Advances in the Liquid-Phase Synthesis of Inorganic Nanopowders

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Overview

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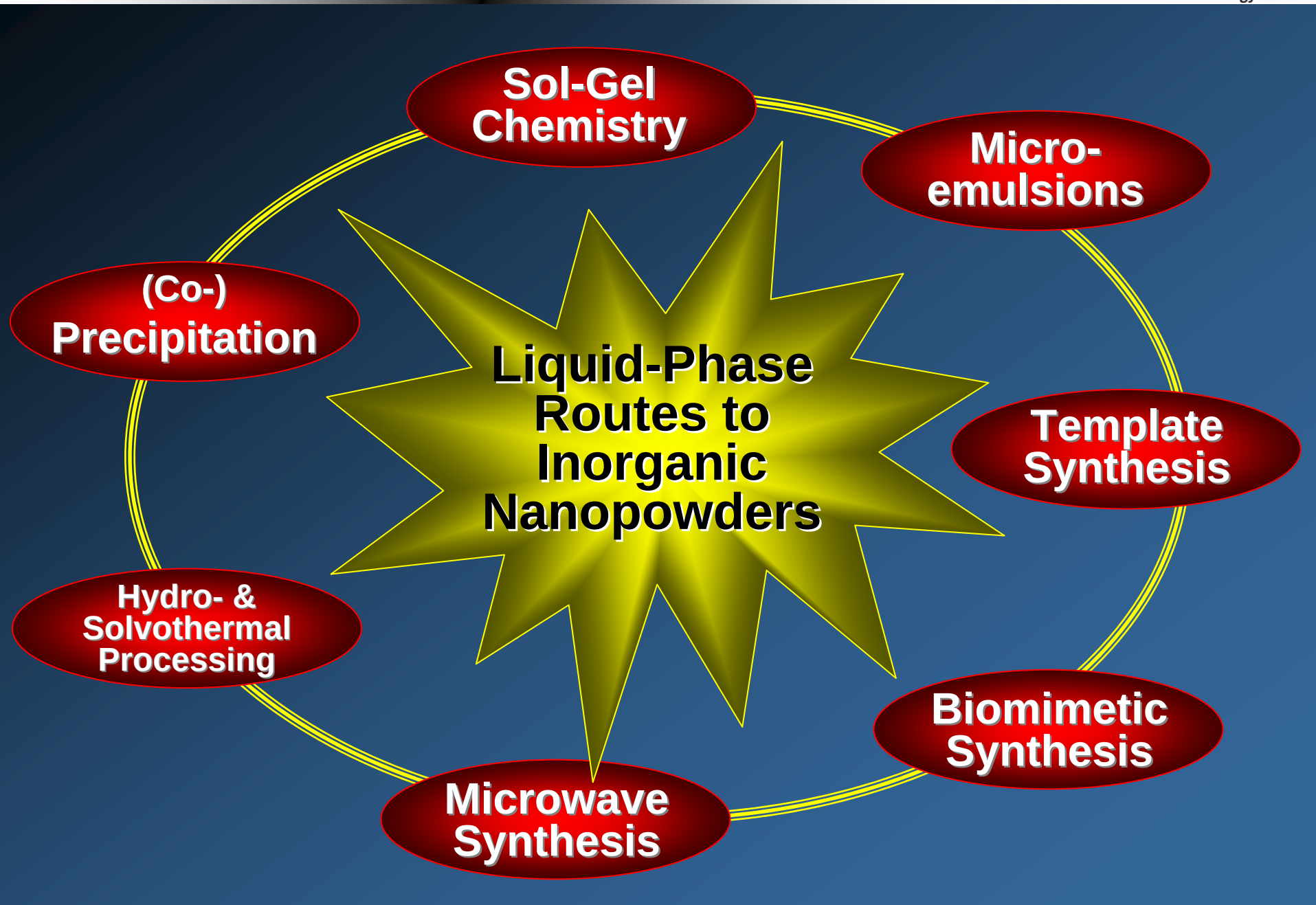

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Hot-Injection Method

J. Am. Chem. Soc. **1993,** *115,* 8706–8715

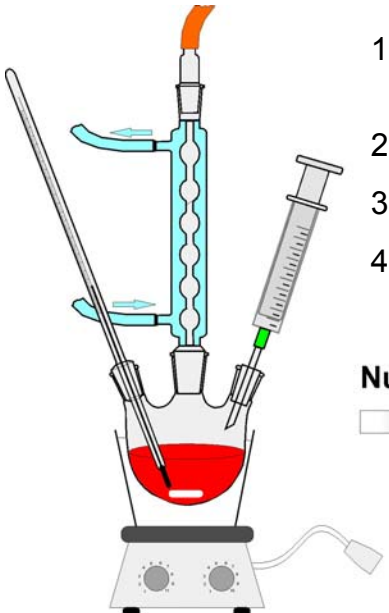
Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites

C. B. Murray, D. J. Norris, and M. G. Bawendi*

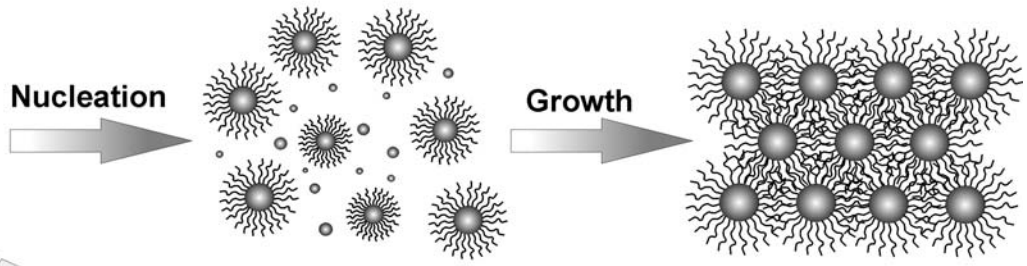
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 22, 1993

Times Cited: 2615



1) Injection of a „cold“ precursor solution to a hot (molten) surfactant or surfactant/solvent mixture
2) Nucleation and growth
3) Surfactant controls size, shape, and surface properties
4) Precipitation by addition of a „nonsolvent“



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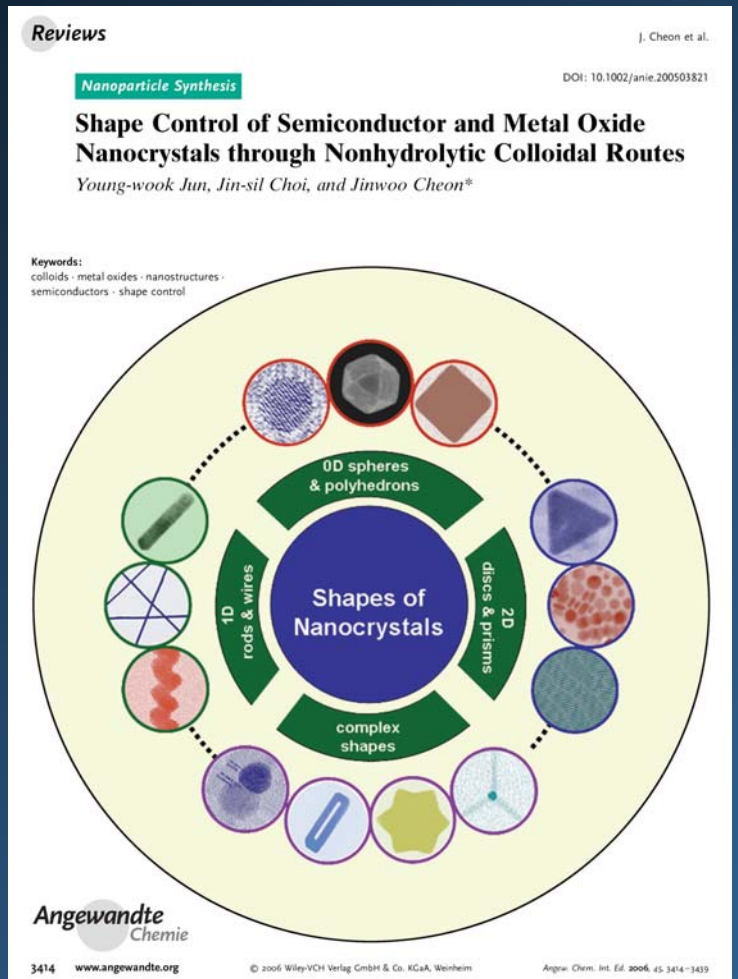
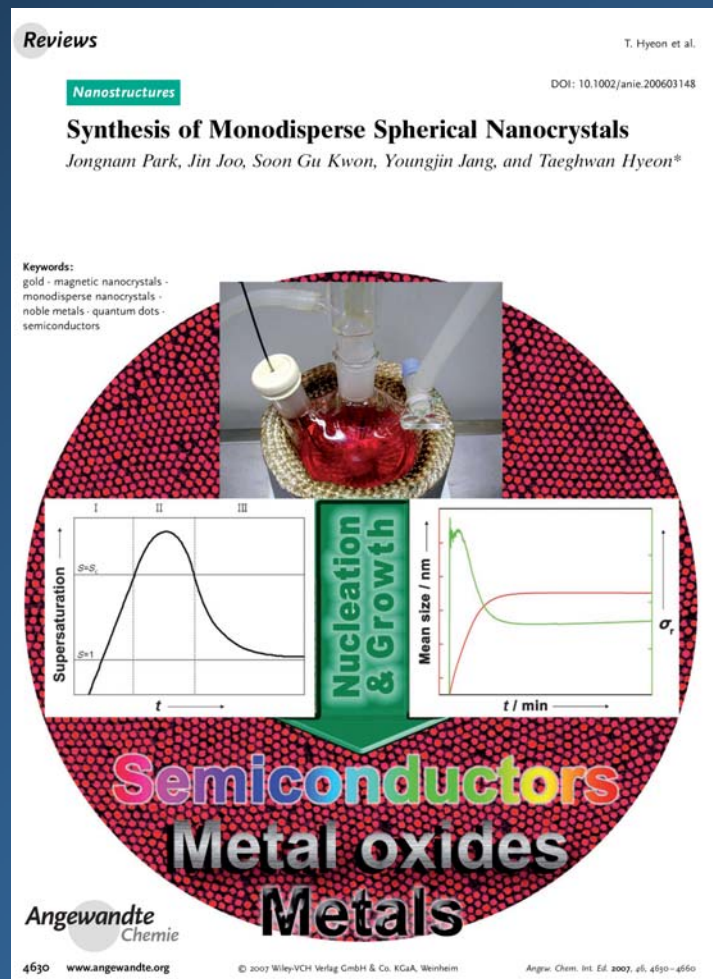
„Consequences“ of the Hot-Injection Method:

Surfactant-Directed Nonhydrolytic Routes





Synthesis

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„Molecular“ Precursor(s) + { **Molten Surfactant(s)** / **Surfactant(s)/High Boiling Solvent(s)**

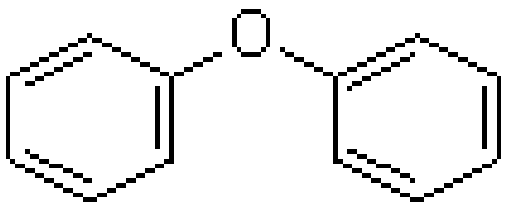
⇩ **T = 100 – 350 °C**

Inorganic Nanoparticles

Metal Organic Compounds: Metal Alkoxides $M(OR)_n$,..

