Mastering size and shape of CoPt nanoparticles by flash laser annealing

A major step towards the understanding of intrinsic properties of nano-objects depends on the ability to obtain assemblies of nanoparticles of a given size with reduced size dispersion and a well-defined shape. The control of these parameters is a fundamental challenge. In this newsletter, we present a new method to tailor in an easy way both size and shape characteristics of nanoparticles by using laser irradiation in the nanosecond regime. The CoPt nanoparticles have been prepared by Pulsed Laser Deposition (PLD) in ultra high vacuum, using a KrF excimer laser at 248 nm with pulse duration of 25 ns. CoPt nanoparticles were formed by an alternative metallic vapor phase deposition on amorphous alumina substrate heated at 550°C. The particles are then covered by a protective thin alumina layer. After the synthesis, the sample was irradiated by using the same laser as the one used for the PLD, but the energy of the laser is well below the ablation threshold of CoPt and Al₂O₃ in order to avoid the vaporization of the sample. For that purpose, a focusing lens is placed between the laser and the sample. The energy density on the nanoparticles is controlled by the distance between the back focal plane of the lens and the sample. In our experiment it was fixed to 47 mJ/cm².

Figure 1a shows the morphology of as-grown CoPt nanoparticles. Due to the tendency of the metals to wet alumina the shape of these particles is elongated in the substrate plane. The morphological changes induced by the laser irradiation as a function of the number of laser pulses is presented in figure 1b and 1c. We observe that this irradiation has two effects. First of all, the morphology of the particles evolves from flat to spherical shape. In the same time, the mean size, the polydispersity (ratio between the standard deviation and the mean size) and the coverage ratio decrease dramatically (table associated to fig. 1). The mechanisms involved in this experiment can be explained as follow: CoPt nanoparticles absorb the laser light. This absorption results in the increase of the temperature of the nanoparticles and makes possible the desorption of Co and Pt atoms from the particle surface. Due to the increase of the absorption cross section of the UV radiation as the particle size increases, these desorption phenomena are more effective on the biggest particles leading to the reduction of the size and the size dispersion of the particles. In parallel, the laser intensity induces the solid-liquid transition of the alloy leading to a complete reshaping of the particles. This solid-liquid transition is evidenced by the shape of the particles (fig. 1c) similar to small water droplets on clean glass substrate and the formation of twin boundaries characteristic of a solidification process. CoPt alloy presents two atomic arrangements depending on temperature: a L1₀ ordered phase under 825°C and a FCC disordered phase for higher temperature. Same irradiation experiment performed on fully ordered particles induce a phase transformation into the disordered phase, similarly to a quenching of the particles from high temperature phase. CoPt nanoparticles composition is not affected by irradiation. Flash laser annealing is an effective way from fundamental and industrial points of view to control size and shape of nanoparticles for the study of their magnetic properties and their applications in high density recording media.

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Building from the “bottom up”: new nanocomposite architectures

Driven in parallel by the demands of technology and the inquisitiveness of basic sciences and engineering, the last decade has brought an explosion in the development of new materials especially in the nanoscale domain. Dr. Meletis’ group (Surface and Nano Engineering Laboratory, SaNEI) in University of Texas at Arlington has recently discovered evidence of self-organization on a very intriguing nanostructured system in a research project funded by the National Science Foundation. Nanocomposite Co/diamond-like carbon (DLC) films synthesized by a plasma-assisted, hybrid CVD/PVD method were found to exhibit Co nanorods (~10 nm in diameter) with narrow size distribution via self-organization (Fig. 1).

Powered by the search of novel properties based on the confinement effect, these self-organized nanostructures offer the opportunity to exhibit novel magnetic properties offering an enormous potential for the development of new devices within the frame of nanotechnology. Traditional manufacturing techniques have been successfully applied in the past in a top-down approach to fabricate components and devices down to the micron scale region. However, such manufacturing practices are merely impossible to apply to the nanoscale regime since entirely different phenomena dominate the behavior of the materials in that domain. Thus, novel manufacturing approaches are needed in order to take advantage of the enormous potential of nanoscale structures.

