Metal oxide nanoparticles: Synthesis and Reactivity

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Environmental Nanotechnologies, 7-8 July 2011, Aix en Provence, France
Stage 1: List of Endpoints

- Nanomaterial Information/Identification
- **Physical-Chemical Properties and Material Characterization**
- Environmental Fate
- Environmental Toxicology
- Mammalian Toxicology
- Material Safety
List of Manufactured Nanomaterials (14)

- Fullerenes (C60)
- Single-walled carbon nanotubes (SWCNTs)
- Multi-walled carbon nanotubes (MWCNTs)
- Silver nanoparticles
- Iron nanoparticles
- Carbon black
- Titanium dioxide
- Aluminium oxide
- Cerium oxide
- Zinc oxide
- Silicon dioxide
- Polystyrene
- Dendrimers
- Nanoclays
Formation of natural crystals in geological conditions
Aqueous Sol-Gel Process for nanoparticle synthesis

[Ti(OH)₆]³⁺

hydrolysis

[Ti(OH)₄(OH₂)₂]⁰

H₂O → M–OH → M–OH₂

Condensation: olation

Strong acidity: Catalysis of oxolation

[HO – M – O – M – OH]

Weak acidity: olation then oxolation

Bottom-up Approach
Morphology and Nanoparticles

Goethite

Anatase

Rutile

Duruphy, O.; Bill, J.; Aldinger, F. Cryst. Growth Des. 2007, 7, 2696


JACS, 2007, 129 (18), 5904
How control the nanocrystal growth?

Goethite

Anatase

Rutile

Durupthy, O.; Bill, J.; Aldinger, F. Cryst. Growth Des. 2007, 7, 2696


JACS, 2007, 129 (18), 5904
Surface energy : origin

Solid formation

\[ \Delta G_{\text{formation}}^\circ = n \Delta G^\circ_{\text{Bulk}} + \Delta G^\circ_{\text{surface}} \]

>0

Variation of surface energy with the particle size (Sodium Chloride):

<table>
<thead>
<tr>
<th>Side (cm)</th>
<th>Total Surface area (cm²)</th>
<th>Surface Energy (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>28</td>
<td>5.6 \times 10^{-4}</td>
</tr>
<tr>
<td>0.01</td>
<td>280</td>
<td>5.6 \times 10^{-3}</td>
</tr>
<tr>
<td>10^{-4} (1\mu m)</td>
<td>2.8 \times 10^{4}</td>
<td></td>
</tr>
<tr>
<td>10^{-7} (1nm)</td>
<td>2.8 \times 10^{7}</td>
<td></td>
</tr>
</tbody>
</table>

Huge surface energy for nano-solids - Thermodynamically unstable system

Calculation for a cube of Sodium Chloride

Surface Sci. 60, 445, 1976
Unstability of nanometric colloidal dispersion:

\[ \Delta G^\circ = n\Delta G^\circ_{\text{Bulk}} + \Delta G^\circ_{\text{surface}} \]

Spontaneous evolution of nanoparticles to minimise the surface contribution

**Surface : motive power of growth**

**How determine the surface energy?**
Surface energy: origin

$$\Delta G^\circ = n \Delta G^\circ_{\text{Bulk}} + \Delta G^\circ_{\text{surface}}$$

$$\gamma = (\delta G / \delta A)_{n_i, T, P}$$

\(\gamma\) : surface energy
energy required to create an unit of area

$$\gamma = \frac{1}{2} N_b \varepsilon \rho_a$$

Bond strength
Surface atomic density
Number of broken bonds per atom

Rough estimation of surface energy:
- surface relaxation
- surface restructuring with formation of new chemical bond
- same value of \(\varepsilon\) for all the atoms
- no entropic consideration/ pressure or volume

Surface Sci. 60, 445, 1976
Surface energy depends on the index of facets:

- Low index facets = low surface energy
Shape of nanoparticle: total surface energy reaches minimum

Wulff construction

Equilibrium crystal

Morphologies for a 2D crystal for 10 and 11 faces

Bi doped with Cu
Surface energy at the atomic scale

Model of multsite complexation, MUSIC$^2$

\[ K_{\text{protonation}} = f(\text{structure, hydratation}) \]

\[
\begin{align*}
M_nO^{(nv-2)} + H^+_{\text{solv}} & \rightleftharpoons M_nOH^{(nv-1)} & K_{n,1} \\
M_nOH^{(nv-1)} + H^+_{\text{solv}} & \rightleftharpoons M_nOH_2^{nv} & K_{n,2}
\end{align*}
\]

\[-\ln K_{n,x} = -A(\Sigma S_j - 2 + m)\]

\[ A = 19.8 \]

\[
\begin{align*}
\Sigma S_j &= \Sigma_i S_{Me} + p S_H + m(1 - S_H) \\
S_H &= 0.8
\end{align*}
\]
Model of multisite complexation, MUSIC²

