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2010 : March 2010 - Fast Moving Fronts : Highly Cited Scientist Younan Xia Discusses Metal Nanocrystals

## FAST MOVING FRONTS - 2010

**March 2010**

PDF

**Younan Xia talks with *ScienceWatch.com* and answers a few questions about this month's Fast Moving Fronts paper in the field of Materials Science. The author has also sent along images of his work.**

**Article: Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics?**
Authors: **Xia, Y**;Xiong, YJ;Lim, B;Skrabalak, SE
Journal: ANGEW CHEM INT ED, 48 (1): 60-103, 2009
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**SW: Why do you think your paper is highly cited?**

Our paper provides a comprehensive review and critical assessment of research activities centering on the syntheses and applications of metal nanocrystals with well-controlled shapes and facets. This article is highly cited simply because it touches upon an extremely important subject that is being actively pursued by many research groups.

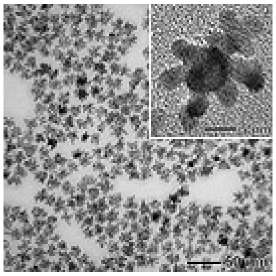
Controlling the shape of a metal nanocrystal offers one of the most powerful means for maneuvering its properties and enhancement of its usefulness for a given application. For example, it has long been recognized (mainly through theoretical modeling) that the number and positions of surface plasmon resonance (SPR) peaks of a silver or gold nanocrystal are strongly correlated with the shape.

A nanocube exhibits three resonance peaks while a spherical counterpart only displays one major peak. The shape also controls how local electric fields are distributed on the surface of a nanocrystal and thus its efficiency in applications such as surface-enhanced Raman scattering (SERS).

In catalysis, it is well-documented that metal nanoparticles can speed up reactions with different activity and selectivity depending on the crystallographic planes (i.e., facets) exposed on the surface, with the {100} and {210} facets of platinum working the best for reactions that involve hydrogen and carbon monoxide, respectively.

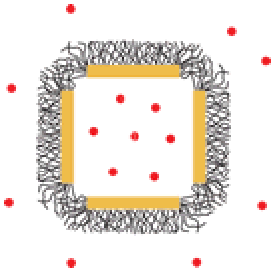
Despite the technological importance, the challenge to synthetically and systematically control the shape of metal nanocrystals had been met with only limited success until eight years ago when we reported a breakthrough (Y. Sun and Y. Xia, "Shape-controlled synthesis of gold and silver nanoparticles," *Science* 298: 2176-79, 2002).

Figure 1 [+] details



Transmission electron microscopy images...

Figure 2 [+] details



An illustration showing how...

Although that paper only described two case studies on cubic nanocrystals of gold and silver, the methodologies were later extended by my and many other groups to cover essentially all noble metals and a myriad of different shapes. As a result, that paper has stimulated an exponential growth of research by enabling a broad range of exciting new demonstrations.

It is the outcomes of these research activities that form a basis for the current review article. Based on the citation data for this review article, it looks like the momentum created by that *Science* report is even getting stronger with time, as more people are moving into the research area of shape-controlled synthesis.

**SW: Does it describe a new discovery, methodology, or synthesis of knowledge?**

Since this is a review article, its major role is to present an intellectual framework, including the rationale, methodology, and mechanism for the synthesis of metal nanocrystals with well-controlled shapes.

We begin with a brief introduction to nucleation and growth mechanisms in the context of metal nanocrystal synthesis, followed by a discussion of the possible shapes that a metal nanocrystal might take under different conditions.

We then focus on a variety of experimental parameters that have been explored to manipulate both the nucleation and growth pathways in solution-phase syntheses in an effort to generate the specific shapes.

We also elaborate on these approaches by selecting good examples in which there is already reasonable understanding of the observed shape control or, at least, the protocols have proven to be both reproducible and controllable.

Towards the end, we highlight a number of applications that have been enabled and/or enhanced by the synthesis of metal nanocrystals with well-controlled shapes. We conclude this article with personal perspectives on the directions toward which future research in this field might lead us.

