Classical and Novel Synthetic Routes toward Nanostructures

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Introduction into the world of nanosized materials

1. What nanoparticles are
2. What makes nanoparticles so special
3. Nanoparticles properties and potentialities
4. How old nanoparticles are?
5. Synthesis: top down and bottom up approach
6. Classical and novel synthetic routes
7. Applications (examples)
8. Are nanoparticles dangerous?
An Idea of Nano

Apple of ~8 cm (80 million nm)
Ant of ~5 mm (5 million nm)
A bacteria ~100 nm
A virus ~50-100 nm
A protein
DNA ~2 nm
Fullerene ~1 nm
Atom ~0.1 nm
Nanoparticle Definition

Nanoparticles are…

Atomic/molecular aggregates with dimensions of 1–100 nm (1nm=10⁻⁹m) Remarkable effects are observed in the range 1-20 nm

Important: Size of some molecules (e.g. bio-molecules) range in nm scale
BUT individual molecules are NOT nanoparticles

A nanoparticle is defined as a small object that behaves as a whole unit in terms of its properties
**Nanoparticles Properties**

**Main Characteristics**

High surface area

Size-dependent properties → Different properties compared to bulk materials

At the nanoscale the traditional concept of “intensive properties” (properties independent of the amount of material, such e.g. melting point, conductivity, malleability, etc.), is no longer valid, because all properties can change depending on scale.

Devices with components as small as possible but simultaneously with enhanced properties
Tailored functionalities simply by controlling nanoparticle size
New materials with well-defined and tuneable properties
### Different properties compared to bulk materials

<table>
<thead>
<tr>
<th>Gold bulk</th>
<th>Nanosized gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shiny (metallic)</td>
<td>Insulator</td>
</tr>
<tr>
<td>yellow</td>
<td>red (~10 nm particles absorb green light)</td>
</tr>
<tr>
<td>noble metal</td>
<td>excellent catalysts (2–3 nm nanoparticles)</td>
</tr>
<tr>
<td>fcc structure</td>
<td>icosahedral symmetry</td>
</tr>
<tr>
<td>non-magnetic</td>
<td>magnetic</td>
</tr>
<tr>
<td>melts at 1064°C</td>
<td>Much lower melting temperature (sizes depending)</td>
</tr>
</tbody>
</table>

- **Bulk material**
  - constant physical properties regardless of its size

- **Nano-sized material**
  - size-dependent properties
Nanoparticles Features: size-dependent properties

Oxidation CO → CO₂

The change of melting point is the effect of high surface energy in small size nanoparticles

Remarkable change are observed d<5 nm

The change of melting point is the effect of high surface energy in small size nanoparticles

Size-dependent properties: Surface Plasmons

Gold bulk (1 m, 1 cm or 1 mm) is shiny, golden and exhibits metallic properties such as malleability and conductivity. On the macroscale, all of these properties remain the same.

On the nanoscale, the color of gold particles becomes very sensitive to size. At sizes ~ 20 nm, it is red, loses its metallic properties and does not conduct electricity.

What is the origin of color changes in nanosized Au?

The “surface plasmons”!
Nanoparticles in Ancient Materials

Ancient stained-glass makers knew that by putting varying, tiny amounts of Au and Ag in the glass, they could produce the red and yellow found in stained-glass windows.

The New York Times, February 22, 2005
Nanoparticles in Ancient Materials

Surprisingly nanoparticles are not an invention of modern science

Between myth and reality: Elixir of long life…

Colloidal Gold used since ancient Roman as a method of staining glass

Lycurgus Cup (Roman pottery, 400 A.C) stored in the British Museum,
Red color from nanosized gold
Nature 2000, 407, 691

Paracelsus and the “Aurum Potable” (XVI century)
The first description in scientific terms of nanometer-scale properties was provided by Faraday in 1857.

Faraday gold NP suspensions
British Museum (London)
(obtained by using phosphorous to reduce a solution of AuCl₃)
The Tyndall Effect

Tyndall Effect: Laser Pointer traveling through a solution (right) and through a colloidal suspension (left).

A: Solution
B: Colloidal Suspension
   Transparent
C: Colloidal Suspension
   completely absorbing light
Nanoparticles in Ancient Materials
An Ancient synthetic Route

Special coloured metallic glitter on pottery from the Middle Ages and Renaissance is due to NP dispersed homogeneously in the glassy matrix of the ceramic glaze.

These NP were created by adding Cu and Ag salts and oxides together with vinegar, ochre and clay on the surface of previously-glazed pottery. The object was then placed into a furnace and heated to ~600 °C in a reducing atmosphere.