Formation of Co nanorods and their self-organization was found to depend critically on processing parameters. Additional convincing evidence in that direction is provided by carefully examining results of previous morphological studies on similar systems. Clear signs of self-organization are evident but they may have been difficult to recognize, since the nanostructures were only partially formed under the prevailing deposition conditions. One is struck by the limited information existing in the literature on detailed structural and microstructural characterization of such nanostructured films especially with sensitive probes such as high-resolution transmission electron microscopy (HRTEM). Recent work revealed that the Co nanorods nucleate from ordered, self-organized nanodots [Meletis and Jiang, JNN 6(6), 1807 (2006)]. The nanodots that form in 2D, hexagonal arrays, have a uniform size of ~5 nm and are encapsulated by 1-2 nm amorphous DLC matrix (Figure 2). Synthesizing such ordered, self-organized, 2D arrays offers the opportunity to form also new, nanocomposite 3D architectures, Figure 3(b). Self-organization of these nanostructures and their morphological characteristics depend strongly on the processing parameters (deposition temperature, arrival rates, etc.) which in turn influence fundamental processes taking place during deposition (i.e., diffusion, etc.). Developing an understanding of the mechanisms that govern these phenomena provides a challenging and unique opportunity to control the self-organization of unit blocks in these systems, that can be utilized to develop a novel, “bottom-up”, nanomanufacturing process.

**Further information:**

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Lasers have been particularly valuable tools for the manufacturing of a range of new products and materials in recent years. They have been key elements of manufacturing in the automotive, aerospace and in machining applications due to the degree of control and manipulation that is possible with lasers. High powered lasers have increased the manufacturing rate of many components and materials. For femto-second lasers have been used to produce channels in surfaces which promote cellular communities in specific direction in an ordered fashion. Such nanomanufacturing techniques are likely to have a major impact in the field of medicine particular for tissue engineering. Researchers at the University of Yale and Ohio state University have been working at developing these techniques to produce nanofibres for tissue engineering applications using both Q-Switched and femto second lasers. These have used to enhance biofunction whilst at the same time preserving the structures of individual nanofibres.

Lasers have also been combined with whole range of analytical tools for various other applications. For example Wang in 2005 combined a laser with a scanning tunnelling microscope to investigate the mechanisms of laser assisted laser nanostructuring. Even though considerable amount of work has been done on laser assisted STM surface nanostructuring nobody, to date, really understands the exact mechanism. There are also irregularities on the final structures produced. However, it is highly desirable to obtain a better quantitative understanding of laser assisted processes so that nanostructures can be manipulated to achieve the desired functionality at the nanoscale level. Considerable work is on going in order to obtain a fundamental understanding using both modelling and practical approaches.

Researchers at the Purdue University are using concentrated light in a nanoscale domain, i.e., much smaller than the diffraction limit. Optical antenna based on ridged waveguide concept have been developed for this purpose. These nanometer size, high intensity light spots are used as light sources for nano-lithography applications. Arrays of antennas are used for parallel manufacturing, thus, increasing the throughput of the manufacturing process. They have also developed numerical methods for the investigation and optimization of nanoscale antennas, in near field scanning optical microscopes for characterizing field distributions of the antennas. They have developed a novel lithography technique using high transmission ridge apertures for next generation nano-manufacturing. Experimental results show enhanced transmission and light concentration properties of C, H and bow-tie apertures compared to square and rectangular apertures of the same opening area.

In the light of these and other recent developments, it is envisaged that laser will be an important role player in nanomanufacturing in the next few years due to their versatility, high degree of dimensional and directional control for development of novel and improved functional products in a range of industrial arenas.