Metal Salts: Chlorides MCl_n, Acetates $M(OOCCH_3)_n$, Nitrates $M(NO_3)_n$,…

Organometallic Compounds: Metal Carbonyls $M(CO)_n$,…



Diphenyl ether $(C_6H_5)_2O$

Boiling Point: 259 °C

Trioctylphosphine oxide (TOPO)

Melting point: 201 °C

Shape Control

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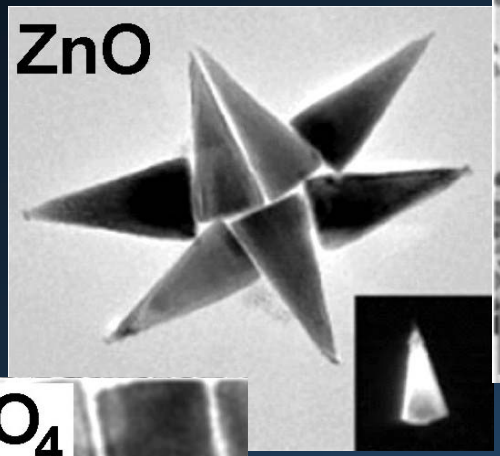
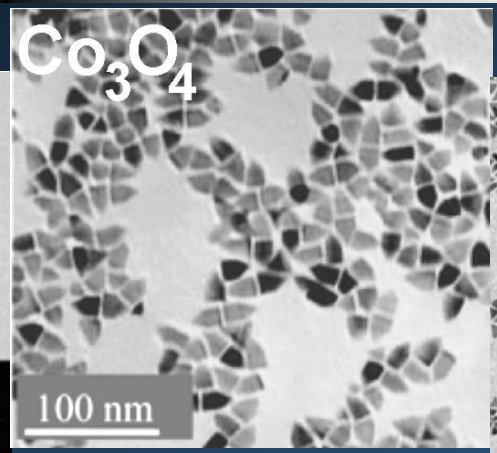
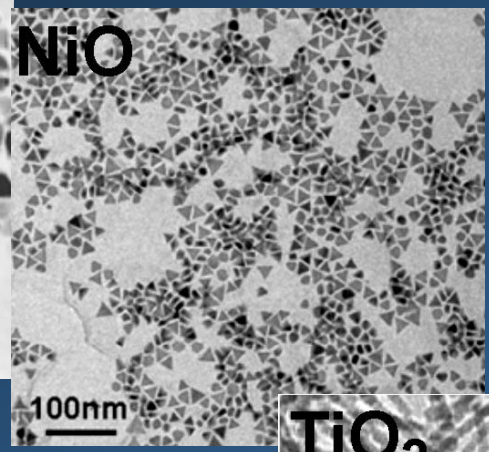
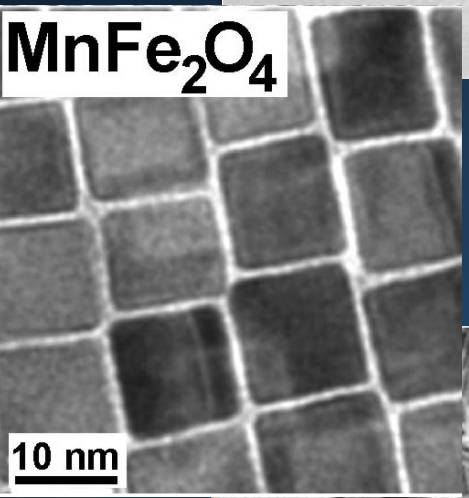
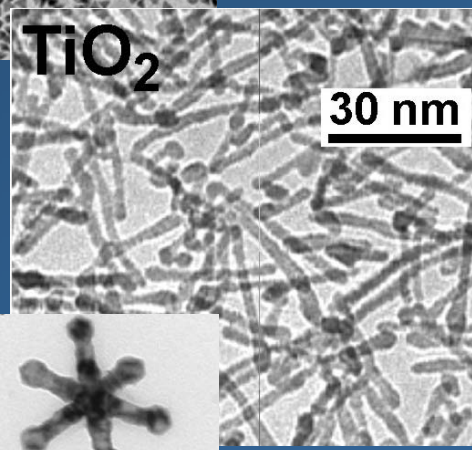


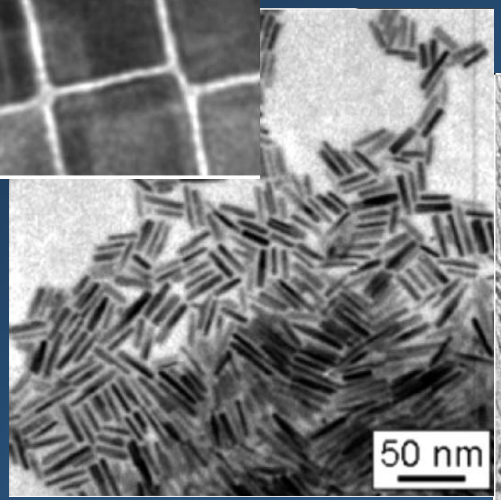


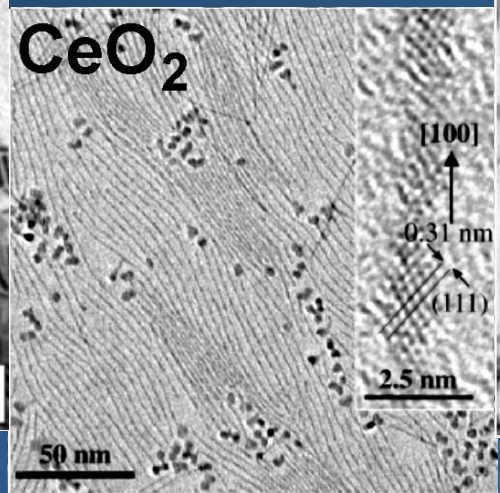


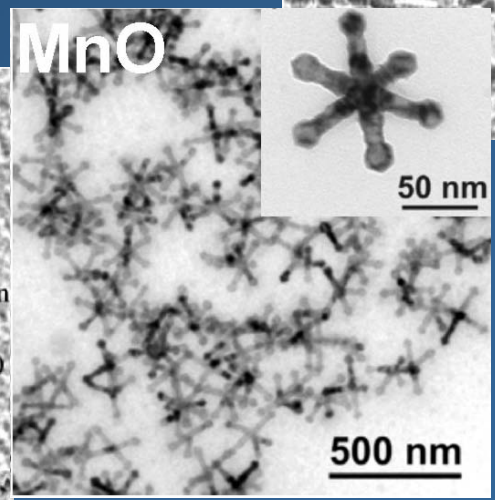


But: **No Prediction possible!**









Size Control

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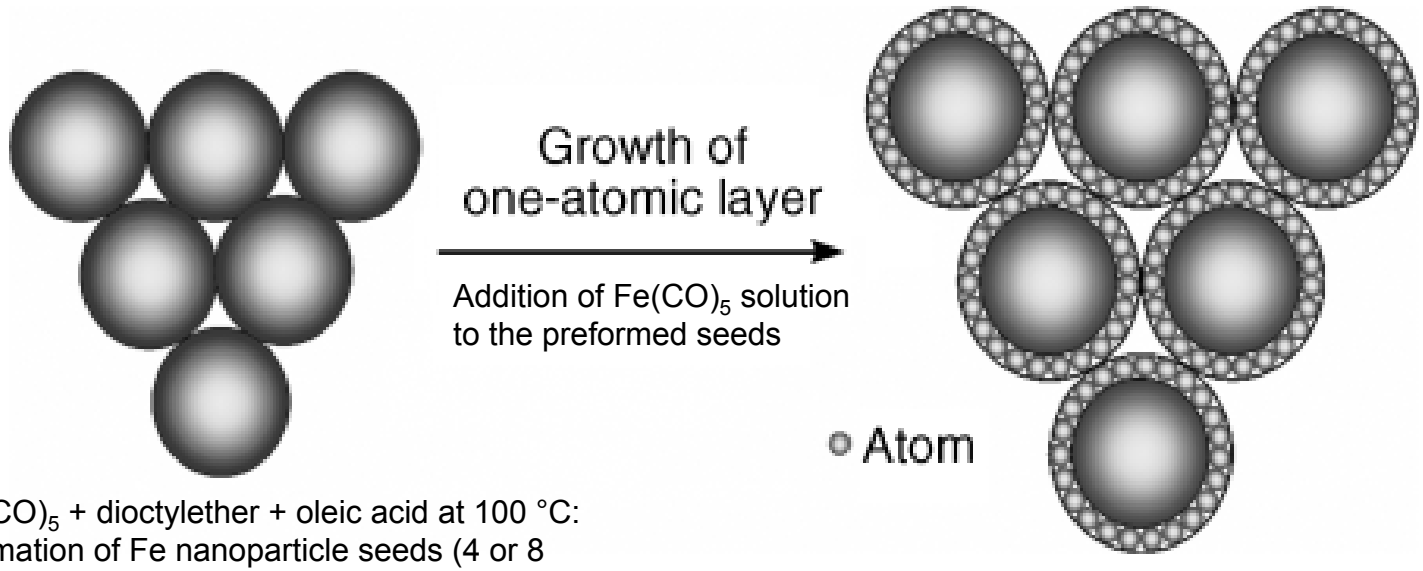

$Fe(CO)_5$ + dioctylether + oleic acid at 100 °C: Formation of Fe nanoparticle seeds (4 or 8 nm)

Oxidation in air: γ-Fe_2O_3 (maghemite)

Table 1: Size of final iron nanoparticles produced from combinations of initial monodisperse iron nanoparticles and iron oleate solutions.