In the heat the glaze would soften, causing Cu and Ag ions to migrate into the outer layers of the glaze. There the reducing atmosphere reduced the ions back to metals, which then came together forming the nanoparticles that give the colour and optical effects.

15th and 16th centuries (Renaissance)

Pottery of Deruta (Umbria, Italy)
Glazes containing copper and silver nanoparticles
The Beginning of the Nano-Age

Die Welt der vernachlässigten Dimensionen
(The world of the neglected dimension)
Wo. Ostwald
1914

There's plenty of room at the bottom
R. Feynman
1959
Nanoparticles: what’s new then?

Development in synthetic techniques and ability to readily characterize materials on nano-scale

Advanced computer technology makes the characterization easier and faster but also helps to predict properties via modelling and simulation

Nanoparticle characterization is necessary to understand and control of nanoparticle synthesis. Common techniques are:

- Electron microscopy: TEM, SEM
- Scattering: SANS, SAXS, WAXS, DLS
- Spectroscopic: XPS, UV-VIS, FT-IR
In particular by STM (scanning tunneling microscopy) since the early 1980s, scientists are able to see the nature of the surface structure with atomic resolution.

**Principle of STM:**
Applying a negative sample voltage yields electron tunneling from occupied states at the surface into unoccupied states of the tip. Keeping the tunneling current constant while scanning the tip over the surface, the tip height follows a contour of constant local density of states.
Nanoparticles: what's new then?

Ernst Ruska/Max Knoll (1931)

Fe₃O₄ nanoparticle
Nanoparticles: what’s new then?

Normal TEM measurement
Just the grid preparation is different!

Au nanoparticles (1.8 ± 0.3 nm)
Pt Nanoparticles (2.5 ± 0.4 nm)
Pd nanoparticles (2.4 ± 0.5 nm)
Rh nanoparticles (1.6 ± 0.3 nm)

Metal salts
NaBH$_4$

Metal ions
Metal nanoparticles
Synthesis:
Classical and Novel Approaches
Nanoparticle Synthesis

Top-down approach: breaking down of large pieces of material to generate nanostructures.

Bottom-up approach: assembling single atoms/molecules into larger nanostructures.

Physical methods or Chemical methods

- Use of template or confining systems
- Microwave synthesis
- Gas Phase synthesis
- Sol-gel based process
- Hydrothermal methods
- Microencapsulation

High-Energy ball milling

- Sonochemistry
- Wet chemical co-precipitation
- Ionothermal route
- Vapor Spray Deposition
Nanoparticle Synthesis

Conventional Top down

Konventionelle Fotolithografie

Ein Laserstrahl schreibt die Schaltkreisstruktur für einen Mikrochip in eine lichtempfindliche Polymerschicht, die als Überzug eine Chromschicht auf einer Glasplatte bedeckt. Die vom Strahl getroffenen Bereiche des Polymers werden danach selektiv entfernt.

Das freigelegte Chrom ätzt man weg und löst schließlich den Rest des Polymers ab. Das Ergebnis ist eine Maske aus Chrom – ähnlich einem Fotonegativ.

Die Maske kommt in eine Art Projektionsapparat mit ultraviolettem Licht. Eine Linse wirft ihren Schattenriss verkleinert auf die Fotolackschicht eines Siliziumwafers.

Die belichteten Teile des Fotolacks werden entfernt, und man erhält das Positiv des Strukturmusters in Miniatur auf dem Siliziumchip.
**Nanoparticle Synthesis**

Conventional Top down

---

**Carbon Nanotubes for Nanolithography**

Preliminary simulation and experiment show:

* the world’s tiniest and strongest nanopencil
* never needs sharpening

TEM image: SiO₂ lines (10 nm width) on Si Surface, written by a CNT tip
Nanoparticle Synthesis

Example of bottom up approaches

Soft nanoreactors
- Reverse micelle
- Filled reverse micelle

Hard nanoreactors
- Porous material
- Filled porous material
Nanoparticle synthesis

Synthesis in Microheterogeneous Systems
**Co**$_x$[Fe(CN)$_6$] Nanoparticles

**Solid-Solid reactions in liquid phase**

\[
\begin{align*}
&x \text{CoCl}_2 + K_4\text{Fe(CN)}_6 \rightarrow Co_x[\text{Fe(CN)}_6] \\
&x \text{CoCl}_2 + K_3\text{Fe(CN)}_6 \rightarrow Co_x[\text{Fe(CN)}_6]
\end{align*}
\]