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Dr N. Ali (n.ali@nano-society.org)
Size enabled elucidation of core-electron energy and dimer-vibration frequency

Information regarding the energy levels of an isolated atom and the vibration frequency of an isolated dimer and their shifts upon bulk formation are of great scientific importance, which seemed yet to go beyond the scope of currently available experimental techniques and theoretical approaches. For instance, using a combination of the most advanced laser-cooling technology and x-ray photoelectron spectroscopy (XPS), one could only measure the energy separation between different energy levels of the slowly-moving gaseous atoms trapped by the laser beams but yet the individual core-level energy of the isolated atom [Phillips W. D., Rev. Mod. Phys. 70, 721(1998)]. However, the new degree of the freedom of size may turn a new leaf, giving us an opportunity.

An incorporation of the BOLS correlation theory [Nano Affair 1, 56 (2007)] to the measured size and shape dependence of the XPS and Raman optical phonon shift has led to such kind information. According to the BOLS correlation, the energy shift of the energy level (E_i) of an isolated atom [Sun C.Q., Phys Rev B 69, 045106 (2004)], or the frequency shift (Dw) of an isolated dimer upon nanosolid formation [Sun C.Q. et al, Phys Rev B 72, 134301 (2005)] follow the scaling relation with Q being a detectable quantity and q the density of Q:

\[ \frac{Q(K_i) - Q(\infty)}{Q(\infty) - Q(1)} = \sum_{i=0}^{n} \gamma_q \left( \frac{q_i}{q_0} - 1 \right) \quad \text{and,} \quad q_i = \left( \frac{\omega_i}{E_i} \right)^{2/12} \frac{d_i}{\gamma_i} \quad \text{(Raman - frequency)} \]
\[ E_i = \left( \frac{\omega_i}{E_i} \right)^{2/3} \gamma_i \quad \text{(Core - level - energy)} \]

where K_i = D_i/2d is the dimensionless form of size with D_i the diameter of a spherical dot, a cylindrical rod or the thickness of a film. Q(\infty) is the bulk value for reference with q_0 as its density. \( \gamma_q \) is the volume ratio of the under-coordinated atoms in the surface skins over the entire of solid.

The z_i, d_i, and E_i are the coordination number, bond length, and single bond energy of a specific atom in the ith atomic layer of the solid. Figure 1 shows the matching of predictions to the typically measured size and shape dependence of (a) energy level shift of Au nanosized specimens on different substrates and (b) the Raman frequency shift of Si nanosolids with derived information of the energy levels of an isolated atom, E_0(1), and the dimer vibration frequency, w(1), and the corresponding bulk shift, with the given bulk values as references, as given in Table 1. Results for Au nanostructures of different shapes on different substrates show consistently high accuracy. Errors arising from determination of shape and size and the operation conditions may fall within the limit of deviation. Nevertheless, preliminary results are quite encouraging, which demonstrate the impact of the new degree of the freedom of size that not only allows us to tune the physical properties of the nanomaterials but also enables us to reveal such information that is beyond the scope of conventional approaches. Exercises may open a promising way of amplifying the capability of existing probing techniques for new information.

![Figure 1. Agreement between BOLS predictions (solid lines) and the measured (scattered data) size and shape dependence of: (a) XPS E-4f energy of Au nanostructures on different substrates; (b) the Raman 521 cm\(^{-1}\) redshift of Si nanostructures.](image)

<table>
<thead>
<tr>
<th>XPS</th>
<th>Au/</th>
<th>Au/</th>
<th>Au/Pt</th>
<th>Si-2p</th>
<th>Raman</th>
<th>CdSe</th>
<th>InP</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octan</td>
<td>E_0((\infty))/eV</td>
<td>-84.37(4)</td>
<td>-99.20</td>
<td>210</td>
<td>347</td>
<td>520</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO_2</td>
<td>E_0(1)/eV</td>
<td>-81.504</td>
<td>-81.504</td>
<td>195.2</td>
<td>333.5</td>
<td>502.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DE_0((\infty))/eV</td>
<td>2.866</td>
<td>2.866</td>
<td>14.8</td>
<td>13.5</td>
<td>17.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. XPS-E_0(K_i) and Raman - w(K_i) derived information regarding (i) the Au-E_0(1) and Si-E_0(1) of an isolated atom and the crystal binding energy of DE_0(\(\infty\)) and (ii) the Si-w(1), InP-w(1), and CdSe-w(1) of an isolated dimer and their bulk shifts Dw(\(\infty\)) = w(\(\infty\)) - w(1) provided with the given bulk values.

