Colloidal Chemical Synthesis of Magnetic Nanoparticles

Synthesis of Monodisperse cobalt nanocrystals and their assembly Into magnetic superlattices

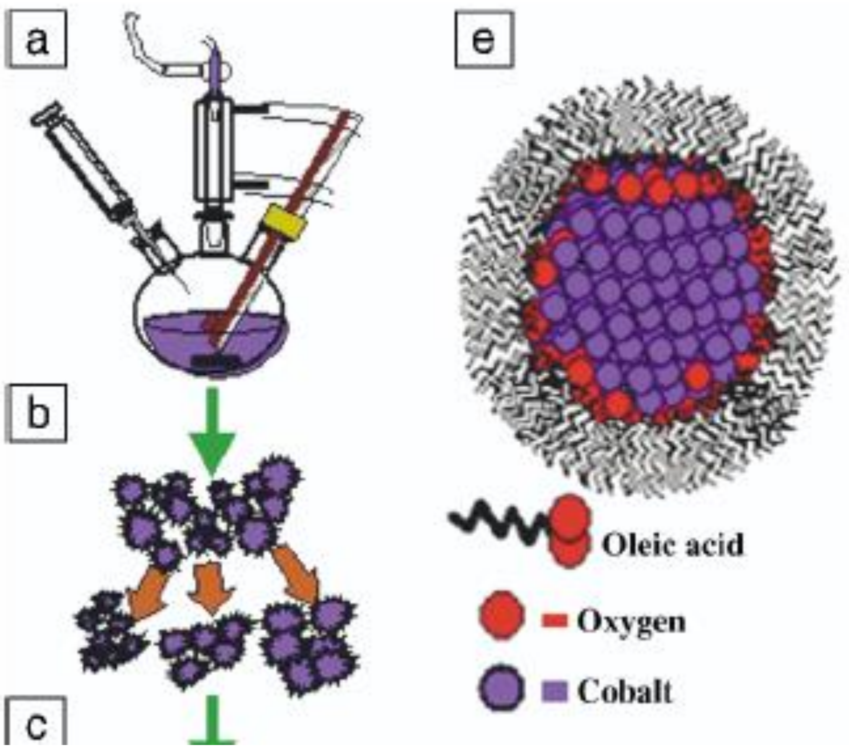
Sun (now at Brown U.) and Murray (now at U. Penn) (IBM),

J. Appl. Phys. **1999**, 85, 4325.

1) Injection of dioctylether superhydride ($LiBEt_3H$) into $CoCl_2$ dioctylether solution in the presence of oleic acid $(CH_3(CH_2)_7CH=CH(CH_2)_7COOH)$

2) Size fractionation to get monodisperse particles

Colloidal Chemical Synthesis of Cobalt Nanoparticles



(a) nanoparticle (NP) synthesis by high-temperature solution-phase routes;

(b) size-selective precipitation, used to narrow nanoparticle size distributions;

C. B. Murray, S. Sun, H. Doyle, T. A. Betley, *MRS Bull.* **2001**, *26*, 985.

Colloidal Chemical Synthesis of Cobalt Nanoparticles

High temp. reduction of cobalt chloride to yield ε-Co nanoparticles.

Injection of superhydride ($LiBEt_3H$) solution in dioctyl ether

into a hot cobalt chloride solution in dioctyl ether (200 ^{o}C)

in the presence of oleic acid and trialkylphosphine.

Addition of $LiBEt_3H$ (superhydride) into solution containing $CoCl_2$,

oleic acid, diotylether, $P(Bu)_3 \rightarrow$ aging at 200 C

Colloidal Chemical Synthesis of Cobalt Nanoparticles

Particle size was controlled by the steric bulkiness of surfactants.

Short-chain alkylphosphines allowed faster growth, and resulted in the bigger particles, while bulkier surfactants reduced particle growth and favored production of smaller NPs.