PhD thesis of C. Giordano

**Synthesis of Metallic NP: Bottom Up and Top Down Procedure**

**Example of bottom up way**

A Chemical pathway

**Reduction of HAuCl₄**

<table>
<thead>
<tr>
<th>Au(III)/AOT/n-heptane</th>
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<td></td>
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**PhD thesis of C. Giordano**

**Example of top down way**

A physical pathway

**Vaporization of pure gold leaf**

<table>
<thead>
<tr>
<th>Au° in reverse micelles (e.g. AOT)</th>
</tr>
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</table>

**Clear and stable solution**


Nanoparticle synthesis

Example of bodinging-systems

Hard nanoreactors

Porous material

Filled porous material

Nanoparticle synthesis

Sol-Gel Synthesis

A wet-chemical technique used primarily to prepare metal oxides starting from a chemical solution (sol) as precursor for an integrated network (gel) of either NP or network polymers. Metal alkoxides and chlorides are typical precursors which undergo various forms of hydrolysis and polycondensation reactions.

\[
\text{TEOS in water} \quad \begin{array}{c}
\text{Si}(	ext{OR})_4 + \text{H}_2\text{O} \rightarrow \text{HO-Si(OR)}_3 + \text{R-OH}
\end{array}
\]

Polymerization is associated with the formation of a 1, 2, or 3-dimensional network of siloxane [Si–O–Si] bonds accompanied by the production of H-O-H and R-O-H species.

SEM micrograph of amorphous colloidal silica particles (average particle diameter 600 nm) formed in basic solution.
Using the solvothermal route gains one the benefits of both the sol-gel and hydrothermal routes. Thus solvothermal synthesis allows for the precise control over the size, shape distribution, and crystallinity of TiO₂ nanoparticles or nanostructures. These characteristics can be altered by changing certain experimental parameters, including reaction temperature, reaction time, solvent type, surfactant type, and precursor type.
Nanoparticle synthesis

Solvothermal Synthesis

• Semiconductor nanoparticles (CdE (E = S, Se, Te))

\[
\text{CdC}_2\text{O}_4 + E \xrightarrow{\text{solvent}} \text{CdE} + 2\text{CO}_2 \uparrow \quad \text{E; Chalcogenide (S, Se, Te)}
\]

• Ethylenediamine
• Pyridine

En ; nanorod

Py ; nanoparticle

200 nm

100 nm
**Sol-gel based routes**

At MPI-KG we have been using a modified sol-gel process to produce nanoparticles. The procedure is fast, cheap and rather simple.

\[ \text{MCl + EtOH} \rightarrow \text{Gel-like, glassy phase} \]

The "Urea-Glass" Route

The Importance of Being a „Gel“…
Tailored morphologies for specific applications

Giordano C., Antonietti M., Review in NanoToday, in press
The Importance of Being a „Gel“…

Tailored morphologies for specific applications

After washing with NaOH to remove SiO₂

The „wolverin“ leaf

Complex hierarchical magnetic/conducting structures

Lignin-rich leaf skeleton templated

Helical Xylem replicated as magnetic Fe₃C

Schnepp Z.; Yang W.; Antonietti M.; Giordano C.; *Angewante Chemie Int. Ed.*, 2010, 49, 6564
Ionothermal synthesis

Nickel Boride

Hafnium Boride

400 nm

200 nm
Where are we moving to…

3D structure, hierarchical structures,
Self-assembling
Nanocomposites and hybrids materials
np@C
Applications
and
Specific Synthetic Routes
Applications: Overview

Nanosized materials application area is extremely broad and it includes:

Electronics
Computing and data storage
Communications
Aerospace
Sporting materials
Health and medicine
Energy
Environmental
Food packaging (containers, films)
National defence applications
Transportation
Automobile (gasoline tanks, interior and exterior panels, etc.)
Construction (shaped extrusions, panels, etc.)
Nanocomposites: old example

Carbon Black has long been used as a reinforcement in rubber tires

Improved strength and tensile properties, tear and abrasion resistance, and increased hardness

To be note:
Absolute strength of nanocomposite initially increases with the addition of carbon because of the reinforcement from carbon grains, then decreases due to the dilution effect when too much carbon black is present.