**SW: Would you summarize the significance of your paper in layman's terms?**

This article provides the reader with an updated account of the protocols and mechanisms with respect to the synthesis of metal nanocrystals having well-defined and controllable shapes. In a sense, this article is a nice combination of three major components: a complete collection of reliable protocols, an analytical discussion of many mechanistic studies, and an offering of insightful perspectives based on first-hand experience.

After reading through this article, the reader should be able to know immediately what has been reported in literature; what is the best protocol for producing nanocrystals of a specific metal and with a specific shape (or facets); and what could be some of the potential problems.

The critical analyses running throughout this article can also serve as useful guidelines for someone who is interested in designing and developing a new protocol for the synthesis of metal nanocrystals with a desired shape.

**SW: How did you become involved in this research and were any particular problems encountered along the way?**

I worked with Professor George M. Whitesides as a Ph.D. candidate and then a postdoctoral fellow at Harvard University.* My thesis work involved the development of soft lithography (See: Y. Xia and G. M. Whitesides, "Soft lithography," *Angewandte Chemie International Edition* 37: 551-75, 1998), which represents a top-down approach to the fabrication of nanostructures.

When I launched my own research at the University of Washington in Seattle in 1997, I wanted to explore different routes to nanostructures, and in particular, the bottom-up approach which involves the formation of nanostructures from building blocks with smaller dimensions, such as atomic and molecular species. That is how I got started on the development of new chemical methods for the synthesis of nanocrystals.

From the perspective of methodology, all chemical syntheses of nanocrystals share the same physics: that is, nucleation and growth. However, the exact details of these two steps can be substantially different, depending on the materials and nanocrystals involved. That means we have to develop a specific protocol for each type of nanocrystal, which makes it much more complicated compared to a top-down approach, where the technique (e.g., electron beam writing) can often be applied to all sorts of materials and nanostructures.

*"Our paper provides a comprehensive review and critical assessment of research activities centering on the syntheses and applications of metal nanocrystals with well-controlled shapes and facets"*

For chemical synthesis, an understanding of the nucleation and growth mechanisms becomes of paramount importance, as it allows one to see why a specific shape is formed or not formed during a synthesis.

For example, after many years of study, we finally established that the final shape of a metal nanocrystal is primarily determined by the number of twin defects included in the initially formed seed, with the seed being defined as something larger than a nucleus in which structural fluctuation is no longer an option.

As summarized on the cover illustration accompanying this review article, the product will be a nanocube with various degrees of truncation at corners for a single-crystal seed (with no twin), while a right bipyramid (or a nanobeam with a single-twinned cross-section) will be obtained from a singly-twinned seed and a pentagonal nanorod or nanowire will be grown from a multiply-twinned seed in a decahedral shape.

Whenever twinning becomes random, the synthesis will yield irregularly shaped nanoparticles—a morphology that was reported again and again in thousands of papers prior to the publication of our *Science* report.

Although our results clearly illustrate the one-to-one correspondence between the seed and the resultant nanocrystal, it is still not clear what factor(s) determines the exact number of twin defects formed in a seed during the nucleation process and how to control it experimentally and reliably.

At the current stage of development, oxidative etching (a process similar to rusting) seems to be the most effective method for selectively eliminating different types of twinned seeds and thus generating metal nanocrystals of a specific shape exclusively.

For example, we have clearly shown that oxidative etching based on chloride ions and oxygen—from the air and/or dissolved in the solvent—yields silver or palladium nanocubes with different degrees of corner truncation, while oxidative etching with bromide ions and oxygen generates right bipyramids together with a small portion of nanocubes.

Since the amount of chloride or bromide ions needed for the etching is so little—typically, on the level of parts per million—all the syntheses of metal nanocrystals are highly susceptible to ionic impurities that could be introduced into the chemical reagents during their manufacturing, transportation, and/or storage.

This high sensitivity to oxidative etching also explains why shape-controlled synthesis of metal nanocrystals has been so difficult to achieve although the first chemical synthesis of metal nanocrystals was documented by the British scientist Michael Faraday (1791-1867) in 1847, when he discovered that the optical properties of gold colloids differed from those of the corresponding bulk metal.

Once we have a solid understanding of the roles played by various ionic species and oxygen, then we have a better way to control both nucleation and growth processes and thus, the shapes of nanocrystals, by purposely introducing some specific ionic species into a synthesis at a well-controlled level.