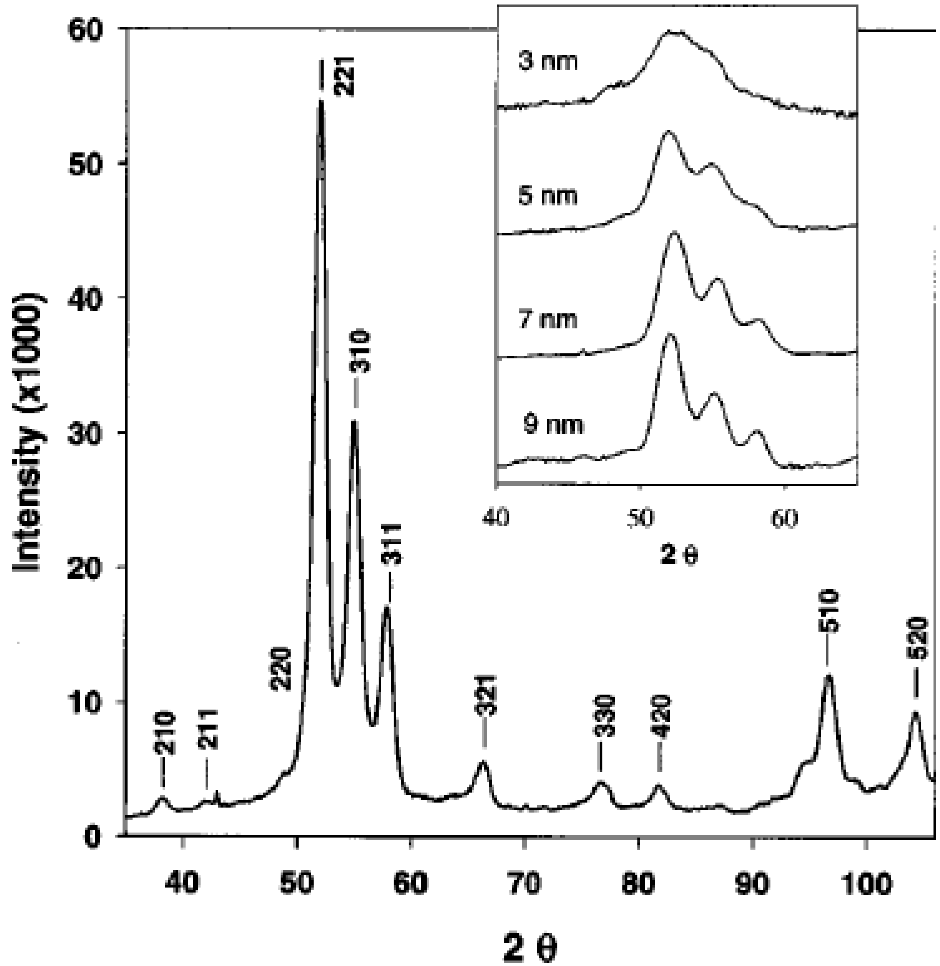
1) $P(C_8H_{17})_3$: 2 – 6 nm. limited growth, 2) $P(Bu)_3$: larger 7 - 11 nm particles. (Steric effect)

A further narrowing of particle size distribution was proceeded using a size selective precipitation by the gradual addition of alcohol.

- Selective precipitation to get monodisperse nanoparticles
- Burst of nucleation followed by steady growth of those nuclei
- Novel ε-Co, annealing at 300 ^{o}C changed to hcp
- Small enough to be superparamagnetic