Carbon black rubber filler in tires $4\text{ billion}$ industry!!!
Modern Applications

Some examples of NP applications in various day to day products:

$\text{TiO}_2 \text{ NP} \rightarrow$ self-cleaning effect (used in detergents) and used as sunscreen by lifeguards (transparent film over white one by bulk)

$\text{ZnO NP} \rightarrow$ superior UV blocking properties (also used in sunscreen lotions)

$\text{Clay}_\text{NP}@\text{polymer matrices} \rightarrow$ increasing reinforcement (stronger plastics)

Various NP in textile fibers $\rightarrow$ creating smart and functional clothing

Photovoltaic cells $\rightarrow$ solar absorption $>>$ in NP materials than thin films
Application of TiO₂

Photo-catalytic decomposition of pollutants and bacteria
Larger surface area leads to faster surface photo-catalytic reactions
Fluorescent dye are frequently used in biological experiments as tags. Problem: even the best fluorescent tags have poor photostability and fluorescence fades quickly over time (usually less than a minute).

Advantages of Nanocrystals:

- Semiconductor nanocrystals exhibit high photostability
  - solid crystal – no simple chemical degradation
  - fluorescence can last days
  - different fluorescence colors simply by changing the size

Quantum Dots: CdSe

Synthesis

- diameters between 2nm to 12nm
- size distributions <3-5%

Quantum Yield ~10% at 300K
Quantum Yield ~80% at 300K

Color in QDs

- The larger the dot, the redder
- The smaller the dot, the bluer
- Color is related to the energy levels of the QD

CdSe/ZnS NP solutions

Reducing size

Increasing $\lambda$

Decreasing size
Application in Medicine

Size- and material-dependent emission spectra of surfactant-coated semiconductor nanocrystals

Prostate cancer cells have taken up fluorescently labelled nanoparticles (in red). RNA aptamers binding to the prostate-specific membrane antigen were used as the targeting molecules on the nanoparticles. The cell nuclei and cytoskeletons are stained blue and green, respectively.

Similarly designed targeted nanoparticles are capable of getting inside cancer cells and releasing lethal doses of chemotherapeutic drugs to destroy the tumours.

Source: American Association for the Advancement of Science (AAAS)
Magnetic Nanoparticles: SPIO’s

- Synthesis can be performed by co-precipitation in an aqueous and supersaturated solution from FeClx in alkaline solution

\[ 2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \]

- Advantage: synthesis very easy
- Disadvantage: control of size and shape difficult
- Electrostatically stabilisation with citrate, advantage: pH stability from 3-12 therefore they can be used in physiological pH (7,4)
- And with citrate you can control the size of nanoparticles \( \rightarrow \) different contrast

Diploma thesis Alexander Kraupner
Comparison of a healthy and a tumour cell incubated with nanoparticles. The phase-contrast light microscopy image shows a prostate carcinoma cell and a fibroblast cell. While the tumour cell shows a high level of pigmentation because of the uptake of a large number of nanoparticles, the adjacent fibroblast cell shows lower levels of pigmentation, that is, no or lower levels of particle uptake.

**Hyperthermia treatment** by iron oxide nanoparticles is induced by exposure of the particles to an alternating magnetic field. A local accumulation of nanoparticles allows for tissue-specific hyperthermia that preferentially addresses the tumour tissue.
Superparamagnetic iron oxides (SPIO) with high relaxivity is used as contrast agents for MRI but for the use in the human body the particles need a coating and specific ligands on the surface e.g. polymers) necessary because: Spio’s are not stable in the physiological pH.

Coating with silane can increase the possibility of further functionalisations for molecular imaging.
Nanocomposites: recent example

Anti-aging for facades

- The slightly tacky surface of the coating film leads to the accumulation of dirt particles.
- Organic dispersion paint
- Inorganic silicate paint
- Nanocomposite coating

- The nanobinder COL 9° offers an optimal balance of surface hardness and elasticity.
- The facade remains resistant to dirt, free of cracks and the color tone stable.
- Mechanical stresses on the surface result in cracking due to the rigid and brittle structure.

This Video is a kind gift from the BASF public relation office
Are nanoparticles dangerous?

For the same reason why NP are interesting, they could be potentially dangerous:
- high surface/volume ratio, brings higher reactivity or superior catalytic properties
- interaction with biological systems (e.g. passing through cell membranes in organisms)

However, free nanoparticles in the environment quickly tend to agglomerate and thus leave the nano-regime, and nature itself presents many nanoparticles to which organisms on earth may have evolved immunity (such as salt particulates from ocean aerosol, terpenes from plants, or dust from volcanic eruptions).

Specific effect are anyway still relatively unknown

Caution: Nanomaterials may have a different toxicity than their bulk counterparts.

Even well known compounds may present unexpected health risks when they are fashioned as nanoscale building blocks.
Everything in life must be balanced...

"Perhaps I overdid the nano and underdid the bio!"

From the web-site „Nanotechnology and Society”

For further questions, please ask! 😊

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