Final iron nanoparticles [nm]	Initial iron nanoparticles [nm]	Iron oleate solution [mmol]
6	4	1.5
7	4	3.0
9	8	1.5
10	8	3.0
12	11	1.5
13	11	3.0
15	11	4.5

Size Control

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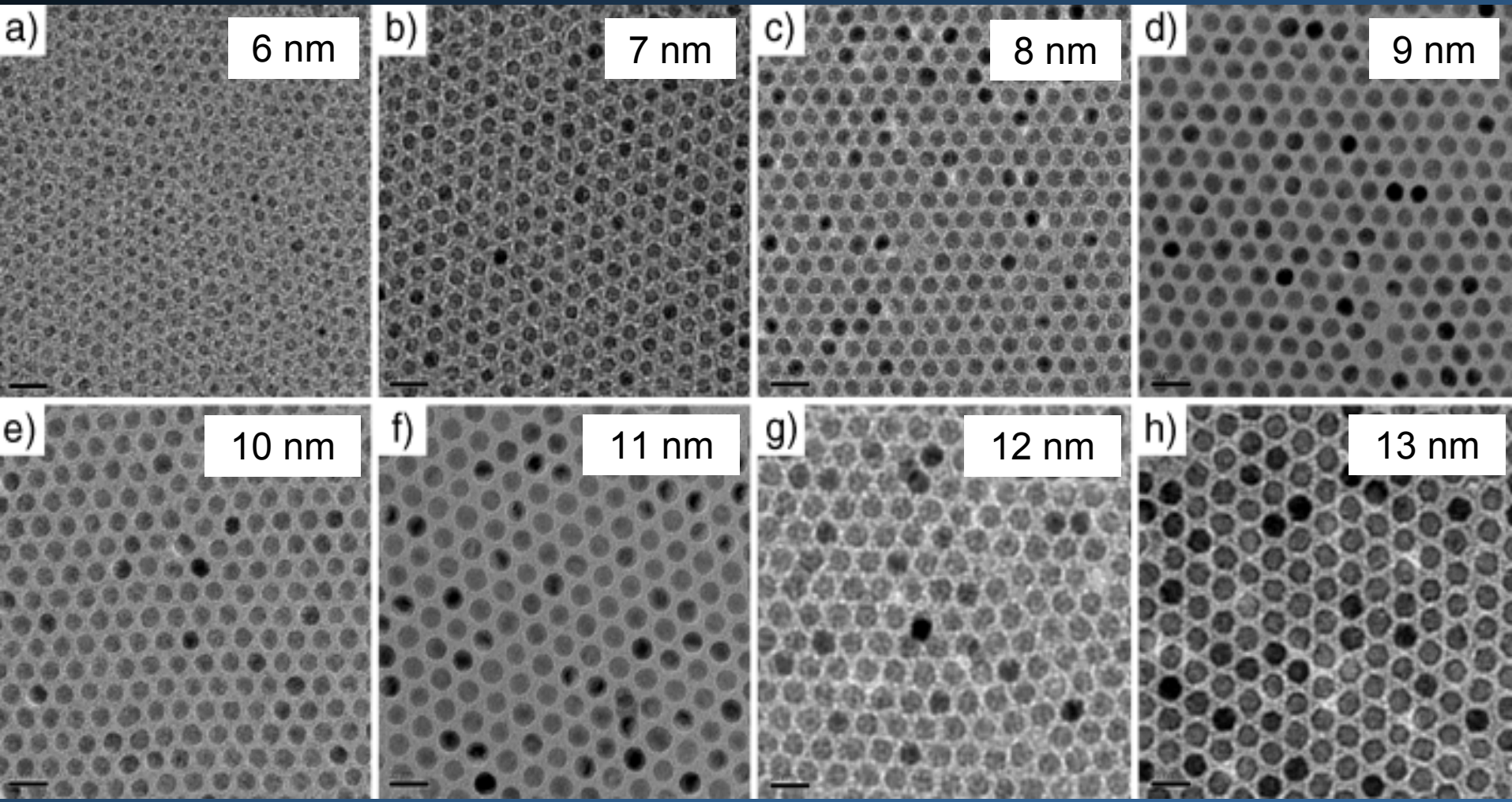
Hyeon et al., Angew. Chem. Int. Ed. **2005**, *44*, 2872



Prediction possible!

Our Research

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Without Surfactants!!!

„Molecular“ Precursor

Organic Solvent

Temperature Treatment

Metal Oxide Nanoparticles

Our Research

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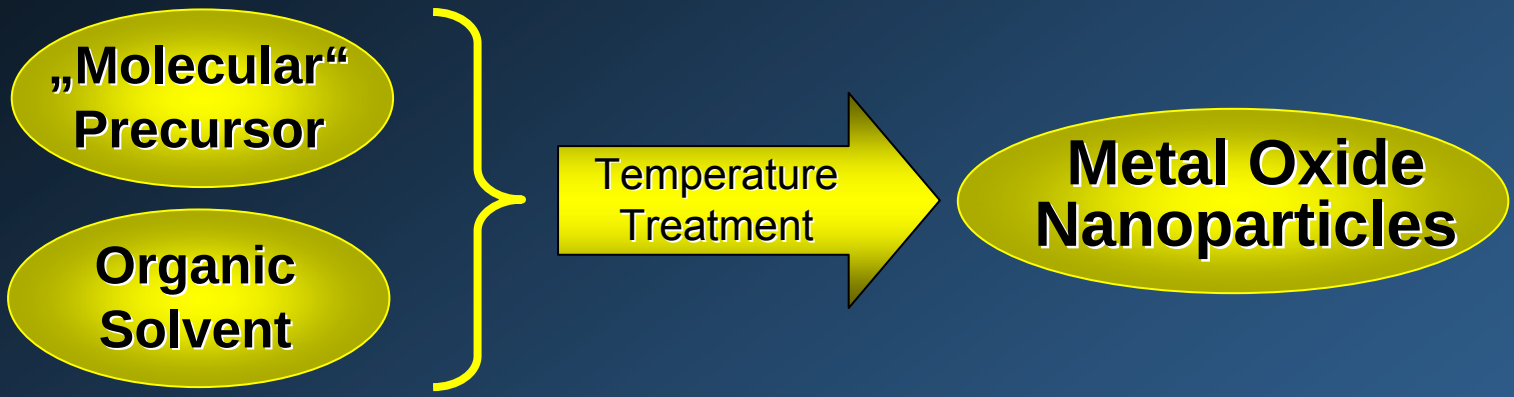
Without Surfactants!!!



\+ Low amount of organic impurities

Nontoxic solvent vs. toxicity of surfactants

Simple, robust, and generally applicable synthesis protocol

Small number of initial components: Study of the mechanisms!

Good accessibility of the nanoparticle surface

\- Less control over size and shape

Broader size distribution

Formation of agglomerates, limited redispersibility

Our Research

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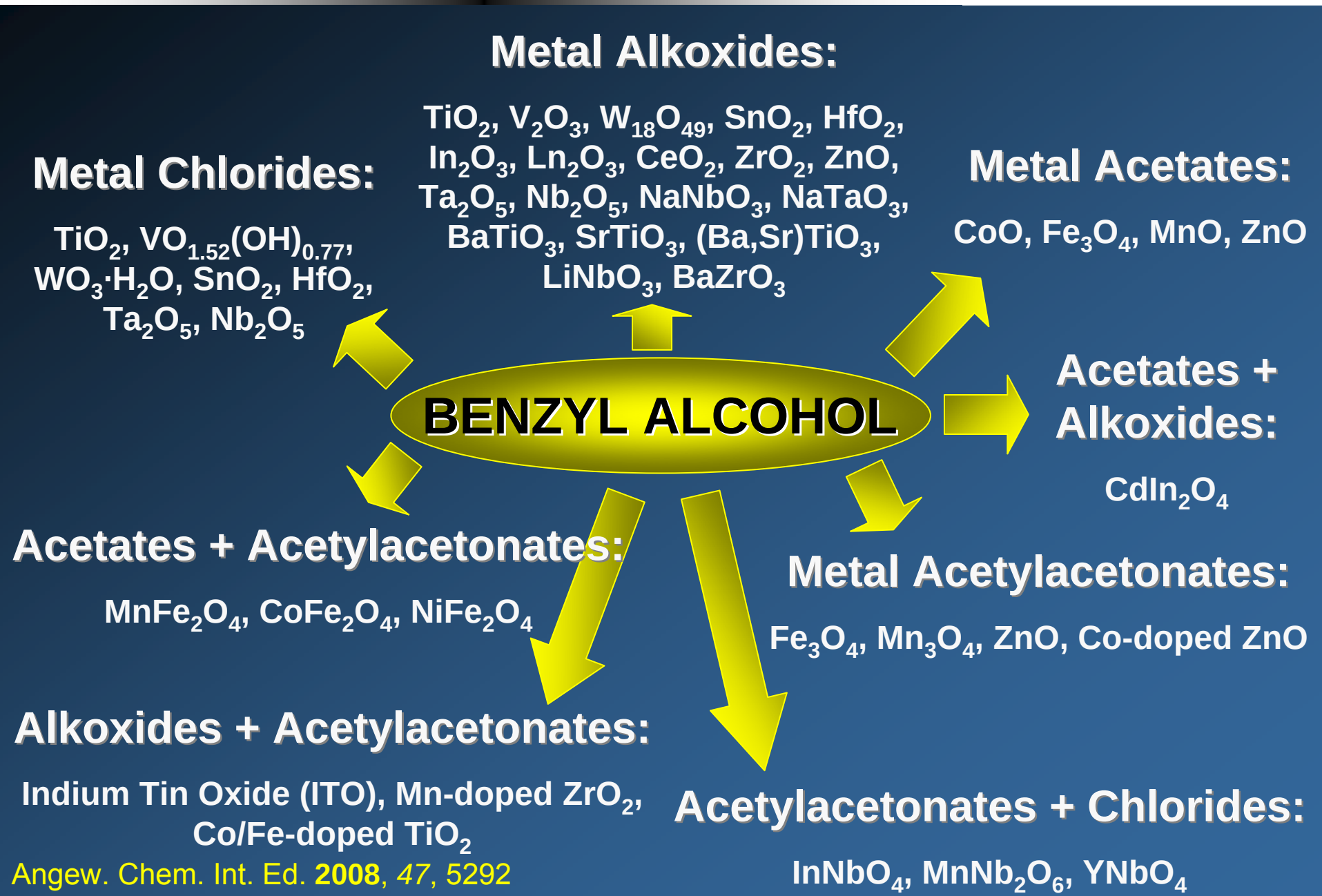