Colloidal Chemical Synthesis of Cobalt Nanoparticles

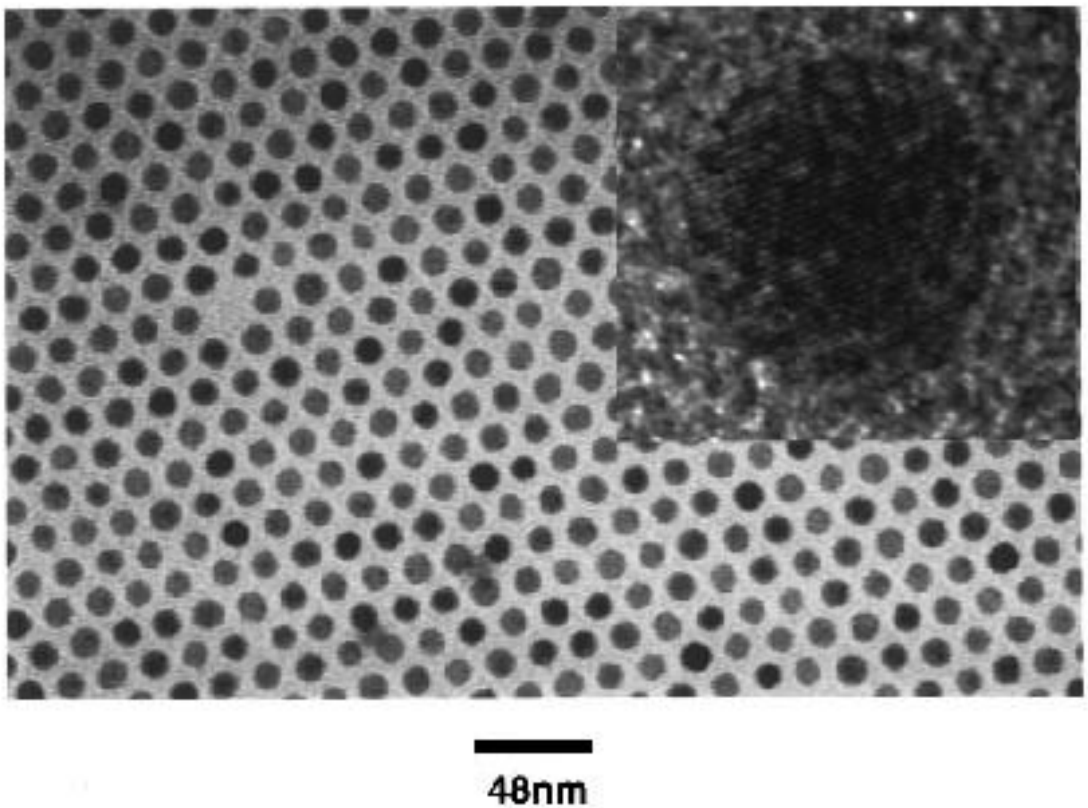
XRD pattern of 11 nm sized ε-Co nanocrystals
and (Inset) size-dependent XRD patterns

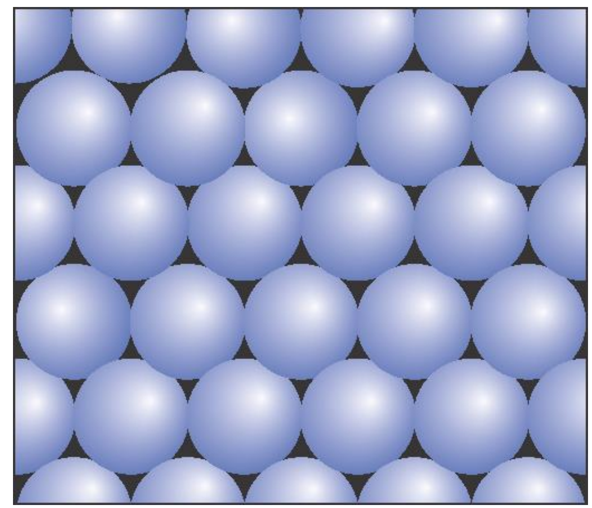


Sun and Murray (IBM), *J. Appl. Phys*. **1999**, 85, 4325.