Example: face $111_{Oh}$ of magnetite, 2 sites $\mu_2$ and $\mu_3$

$pH$  
$3.3$  $10.86$

$Fe_2$-$OH_2$ $+0.8$  $Fe_2$-$OH$ $-0.4$

$Fe_3$-$OH$ $+0.6$  $Fe_3$-$O$ $-1.8$

Good valuation of surface charge and of point of zero charge

Surface energy at the atomic scale
Surface energy at the atomic scale

**Brønsted basic site**

\[ \text{H}^+ \xrightarrow{\text{O}^{\delta-1}} \text{H}_2\text{O}^{\delta-1} \]

\[ \text{H}^+ \xrightarrow{\text{O}^{\delta-1}} \text{H}_2\text{O}^{\delta-2} \]

**Site \( \mu_2 \)**

**Site \( \mu_3 \)**

**\( \Delta G^\circ_{\text{surface}} > 0 \)**

**Gibbs’s Law**:

\[ \Delta \gamma = -\Sigma_k \Gamma_i d\mu_i \]

\[ \Delta \gamma = \gamma - \gamma_0 = \frac{RT}{F} \left( 0.22 \sqrt{I} - 2 \sqrt{0.0136 I + \sigma^2 - \sigma_{\text{max}}} \right) \ln \left( 1 - \frac{\sigma}{\sigma_{\text{max}}} \right) \]

J.P. Jolivet et al., J. Mater. Chem., 2004, 14, 3281
Surface Energy Effect

Metastable Object

\[ \Delta G^\circ = n \Delta G^\circ_{\text{Bulk}} + \Delta G^\circ_{\text{surface}} \]

Two ways

Decrease of \( \gamma \)

Gibbs Law: \( \Delta \gamma = -\Sigma_k \Gamma_i d\mu_i \)

\[ \Delta \gamma = \gamma - \gamma_0 = \frac{RT}{F} \left( 0.22\sqrt{I} - 2\sqrt{0.0136I + \sigma^2} - \sigma_{\text{max}} \right) \ln\left(1 - \frac{\sigma}{\sigma_{\text{max}}}\right) \]

\( \gamma \) decreases when the charge density, \( \sigma \), increases

J.P. Jolivet et al., J. Mater. Chem., 2004, 14, 3281
Surface Energy Effect

As $\sigma = f(pH)$

The surface energy is lesser far from the PZC
Isotropic Nanoparticles

Precipitation of FeCl$_2$ / FeCl$_3$ : Fe$_3$O$_4$ magnetite
ΑRM, Hyperthermia

Precipitation of TiCl$_4$ : TiO$_2$ anatase
Photocatalysis, Photovoltaic

\[ \text{Size} = f(\text{Surface Energy}) \]

Charged surface = stopped growth

\[ \text{Surface charge (C/m}^2\text{)} \]

Isotropic Nanoparticles

**Precipitation of FeCl₂ / FeCl₃ : Fe₃O₄ magnetite**

IRM, Hyperthermia

Size = f(Surface Energy)

After 3 weeks aging at pH 13.5 at 25°C

Stability of nanoparticle = f(solution acidity), reversible phenomena
Anisotropic Nanoparticles

Precipitation of $\text{Al(NO}_3\text{)}_3$ : $\gamma$-AlO(OH) boehmite

Wulff construction:
Equilibrium crystal = faces of lesser energy

Morphology = $f$(Surface Energy of each face)
Anisotropic Nanoparticles

Precipitation of Al(NO$_3$)$_3$ : γ-AlO(OH) boehmite

- **pH = 4.5**
  - $L = 4.5 \text{ nm}$
  - $e = 3.7 \text{ nm}$
  - small aggregated pseudo-isotropic particle

- **pH = 6.5**
  - $L = 8 \pm 1 \text{ nm}$
  - $e = 3.7 \text{ nm}$
  - pseudo-hexagonal platelets

- **pH = 11.5**
  - $L = 13 \pm 4 \text{ nm}$
  - $e = 4.9 \text{ nm}$
  - diamond shape platelets