Further information:

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The European fuel cell research consortium, NANOCOFC (Nanocomposites for advanced fuel cell technology), financed by EC FP6 NMP program, has announced substantial improvements in solid oxide fuel cells material research.

NANOCOFC project involves the seven European countries of Sweden, Finland, Belgium, UK, Italy, Portugal and Turkey and four Chinese partners including the Chinese Fuel Cell Industry. Dr. Bin Zhu, Royal Institute of Technology, Stockholm, is the project coordinator for NANOCOFC.

The materials improvement is based on two-phase material (TPM) composite architecture in nano-scale to create an interfacial superionic conduction in the interfaces between the constituent phases. The new scientific concept is to construct the superionic paths or ion-highways in interfaces.

Recent research discovered that with YSZ (yttrium stabilised zirconia) in nanometer thin film materials, the point defects and the dislocations may form the ionic conduction highways. However, in the single-phase materials (SPM) like YSZ, the point defects and dislocations make it difficult to form the long-path continuous ionic highways. Instead, more localised highly mobile ionic domains may be formed.

TPM allows NANOCOFC to construct the TPM architectures in nano-engineering directly between existing nanoparticles comprised of two different phases to construct the continuous ionic highways and create improved performance at the interfaces.

NANOCOFC’s TPM approach offers a greatly improved new material. The improvement is defined as a powerful “artificial way to develop multifunctional TPMs with many advantages over the SPMs (“artificial” in this instance means at least two readily existing SPMs that create improved performance between them without changing their individual structures).

The new TPM material offers new solutions for relevant fuel cell problems/challenges that will greatly accelerate solid oxide fuel cell commercialisation.

The new TPM technology allows fuel cells to run at much lower temperatures (300 to 600 degrees C) without the use of expensive noble-metal catalysts. Instead, lower-cost transit metal-ceria catalyst electrodes are used. It has already been demonstrated that the new materials with the interfacial superionic conduction highways deliver a power density of approximately 500 mW/cm² at 400 degrees C.

There are still many possibilities in improvements:

1. Use of thin film technology -- currently the demonstrated fuel cell technology uses 100-200 mm thick electrolyte membranes
2. Using the TPM technology, many new materials with superionic conduction via interfacial highways can be developed
3. And, both oxygen ions and protons (produced often from external sources when situated in the fuel cell environment) can be combined through interfaces and interfacial mechanism. Thus dual-phase proton and oxygen ion conduction can function at the same time, which can further enhance the transported ion numbers/concentrations as well as material conductivity and hence fuel cell power output (the current output is proportional to the transported ion numbers/concentrations).

The new materials have not only been successfully demonstrated in the lab but the research has been validated by six experts panel from the United States, Canada, Austria, Finland and Denmark. Furthermore, substantial progress is now being made towards industrial commercialisation for a new generation of low-temperature solid oxide fuel cells.

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EVENTS

3rd International Conference on Surfaces, Coatings and Nanostructured Materials — Barcelona, Spain, 21-24 October 2008

International Conference on Surfaces, Coatings and Nanostructured Materials (NanoSMat) is organised to enable knowledge exchange and also provide an interactive platform for researchers and engineers from industry, research laboratories and academia.

NanoSMat 2007 is the third of this series. Following its success as NanoSMat-2007, NanoSMat 2008 will bring together state-of-the-art developments on all aspects related to the processing, characterization and applications of surfaces, coatings and novel nanostructured materials.

A major aspect of the conference is to foster close collaborations among scientists, engineers, researchers and industrialists thus providing an opportunity to create links for future developments. The conference will provide ample opportunity for the conference delegates to network in a friendly and supportive environment.