Colloidal Chemical Synthesis of Cobalt Nanoparticles

9 nm sized Co nanocrystals form 2-dimensional hexagonal colosed
Packing demonstrates the uniformity of the nanocrystals
Inset HRTEM image demonstrates the high crystallinity



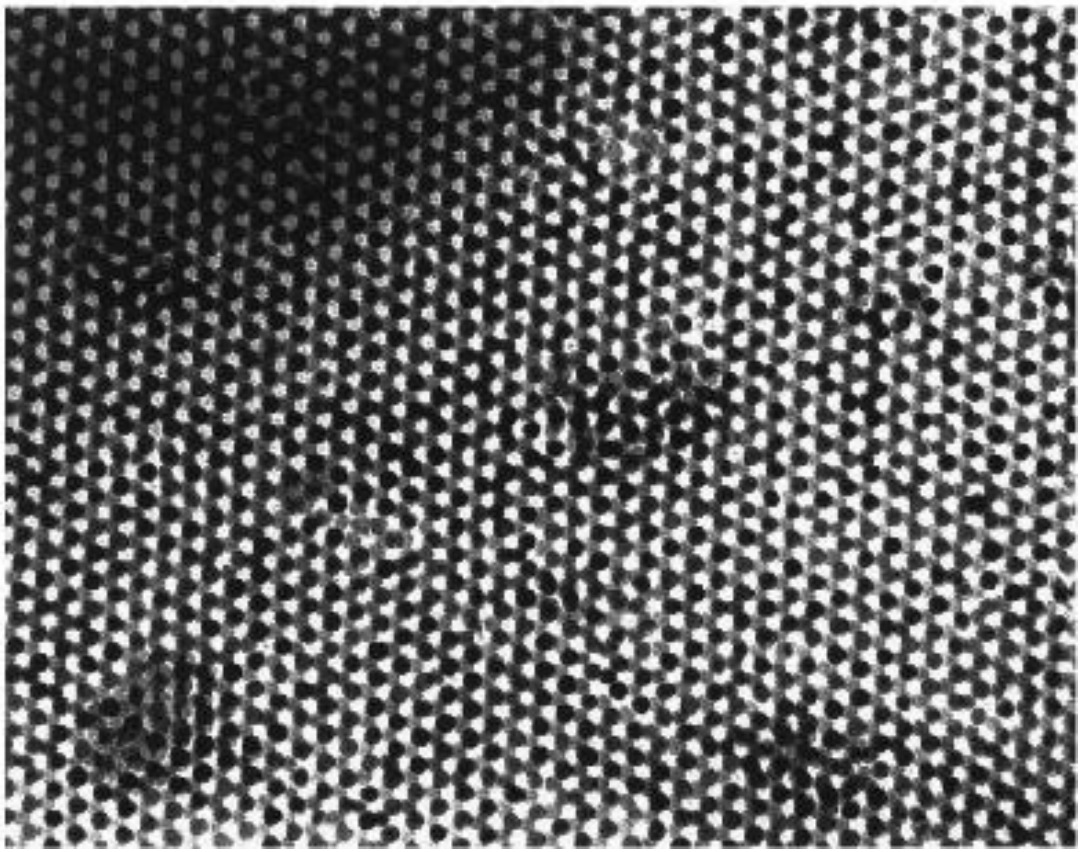


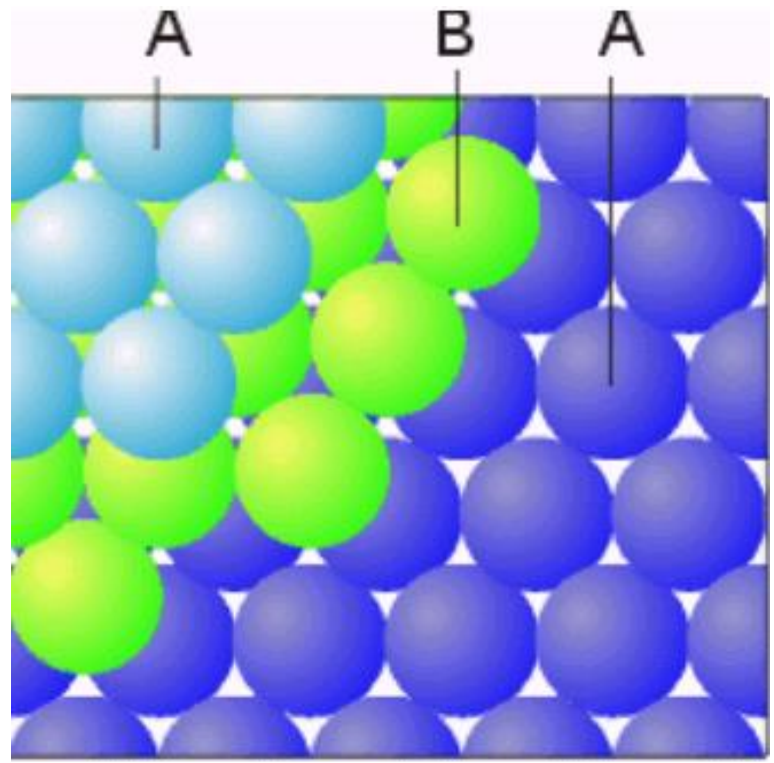
2-D hexagonal close-packing

Sun and Murray (IBM), *J. Appl. Phys*. **1999**, 85, 4325.