Angew. Chem. Int. Ed. **2008**, *47*, 5292

Binary Metal Oxide Nanoparticles

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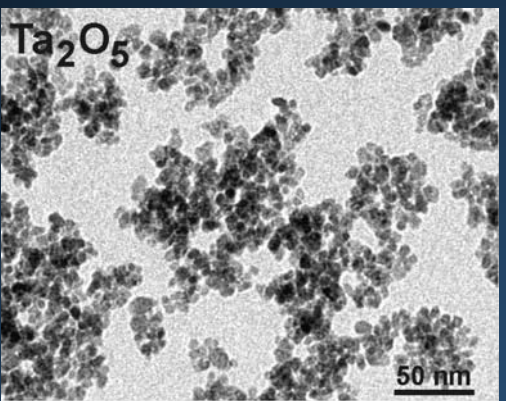
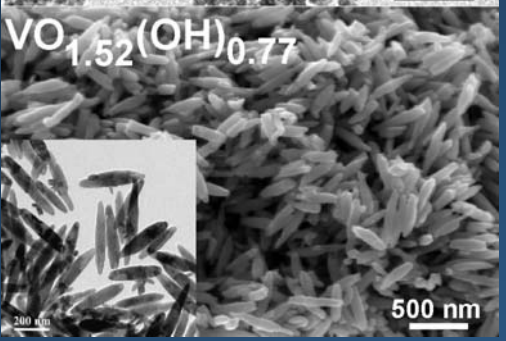
BENZYL ALCOHOL

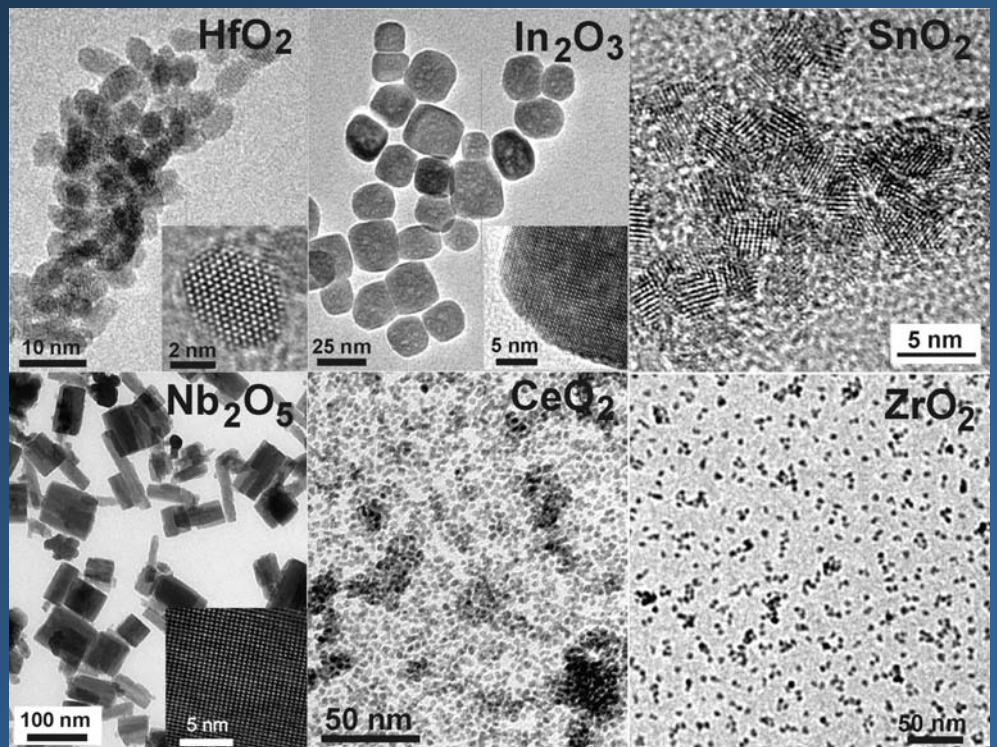
Metal Chlorides
T = 60-220 °C

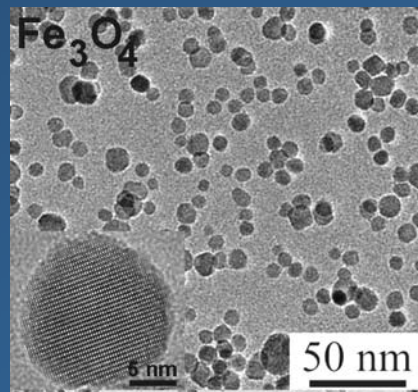
Metal Alkoxides
T = 200-250 °C

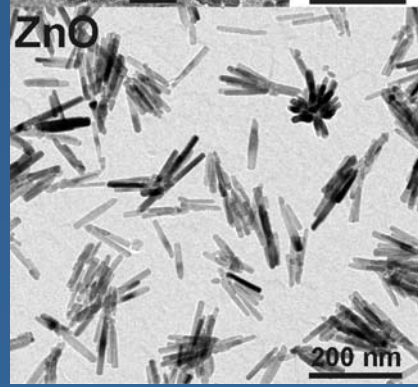
Metal Acetylacetonates
T = 80-200 °C











Ternary Metal Oxide Nanoparticles

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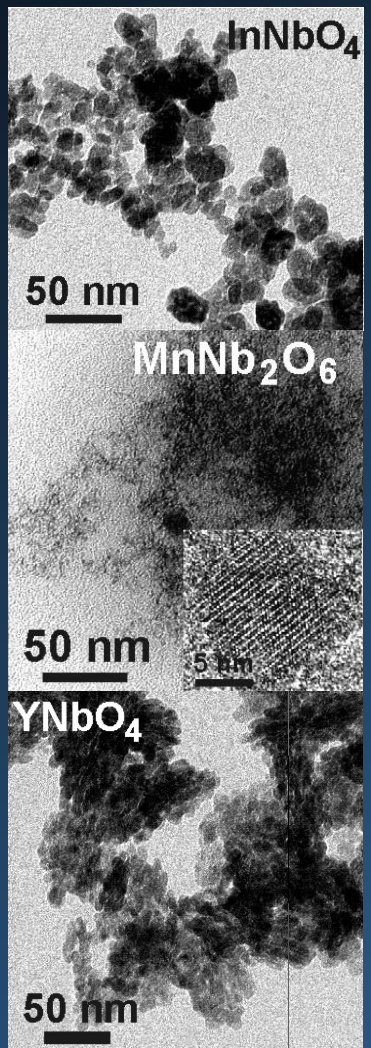
$M(acac)_3$ and $NbCl_5$

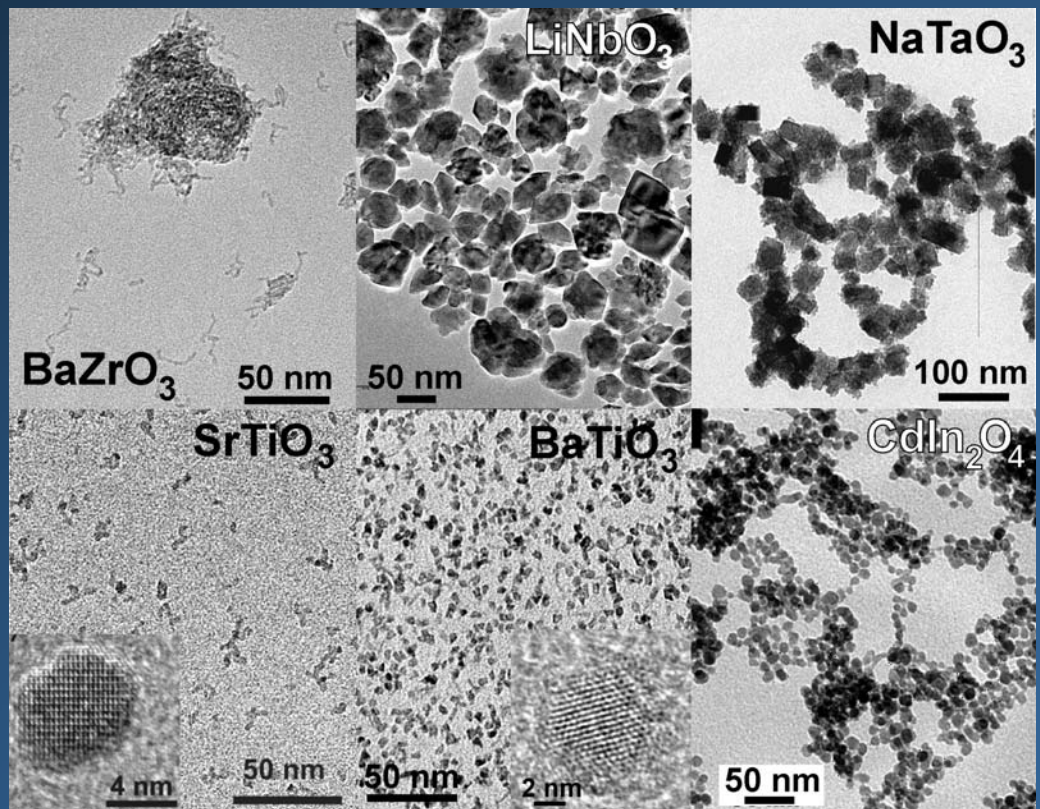
BENZYL ALCOHOL

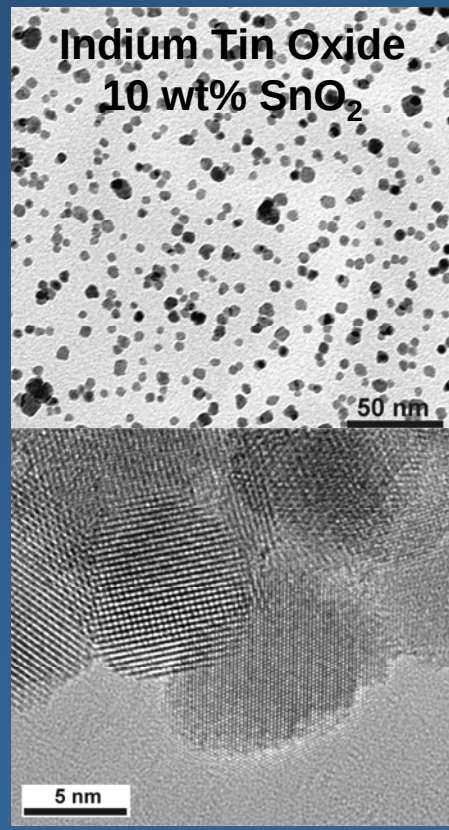
Alkoxides and Acetylacetonates

Metal Alkoxides

T = 200-250 °C







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No water ⟶ Two main questions:

1) Where does the oxygen come from?