Anisotropic Nanoparticles

Precipitation of Al(NO$_3$)$_3$: $\gamma$-AlO(OH) boehmite

Electric Properties = f(Morphology)
Anisotropic Nanoparticles

Boehmite $\rightarrow$ Gama Alumina: topotactic transformation

Boehmite

$$\begin{align*}
(001)_b & \\
(101)_b & \\
(100)_b &
\end{align*}$$

$$\begin{align*}
(110)_b & \\
(111)_b & \\
(001)_b &
\end{align*}$$

calcination

450°C

Alumine $\gamma$

$$\begin{align*}
(110)_\text{al} & \\
(111)_\text{al} & \\
(100)_\text{al} &
\end{align*}$$

$$\begin{align*}
(110)_\text{al} & \\
(111)_\text{al} & \\
(100)_\text{al} &
\end{align*}$$

50 nm

$104^\circ$

450°C

20 nm

$104^\circ$

$\Rightarrow$ Morphology is kept after the heat treatment

Surface complexation

Complexing molecules and growth of cristallites

Precipitation of $\text{Al(NO}_3\text{)}_3$ with polyols: $\gamma$-$\text{AlO(OH)}$ boehmite

$[\text{polyol}] = 0.007 \text{M}$

**Polyols**

<table>
<thead>
<tr>
<th>C2</th>
<th>HO-CH$_2$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>HO-CH$_2$-CH$_2$OH</td>
</tr>
<tr>
<td>C4</td>
<td>HO-CH$_2$-CH$_2$-CH$_2$OH</td>
</tr>
<tr>
<td>C5</td>
<td>HO-CH$_2$-CH$_2$-CH$_2$-CH$_2$OH</td>
</tr>
<tr>
<td>C6</td>
<td>HO-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$OH</td>
</tr>
</tbody>
</table>

**Dicarboxylates**

<table>
<thead>
<tr>
<th>C2</th>
<th>-CO$_2$-</th>
</tr>
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<tbody>
<tr>
<td>C3</td>
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</tr>
<tr>
<td>C4</td>
<td>-CO$_2$-</td>
</tr>
</tbody>
</table>

**Hydroxycarboxylates**

<table>
<thead>
<tr>
<th>C2</th>
<th>-CO$_2$OH</th>
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</tr>
</tbody>
</table>
Surface complexation by polyols

Precipitation of Al(NO$_3$)$_3$ with polyols: γ-AlO(OH) boehmte

pH = 11.5

[Al]=0.07M

éthylène glycol

dulcitol

glycerol

erithritol

dulcitol

The size of nanoparticles decreases with the length of polyols
Surface complexation by polyols

Precipitation of $\text{Al(NO}_3\text{)}_3$ with polyols: $\gamma$-AlO(OH) boehmite

Xylitol: 290 m²/g
Ribitol: 180 m²/g

Stereochemistry effect

Heterogenous Catalysts, Elsevier, 2006, 393
Surface complexation by polyols

Precipitation of Al(NO₃)₃ with polyols: γ-AlO(OH) boehmite

![Polyol images](C2, C3, C4, C5)

- ethylene glycol: R = L/e = 2.2
- glycerol: R = L/e = 1.8
- erythritol: R = L/e = 2
- arabinitol: R = L/e = 1.4

Stabilisation énergétique des faces (101)

Aspect ratio evolution:
Preferential adsorption upon lateral surfaces

Specific adsorption of Polyols on (101) face:
Selectivity of adsorbed species

Surface complexation by polyols

DFT calculations

Preferential adsorption upon lateral surfaces: concavity and stabilization

E_{ads}(0K) = -87 \text{ kJ.mol}^{-1}

E_{ads}(0K) = -118 \text{ kJ.mol}^{-1}

"Nest" effect
Surface complexation by hydroxy carboxylate

poly(hydroxy)carboxylates 0.007M

R = l/e

$\text{succinate} \quad 2,2$

$\text{malate} \quad 1,6$

$\text{tartrate} \quad 1,1$

Size variation is not homothetic: Strong decrease of anisotropy

Selectively adsorption on (101) face

Hydroxy carboxylate chemisorption

Geffroy 1999, Haines 1974, Martell 1984

Acidity of OH groups is strengthened by the complexation
Lower reactivity of (010) face due to $\mu_2$-OH sites.

Increase of (101) face stabilization with the distance between –COOH groups: more available adsorption sites.
Surface complexation and shape of anatase nanoparticles

Anatase nanoparticles obtained without complexant in presence of glutamic acid

30 nm

In presence of glutamic acid

Only 101 faces

Durupthy, O.; Bill, J.; Aldinger, F. Cryst. Growth Des. 2007, 7, 2696

In presence of oleic acid

Ethynediamine

(100) and (001) faces

30 nm

(100) faces


Matijevic, J. Colloid Interface Sci. 103 (1985)
What are the relevant parameters to control the growth of nanoparticles?