Colloidal Chemical Synthesis of Cobalt Nanoparticles

3-Dimensional hexagonal closed packing
of 9 nm sized Co nanocrystals

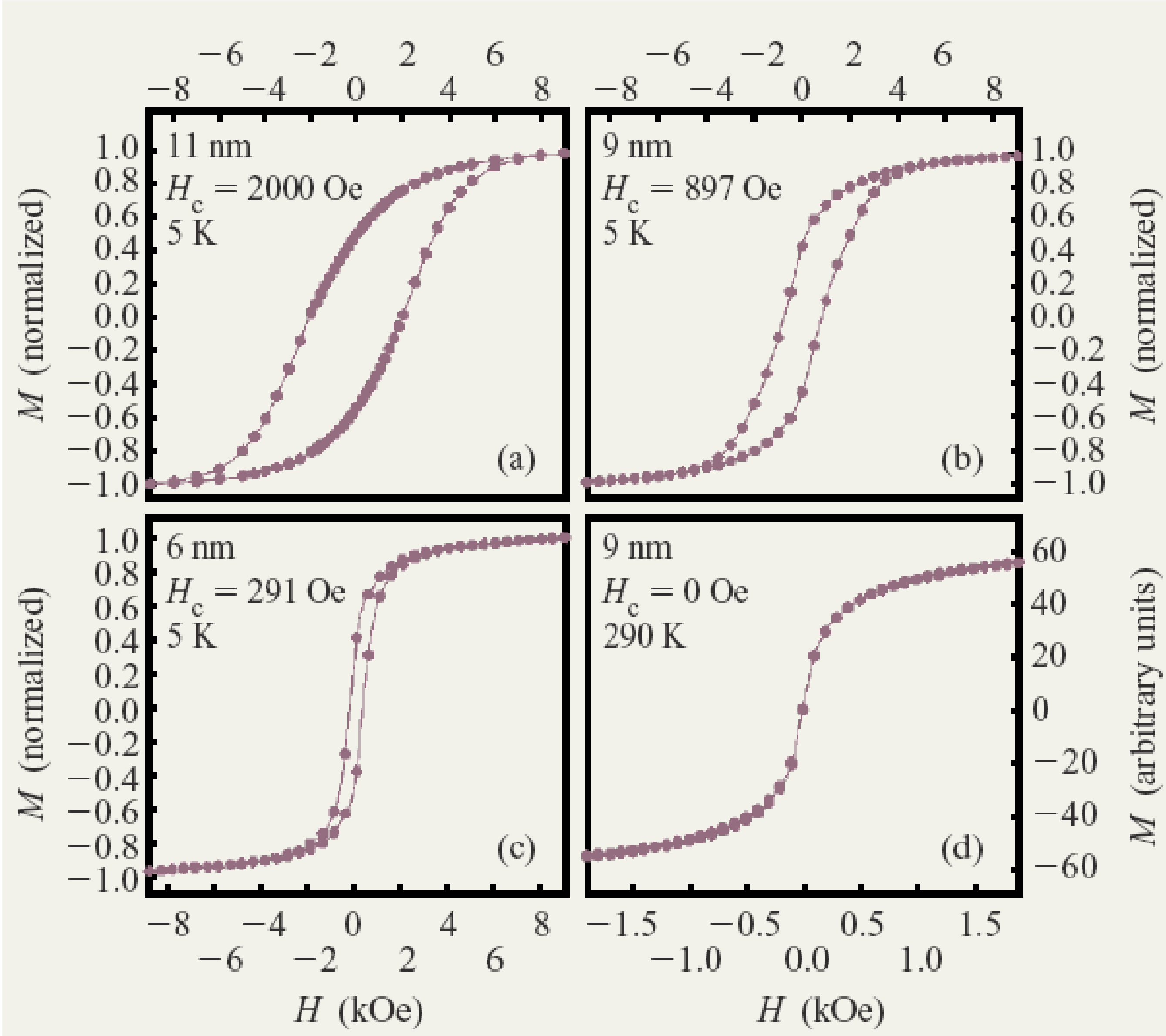




3-D Hexagonal close packing

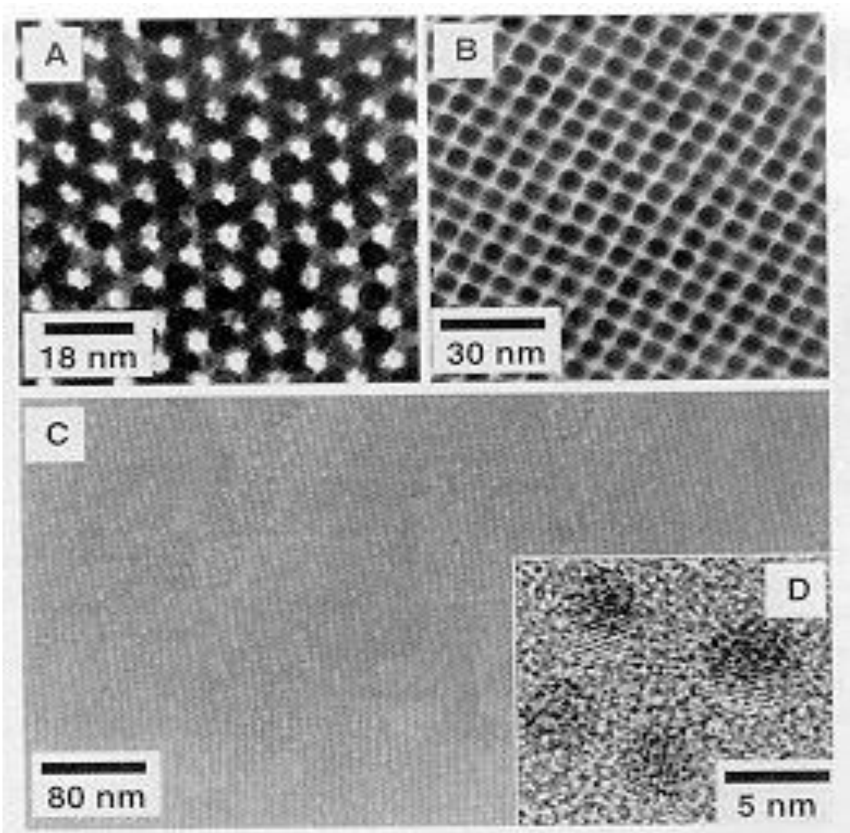
Sun and Murray (IBM), *J. Appl. Phys*. **1999**, 85, 4325.

Cobalt nanocrystals are superparamagnetic and room temp and become ferromagnetic below blocking temperature.



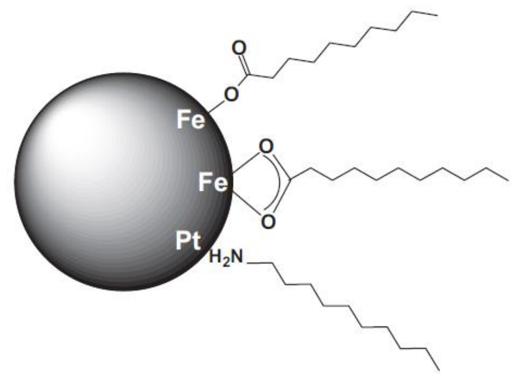
Synthesis of Fe-Pt alloy Magnetic Nanoparticles

