Gold fever

The catalytic potential of gold nanoparticles was overlooked for years, but researchers are making up for lost time, writes Bea Perks
Gold was among the first elements known to man, but it was quite some time before chemists realised it might be useful as well as beautiful. A gold nugget is relatively unreactive but take it down to the nanoscale and it’s a different story.

Gold nanoparticles make exceptionally active catalysts. They are not just good catalysts; they are the very best available for a number of reactions. They are, to use a well-worn cliche, worth more than their weight in gold.

As an active part of a catalytic system specifically designed to break down dangerous groundwater pollutants, for example, there is no question that gold nanoparticles are remarkable, says Trevor Keel, industrial team project manager at the World Gold Council, an organisation that represents leading gold mining companies. ‘Using gold to develop efficient, cost-effective solutions to environmental problems enables less suitable treatments to be removed completely,’ he adds.

World market

The growth of gold’s importance in the field of nanotechnology has had a fairly limited effect on the world’s gold industry overall. In 2009, the world’s gold mines produced over 2500 tonnes of gold. The vast majority of this went into the enormous jewellery and investment markets, with the major industrial use (the electronics market) taking approximately 10 per cent of the total. Overall, nanotechnology may account for just a few tonnes of gold per year worldwide.

But the impact of nanotechnology is much more than just numbers. ‘The field is burgeoning, with new applications and breakthroughs being reported and patented at a staggering rate,’ says Keel. ‘Ongoing advances in nanotechnology are permitting this precious material to be used in an intelligent, cost-effective way opening up a range of new markets.’

The full catalytic potential of gold was underlined in a 2005 review article in Applied Catalysis A by Graham Hutchings at the University of Cardiff, UK, and Masatake Haruta at Tokyo Metropolitan University, Japan.1 ‘The chemical industry would be transformed if selective oxidation of hydrocarbons could be achieved efficiently using cheap and clean oxygen from the air,’ wrote Haruta in the journal Nature the same year. 2 ‘Doing that with gold as a catalyst is a method gaining in allure,’ he added.

Getting to that point, recognising gold’s potential as a catalyst, has been a surprisingly lengthy process, particularly considering the widespread use of platinum and silver based catalysts. Even back in the 1970s, researchers working on hydrogenation had reported that very small gold particles were very active. Alas, reports shortly afterwards suggested that the so-called catalytic activity of gold was probably the result of impurities. The gift of hindsight is a wonderful thing.

‘People had the impression that gold was doing nothing whatsoever,’ says Hutchings. ‘So no one bothered to look.’

In 1985, Hutchings reported that Au3+ could catalyse the hydrochlorination of acetylene to vinyl chloride.3 Gold turned out to be the best catalyst available for hydrochlorination to the vinyl chloride monomer, says Hutchings: ‘we haven’t found anything better.’

The same year, Haruta arrived at the surprising discovery that gold nanoparticles deposited on semiconducting transition-metal oxides were active in carbon monoxide oxidation, even at −76°C. 4

Textbook nanotech

Once gold’s catalytic potential began to be recognised, the flood gates opened. Its impressive catalytic activity is textbook nanotechnology: the smaller the gold nanoparticles, the greater the catalytic activity. Take

The Lycurgus cup is green, but glows red when a light is placed inside due to the gold nanoparticle content

In short

- Gold on the nanoscale is an extremely efficient, green catalyst
- Gold nanoparticles have historically been used in applications ranging from ancient medicines to colourful church windows
- Today, their uses in analytical instruments and gas masks are being explored

Not so new

The fact that the catalytic value of gold nanoparticles was only recognised relatively recently is particularly surprising given that we’ve actually been making gold nanoparticles for over 2000 years.

In traditional Indian ayurvedic medicine, an ash-like substance called swarna bhasma, which contains gold nanoparticles about 56nm in diameter, was used to treat a range of diseases including asthma and arthritis. Hundreds of years later, the Romans were using gold nanoparticles to colour glass. Nanotechnologists often quote the example of a 4th century Roman glass beaker currently in the British Museum in London, the Lycurgus cup, which looks green on the outside, but glows red, courtesy of its gold nanoparticle content, when lit from inside. Church windows are often coloured using a similar technique. In 19th century Britain, Michael Faraday reported that a similar rosy glow could be created by aqueous solutions of gold particles ‘very minute in their dimensions’.

Historically, gold nanoparticles were believed to be spherical. But in the past decade it has become clear that tailoring not only their size but also their shape holds tremendous potential. Gold nanoparticles can now be produced as platonic solids (regular polyhedrons – tetrahedra, hexahedra, octahedra, icosahedra and dodecahedra); nanorods; nanoplates; and branched metal nanocrystals.

Although it is now over 20 years since Haruta reported the spectacular performance of gold nanoparticles in the aerobic
Carbon monoxide oxidation, particularly at low temperatures, holds tremendous commercial potential because of the possibility of removing CO impurities from hydrogen fuel cells, which gold nanoparticles can do without oxidising the valuable hydrogen. But the possibilities don’t end there, with examples of gold nanoparticles as the catalyst of choice extending from acetylene hydrochlorination to the addition of nucleophiles to acetylenes; to selective hydrogenation of NO multiple bonds; alcohol oxidation to acids and aldehydes; and direct formation of hydrogen peroxide.

The catalytic activity of gold has interested researchers not only because gold nanoparticles are such outstanding catalysts, but also because gold offers such a ‘paradigmatic example’ of chemistry on the nanoscale. The catalytic activity of gold is directly related to nanoparticle size in the nanometre length scale, notes Hermenegildo Garcia, professor at the Technical University of Valencia in Spain. The catalytic properties of gold are unique to particles on the nanoscale, he says, ‘and can disappear completely on the micrometric scale’.

### Praise the Lord

The history of gold nanoparticles – from their use in ancient medicines; to colourful applications in glass manufacture; to current use and promising potential as industrial catalysts – has been as exciting as it is varied. Zhu Huai Yong at Queensland University of Technology in Australia recently brought together several strands of this colourful past, with the discovery that the gold nanoparticles in church windows were also able to destroy airborne pollutants.

‘For centuries people appreciated only the beautiful works of art, and long life of the colours, but little did they realise that these works of art are also, in modern language, a photocatalytic air purifier with nanostructured gold catalyst,’ says Zhu.

What took us chemist’s so long to see gold’s potential? It turns out we’d been enjoying the benefits of catalysis by gold nanoparticles for centuries.

### References