2) How is it transferred from the source to the metal center?

Example:

Formation Mechanism of $BaTiO_3$

Chemical Formation Mechanisms

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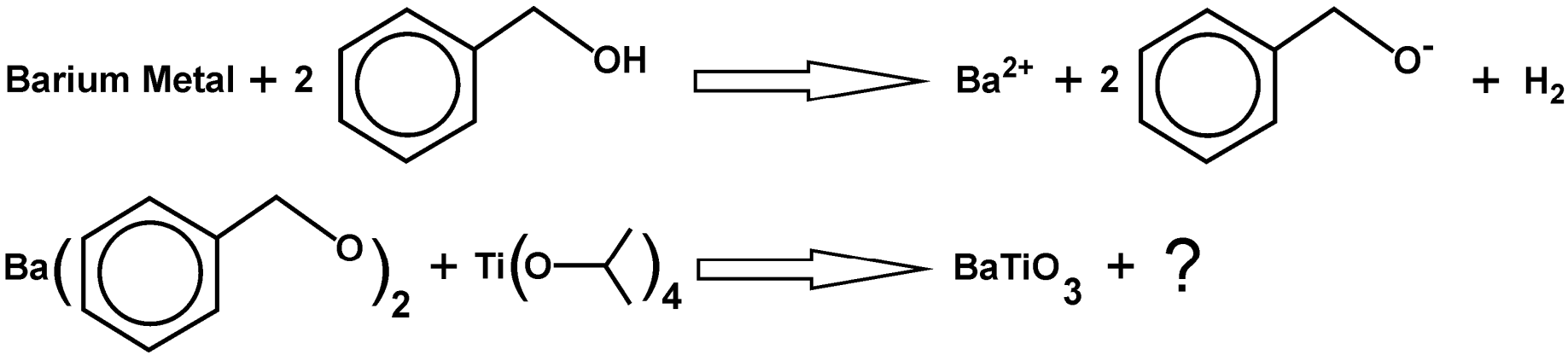
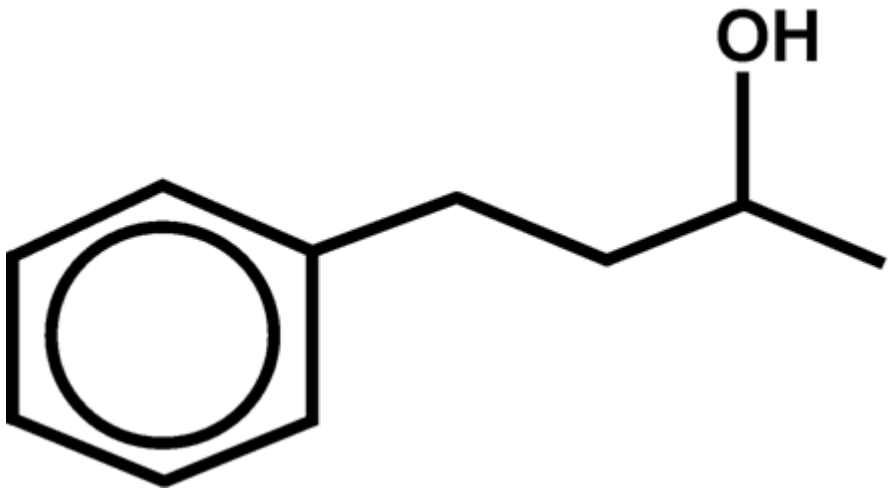


? =



Chemical Formation Mechanisms

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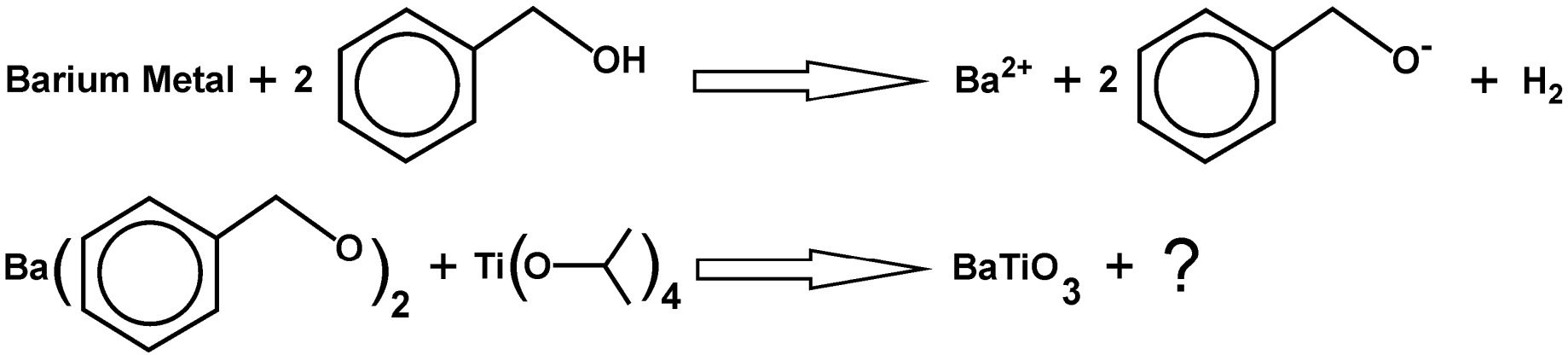