As a result of these new developments, the synthesis of metal nanocrystals is evolving from an art into a science. This is also probably another reason why so many people are moving into this area, as it is getting easier to obtain metal nanocrystals with well-controlled shapes for various applications.

**SW: Where do you see your research leading in the future?**

About four or five years ago, I became interested in finding applications for the nanomaterials my group had developed, including metal nanocrystals, gold nanocages, and polymer nanofibers. I was particularly interested in biomedical applications because I personally see a lot of potentials there for nanomaterials in terms of diagnosis and therapy. It is also a research field that probably has the strongest impact on our society. As a result, I switched my area of concentration from chemistry to biomedical engineering by relocating from the University of Washington in Seattle to Washington University in St. Louis in the summer of 2007.

*"Since this is a review article, its major role is to present an intellectual framework, including the rationale, methodology, and mechanism for the synthesis of*

Our current efforts include the development of nanofibers and other nanostructures that can be used to control the differentiation of stem cells and guide the outgrowth of neurites. This will allow us to address clinical problems related to neural regeneration, peripheral nerve repair, and spinal cord injury recovery.

Meanwhile, we are exploring the use of gold nanocages as contrast agents, drug delivery vehicles (See: M. S. Yavuz, *et al*., "Gold nanocages covered by smart polymers for controlled release with near-infrared light," *Nature Materials* 12: 935-39, 2009), and photothermal therapeutic agents. The end applications include early cancer detection and treatment with better efficacy and less side effects.

On the fundamental side, we are exploring new approaches to studying and *metal nanocrystals with well-controlled shapes."*

controlling cell communication. In one approach, we use gold nanocages to deliver neurotransmitters with high spatial and temporal resolutions in order to study how signals are received and integrated by a neuron and a neural network.

In another approach, we use the unique photothermal properties of gold nanocages to alter the functions of some key enzymes involved in cell communication. Combined together, we hope we can develop a powerful new toolset to reversibly turn on and off a signal transduction pathway.

If successful, this research will enable us to control the behavior of cells at will. As a continuous effort from my chemistry background, part of my group is developing more robust and efficient catalysts which are highly sought after for various applications, including fuel cells and catalytic converters.

**SW: Do you foresee any social or political implications for your research?**

We always want to do cutting-edge research that will have a profound impact on society, one way or another. Regarding the nanomaterials we have invented and developed in the past, some of them have already started to find applications in a wide range of areas that include microelectronics, photonics, spectroscopy, sensing, biotechnology, medical diagnostics, catalysis, and energy conversion/storage.

For example, our technology for silver nanowires has been licensed to Cambrios Technologies Corp., a start-up company in the Bay Area, and is being used to develop flexible, transparent, conductive substrates for touch-screens and other types of display devices.

Our newly developed palladium-platinum bimetallic catalyst (See, for example, B. Lim, *et al*., "Pd-Pt bimetallic nanodendrites with high activity for oxygen reduction," *Science* 324: 1302-05, 2009) is expected to cut the costs of proton-exchange membrane (PEM) fuel cells and eventually help to commercialize this technology.

It will also help to achieve sustainability, as platinum is itself such a rare and expensive metal that is critical for many industrial applications, including the manufacturing of nitric acid, petroleum products, fuel cells, and catalytic converters.

Our technology on gold nanocages is expected to radically change the way cancer is diagnosed and treated. We are quite excited about all these implications that our research will be able to offer.

Figures & descriptions

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KEYWORDS: GROWTH; METAL; NANOCRYSTAL; NUCLEATION; shape control; ENHANCED RAMAN-SCATTERING; LARGE-SCALE SYNTHESIS; SEED-MEDIATED GROWTH; POLYHEDRAL GOLD NANOCRYSTALS; SINGLE-CRYSTALLINE NANOWIRES; SURFACE-PLASMON RESONANCE; UNIFORM SILVER NANOWIRES; HIGH-YIELD SYNTHESIS; STABILIZED RUTHENIUM NANOPARTICLES; COLLOIDAL PLATINUM NANOPARTICLES.

**Additional information:**

- Listen to podcast: MP3¦ WMA
- Younan Xia is featured in ISIHighlyCited.com
- * Read a *ScienceWatch.com classic* interview (2002) with George M. Whitesides.

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