P.94](#)

CHRISTOPHER J. HALE
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Fertilization occurs when two gametes merge to form a zygote. The zygote's genome comprises two sets of chromosomes — one maternal, the other paternal. In animals, the stages of development immediately after fertilization are disproportionately controlled by maternally inherited factors, with the zygotic genome being switched on gradually in waves of activation¹. Whether plants undergo a similar maternal-to-zygotic transition in genomic activity has been a long-standing question. In contrast to previous work², Nodine and Bartel³ show (page 94 of this issue) that a plant zygote's protein-coding transcriptome — its total complement of protein-coding RNA transcripts — contains relatively equal maternal and paternal contributions. It seems, therefore, that plants and animals have evolved distinct strategies for managing the early steps in the transition from two gametes to an organism with maternal and paternal copies of the genome*.

For the plant species *Arabidopsis thaliana*, a wealth of whole-genome sequence data exists for closely related yet genetically distinct lines known as ecotypes⁴. To directly measure the respective contributions of the maternal

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and paternal genomes to the zygotic transcriptome, Nodine and Bartel crossed two of these ecotypes and sequenced the RNA content of the resulting zygote. Using the genetic differences between the parents, they then matched these RNAs to either the maternal or the paternal genome.

The authors observed a near-equal abundance of RNA sequences derived from each parental genome in the plant embryos as early as the one- to two-cell stage. Only a small number of genes showed biased expression. They also performed reciprocal crosses — switching which ecotype provided the male and female gamete. It emerged that most of these cases of bias were probably due to genetic or epigenetic differences (chemical modifications that alter gene expression without affecting the DNA sequence) between the two ecotypes used, rather than being a result of which ecotype was used as the male or the female parent. These findings imply that the plant zygotic genome is essentially switched on only hours after fertilization.

Nodine and Bartel's results are in contrast to other reports^{2,5} suggesting that the maternal-to-zygotic transition in plants is gradual, as is the case for animals. The most comprehensive of these reports², published last year, used a genomics approach similar to that of the current study, and found that more than 80% of the *Arabidopsis* transcriptome in early