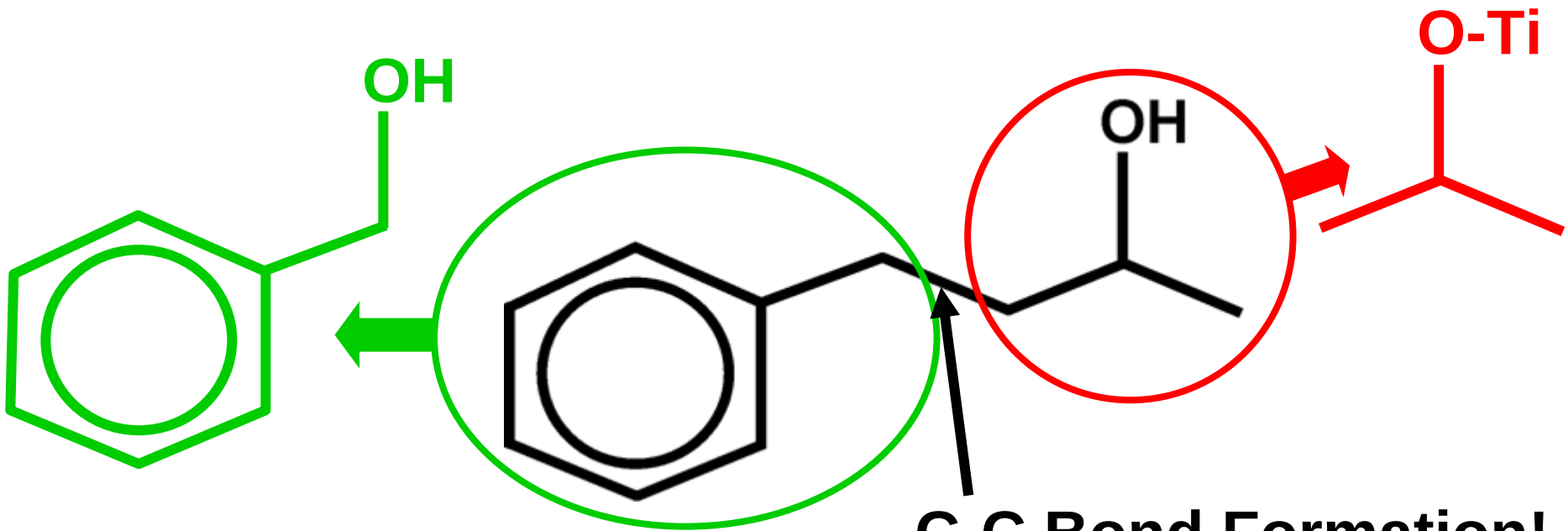

Chemical Formation Mechanisms

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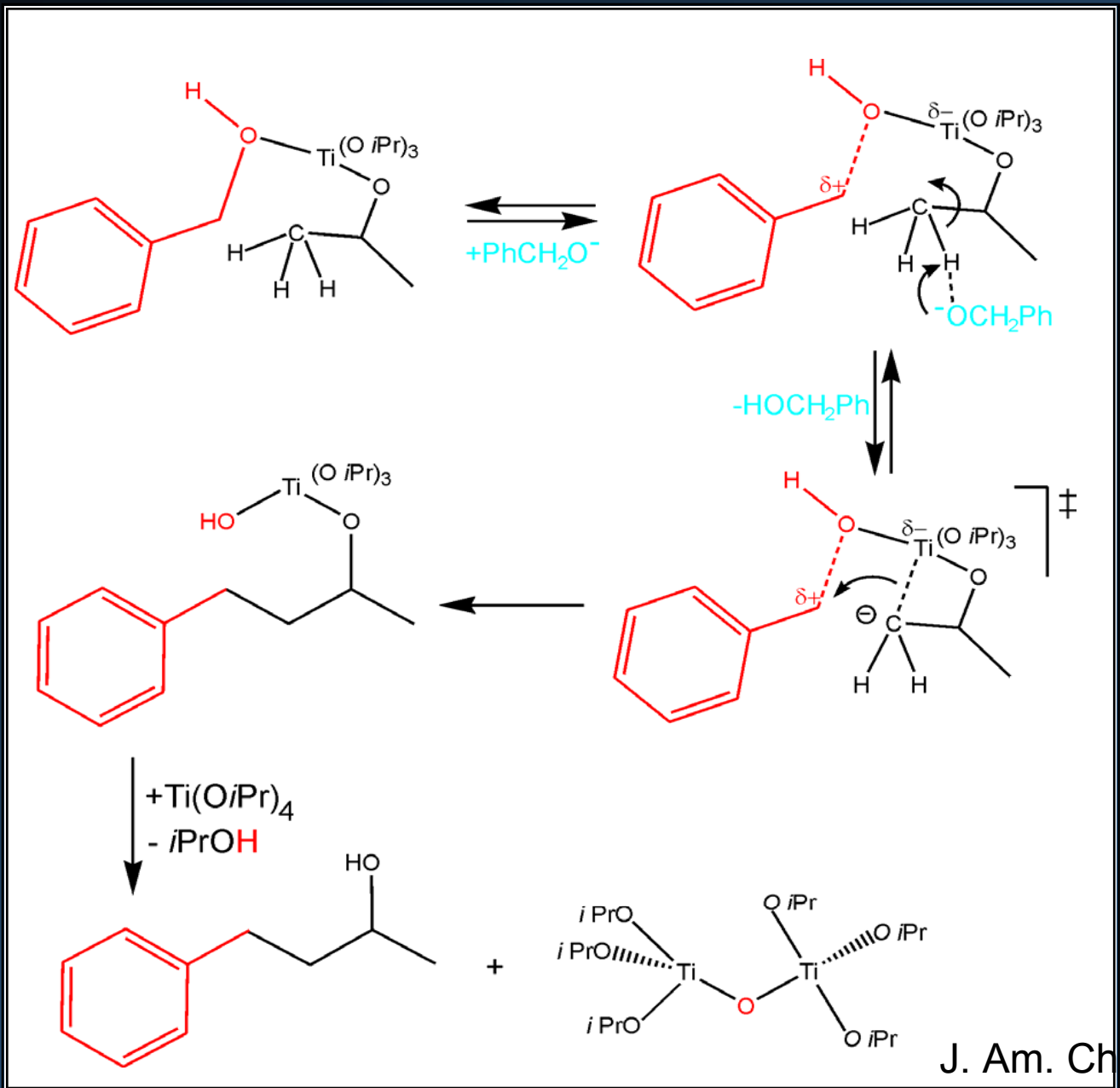

The oxygen is provided by the „OH“ group of benzyl alcohol!

J. Am. Chem. Soc. **2004**, *126*, 9120

Chemical Formation Mechanisms

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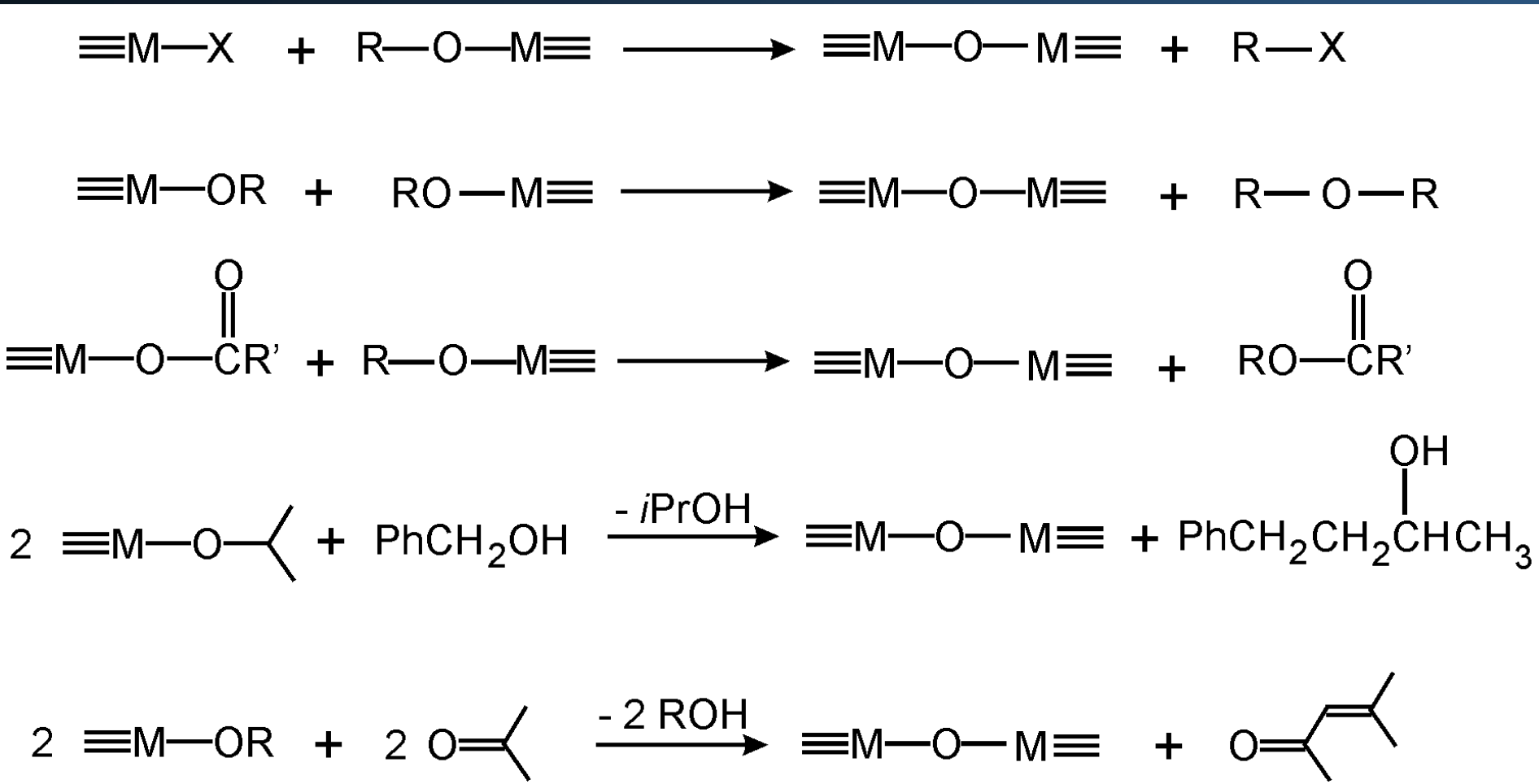

Chem. Eur. J. **2006**, *12*, 7282

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To understand nanoparticle formation on a molecular level (i.e., crystallization and size- and shape-determining parameters), all the organic species (initially present as well as formed *in-situ*) have to be considered!

J. Mater. Chem. **2008**, *18*, 1171

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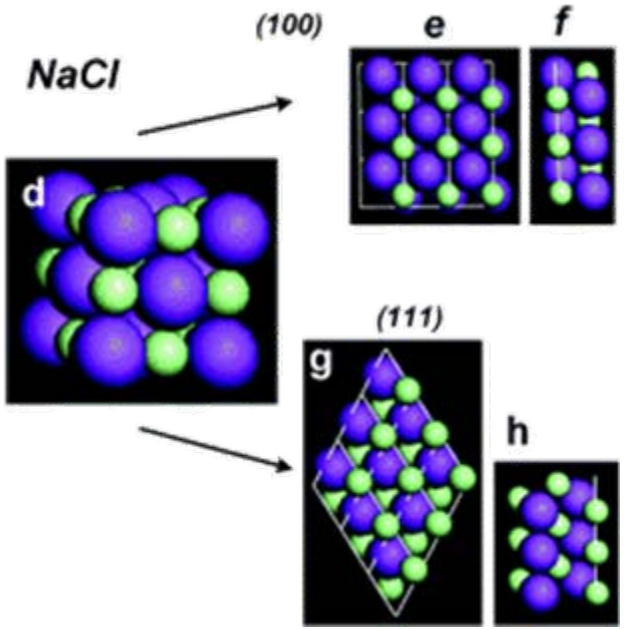
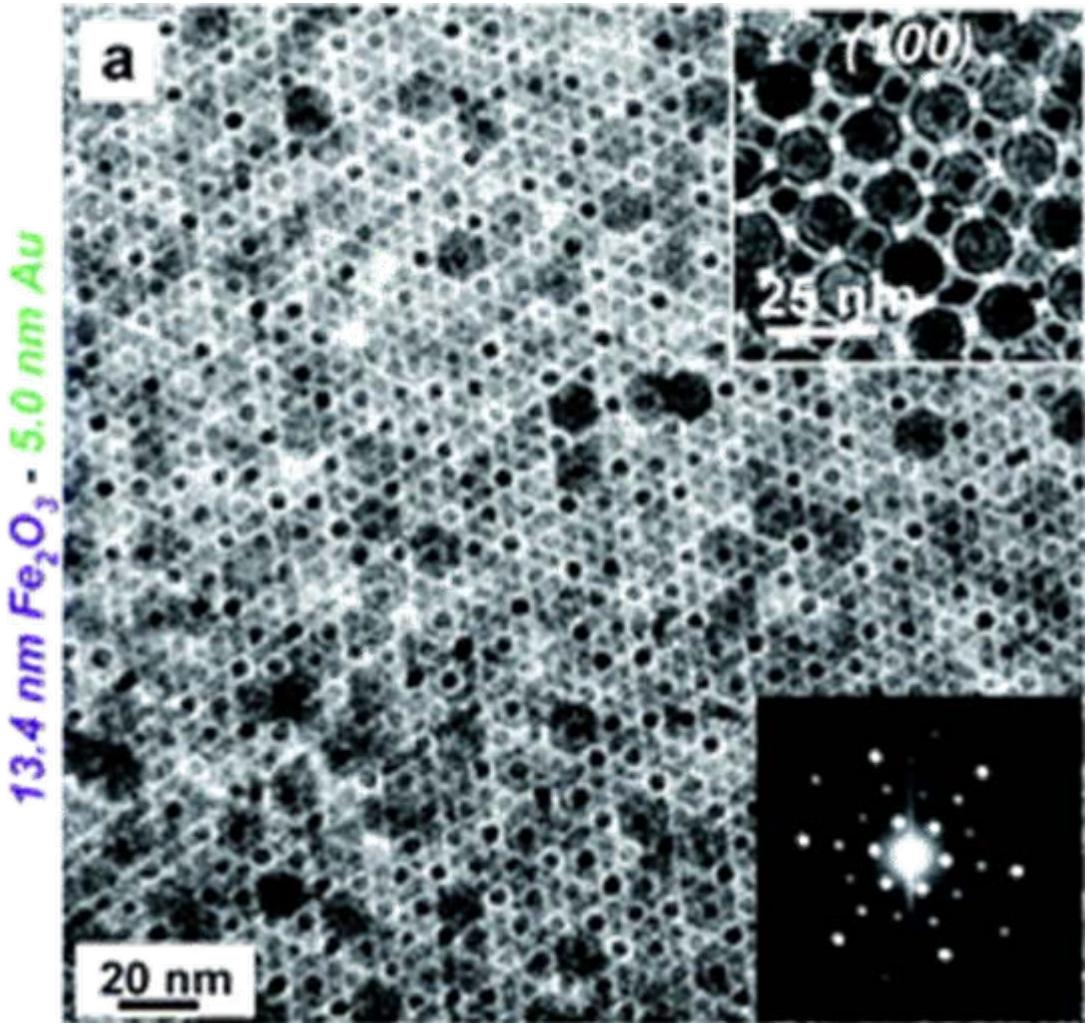
Nanoparticles as Building Blocks (Lego Bricks)