NanoSMat-2008 will host an exhibition and offer several short educational courses relating to nanostructured materials, nanoscience and nanotechnology. For more details visit the NanoSMat homepage: www.nanosmat2008.org

NEW BOOKS

Nanocomposite Thin Films and Coatings: Processing, Properties and Performance

Editors: Sam Zhang and Nasar Ali

Publishers: Imperial College Press, UK.

Publication date: Scheduled Fall 2007

Price: 145 USD or 78 GBP

More details: http://www.icpress.co.uk/nanosci/p502.html

Materials development has reached a point where it is difficult for a single material to satisfy the needs of sophisticated applications in the modern world. Nanocomposite films and coatings achieve much more than the simple addition of the constituents — the law of summation fails to work in the nano-world. This book encompasses three major parts of the development of nanocomposite films and coatings: the first focuses on processing and properties, the second concentrates on mechanical performance, and the third deals with functional performance, including wide application areas ranging from mechanical cutting to solar energy and from electronics to medicine.

Readership: Undergraduates, postgraduates, researchers, scientists, college and university professors, research professionals, technology investors and developers, research enterprises, R&D research laboratories, academic and research libraries.

JOURNAL

Journal of Nano Research (JnanoR) is a multidisciplinary peer-reviewed journal, which publishes high quality work on ALL aspects of nanoscience and nanotechnology. Currently, it stands alone in serving the global “nano” community in providing up-to-date information on all developments and progresses being made in nanoscience and nanotechnology and the future predictions for this extraordinary technology. The topics covered by the journal relate to all “nano” related areas of research and development work. The subjects covered include the following: 1. Physical Sciences 2. Life Sciences 3. Theoretical and Computational Science and Engineering.

Author instructions: http://www.ttp.net/Downloads.html

Note from Nobel Laureate Professor Sir H. W. Kroto (Florida State University, USA):

As Chemistry and Physics at one borderline and Chemistry and Biology at the other become indistinguishable so crossdisciplinary research is leading to the fascinating “new” overarching field of Nanoscience and Nanotechnology (N&N). Ingenious strategies for the creation of molecules and extended atomic structures with complex exactly-specified infrastructures and function are being developed — basically nanoscale devices that “do things” are now being created. New experimental approaches which focus on how atoms assemble are leading to the production of novel nanostructures and research is focusing on the control of self-assembly processes is the bottom-up approach to the production of materials with advanced function. This new approach is leading to novel advanced materials with exciting new applications. Fascinating fundamental insights into formation mechanisms are being revealed and nanoscale devices, which parallel devices in standard engineering are now being created. This new journal, Journal of Nano Research, has been born at the ideal moment and is set to become a leading source of N&N research, essentially the “Frontier Chemistry of the 21st Century”. Breakthroughs are presently being realised which are generating a paradigm shift in synthetic chemical assembly techniques. On the horizon are applications ranging from civil engineering to advanced molecular electronics so promising to transform our everyday technology as well as basic economics.
The Society of Nanoscience and Nanotechnology (SNN) is a worldwide organisation set up to serve the needs of the “nano” community. Currently, it is one of the very few organisations in the world that sets out to serve such a purpose on a global scale. SNN is designed to provide an effective and stimulating platform for world people to foster, develop and promote communication, education, networking, dissemination of knowledge, research and innovations in aspects of nanoscience and nanotechnology.

Aims and objectives:

• Promote all aspects of nanoscience and nanotechnology
• Educate and bring awareness to people about nanotechnology and its impact on society
• Raise, discuss and debate nano-related issues, including government policies on nanotechnology
• Offer different levels of memberships, with benefits, to people working in nanoscience and nanotechnology.
• Organise and manage international nano-related conferences
• Provide an effective advertising platform for companies to promote their business
• Promote education and training through organising workshops, short educational courses, seminars, etc.
• Bringing to the front, current and most recent up-to-date scientific and technical information to the public
• Provide consultancy services to both people from academia and industry
• Alert people about new job opportunities
• Publish journals, reports, books and newsletters.
• National, European and international research projects: identify, link partners and coordinate projects

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