Size, Shape = \( f(\text{Solubility}) \)

Size, Shape = \( f(\text{Surface energy}) \)
Titanium oxide Nanoparticles

3 polymorphs

Anatase (I4₁/amd)

$\Delta H^0_f \ (kJ \cdot mol^{-1})$ -939

$\rho \ (g/cm^3)$ 3.84

Mine Falls Park, Nashua, NH

Brookite (Pcab)

-941

4.17

Mina Maria, Caneca, Sonora, Mexico

Rutile (P4₂/mnm)

-944

4.26

Stony Point, Alexander County, NC

Pigment: paints, papers, plastics, cosmetic and pharmacy

Photocatalysis, photovoltaic ...

Cristalline structure depends on synthesis conditions
Alcalinisation
$2 \leq \text{pH} \leq 6$

Thermolysis in acidic medium
$\text{Ti(OH)}_2(\text{OH}_2)_4^{2+}$
$\approx 100^\circ\text{C}$

Thermolysis with chlorides
$\text{Ti(OH)}_2\text{X}_2(\text{OH}_2)_2^0$

Olation
$\text{[Ti(OH)}_4(\text{OH}_2)_2]^0 \rightarrow \text{TiO}_2$

$\text{TiO}_2$ anatase
$\text{brookite}$
$\text{Thermolysis with chlorides}$
$\text{rutile}$

Titanium oxide Nanoparticles
Weak nucleation: slow precipitation
High solubility: favour the growth

\[ R = \frac{\text{length}}{\text{wide}} \]

Titanium oxide Nanoparticles

Thermolysis of TiCl\(_4\) : TiO\(_2\) rutile

1 M          2 M          4 M

solubility increase

\([H^+]_{sol}\)
Thermolysis of TiCl₄ with chloride: TiO₂ brookite

TiCl₄ 0.15 M / HCl / 95°C 48 hours

17 < Cl/Ti < 35

[Ti(OH)₂Cl₂(H₂O)₂]⁰

Thermolysis of TiCl$_4$ with chloride: TiO$_2$ brookite

Structure control by a complexing agent

Hydrolysis of Ti(III)

\[ \text{Ti}(\text{OH}_2)_6^{3+} \rightarrow 3\text{Ti}^{3+} + 3\text{OH}^- \]

Oxidation
Precipitation

\[ \text{Ti}_x\text{(OH)}_a(\text{OH}_2)_b^{z+} \rightarrow \text{TiO}_2 \]

New Morphologies for TiO\(_2\)

Growth control and Seeding

**TiO$_2$ Rutile : TiCl$_4$ 3 M / HNO$_3$ 15M / 120°C 24 hours**


Seed

+ Growth solution : C(Ti$^{4+}$) = 0.3M

Mesoparticles

Volume fraction : $f = 13.3\%$

Dessombz A., Thesis UPMC-Orsay, Paris 11

JACS, 2007, 129 (18), 5904
Properties of long nanorods

Collaboration: Patrick Davidson, LPS Orsay, Pierre Panine, ESRF Grenoble

Nematic Proportion

Volume Fraction (%)

Isotropic

Biphasic

Nematic droplets

Sample: 100 µm

\( f = 10.6\% \)

\( \phi = 8.2\% \)

\( S = 0.75 \pm 0.05 \)

d \( \sim 50 \) nm

First order transition

Dessombz A., Thesis UPMC-Orsay, Paris 11

JACS, 2007, 129 (18), 5904
Methylene blue degradation (10^-5 M)

Oriented aggregation: Increase of the photocatalytic activity

Photocatalysis study

Dessombz A., Thesis UPMC-Orsay, Paris 11

Collaboration: Patrick Davidson, LPS Orsay, Pierre Panine, ESRF Grenoble

Properties of long nanorods

Oriented Film

Rotated Film

Polarizer

agitation

UV lamp 365 nm, 1h

Methylene blue degradation

Intensity (ua.)

Film oriented (⊥)

Film oriented (//)

Film in rotation
Properties of long nanorods

Anisotropy of electric properties; Photoactivation of current
• Aqueous chemistry of metal cations: environmentally friendly, Low cost

• Versatile way to tune oxide nanoparticles
  Size, shape and crystalline structure

• Identification of relevant synthesis parameters to tune size and shape:
  pH and acidity,
  used of polyfunctionnal complexant : Polyols, Polycarboxylates

**Surface energy and solubility of nanoparticles are the driving force of their evolution**
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