Shevchenko, Talapin, Murray, O'Brien: J. Am. Chem. Soc. **2006**, *128*, 3620

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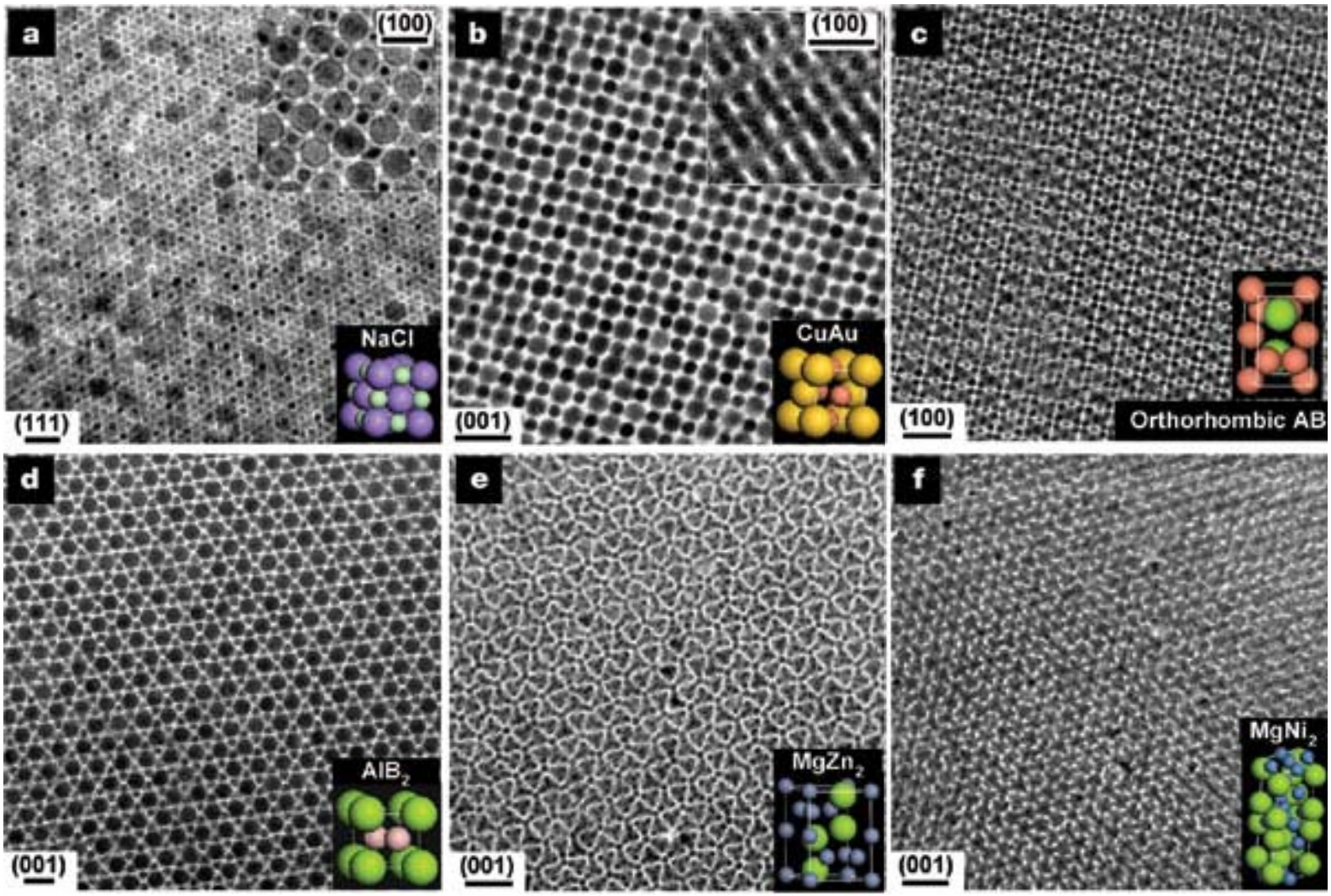

Nature, **439**, 55-59 (2006)

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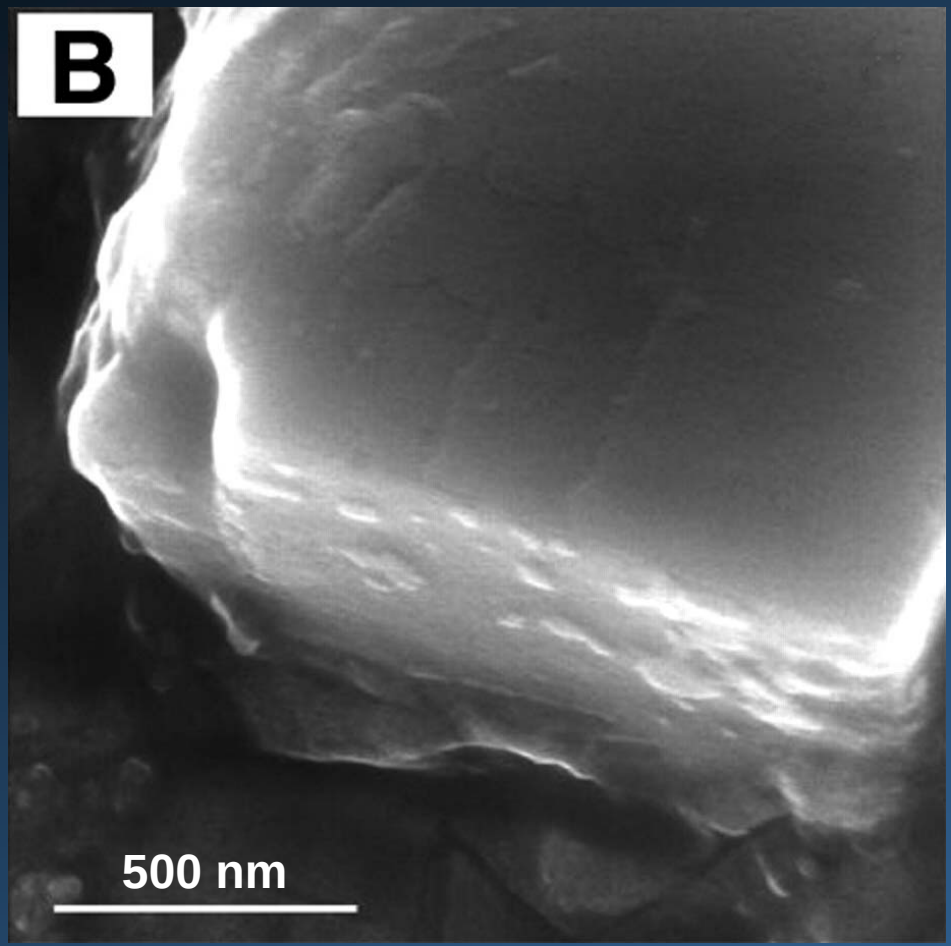
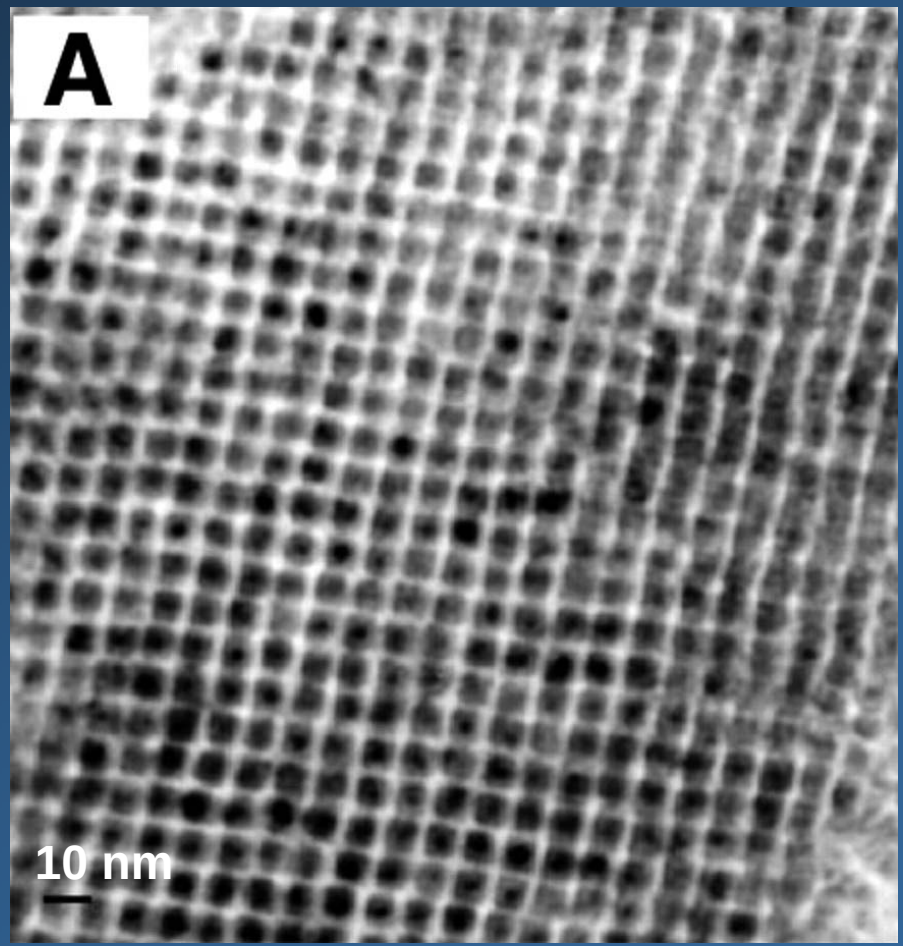
Nanoparticles as Building Blocks (Lego Bricks)





New Properties?

Chaudret et al. Science **2004**, *303*, 821

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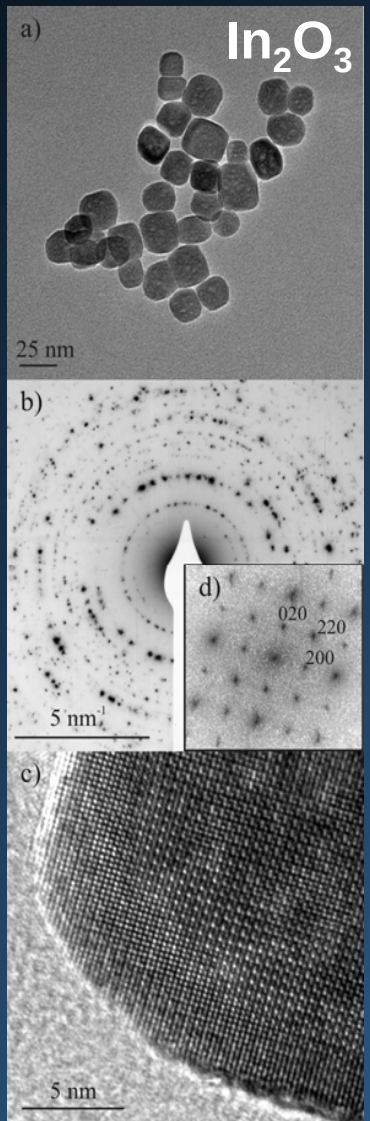
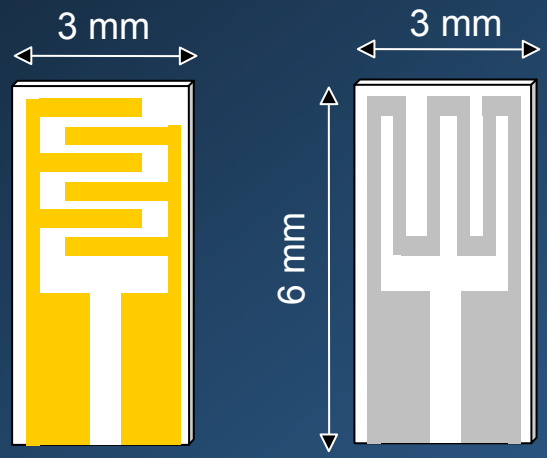
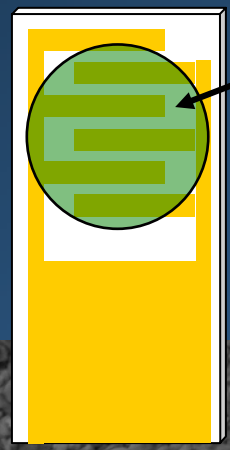
Metal Oxide Nanoparticles for Gas Sensing



Front side
gold electrodes

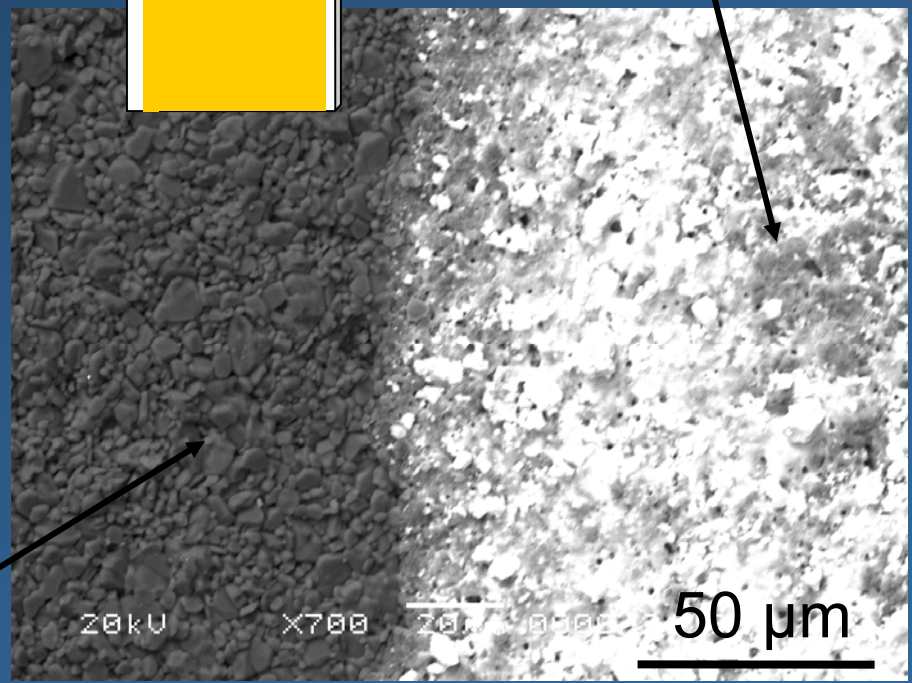
Back side
platinum contacts





Sensing layer

Cross section



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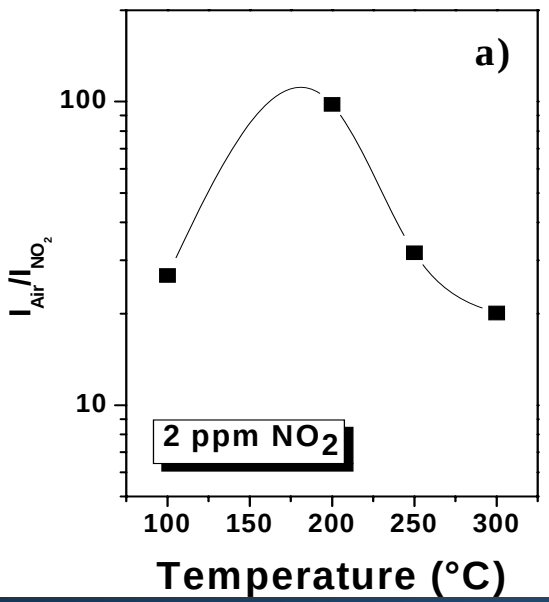
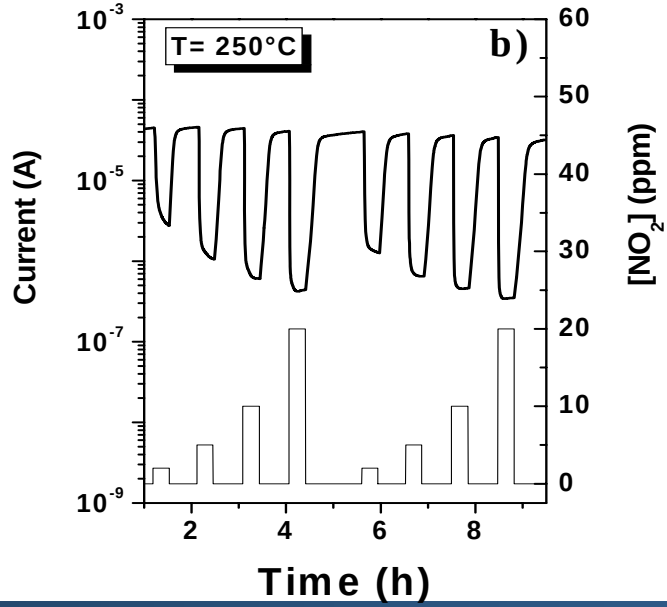
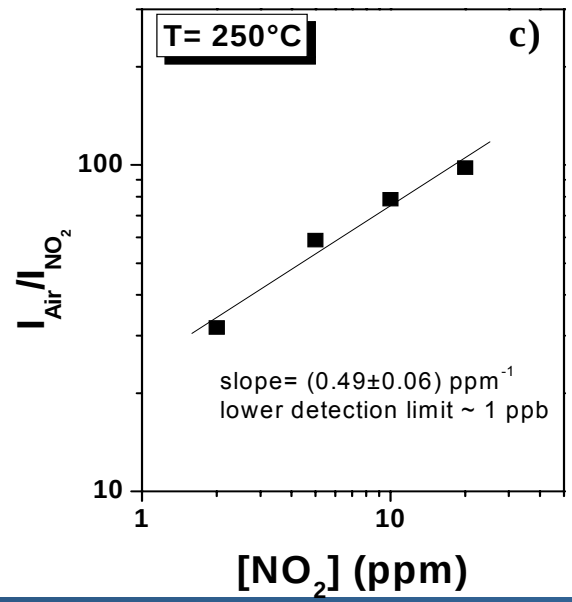
Metal Oxide Nanoparticles for Gas Sensing







(a) Response to 2 ppm of NO_2 versus operating temperature of the In_2O_3 sensor: Maximum sensitivity around 200°C

(b) Dynamic response at 250°C to different and successive concentration pulses of NO_2 (2-20 ppm): Fast response time (less than 60 s)

(c) Calibration curve at 250°C: Detection limit of about 1 ppb for NO_2 in air

Cross-sensitivity tests with CO and CH_4 show no response (T = 100-400°C)

Angew. Chem. Int. Ed. **2004**, *43*, 4345

Conclusions - Outlook

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But: **Doping, Multi Metal Oxides, Heteronanostructures!**

But: **No Prediction! No Rational Synthesis Planning!**

Synthesis in Benzyl Alcohol:

General (> 30 Compositions)

Large Variety of Crystal Sizes and Shapes: Wires, Rods, Platelets, Cubes, Spheres,…

Synthesis

Metal Oxides Nanoparticles

Assembly

1, 2 and 3D Architectures in Selected Cases

Nanocomposites / Organic-Inorganic Hybrid Structures

But: **Study of Collective Properties**

But: **Nanoparticles as Artificial Atoms (Directed Bonding)**

But: **Dispersions of Nanoparticles on Primary Particle Level!**

Multifunctional Materials

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2007