Thermal decomposition of $Fe(CO)_5$ followed by reduction of $Pt(acetylacetonate)_2$ by diol in the presence of oleic acid &Oleic amine



- Thermal annealing converts Fcc to face-center tetragonal Structure

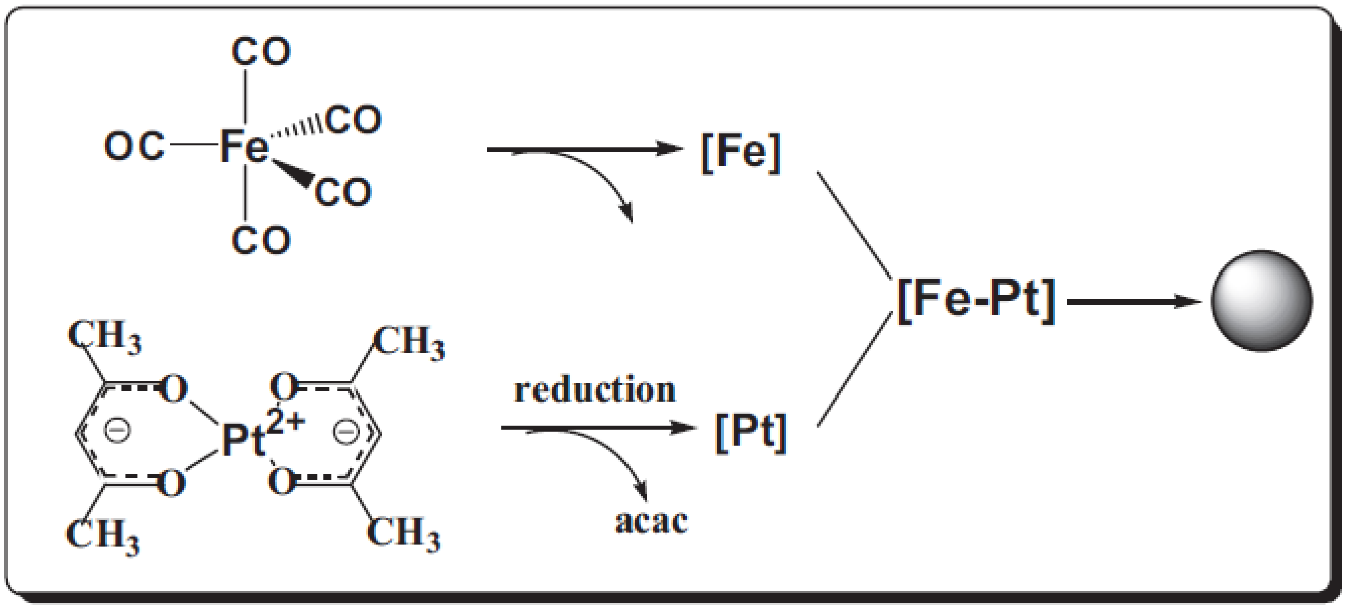
-High-density magnetization reversal transition demonstrated

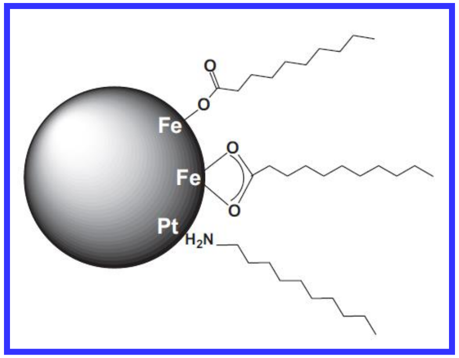


Sun and Murray, *Science* **2000**, 287, 1989.

To prepare FePt nanoparticles

- Combination of oleic acid and oleyl amine to stabilize the monodisperse FePt nanoparticles
- Reduction of $Pt(acac)_2$ by 1,2-hexadecanediol (polyol process)
- Decomposition of $Fe(CO)_5$ in high-temperature solutions.



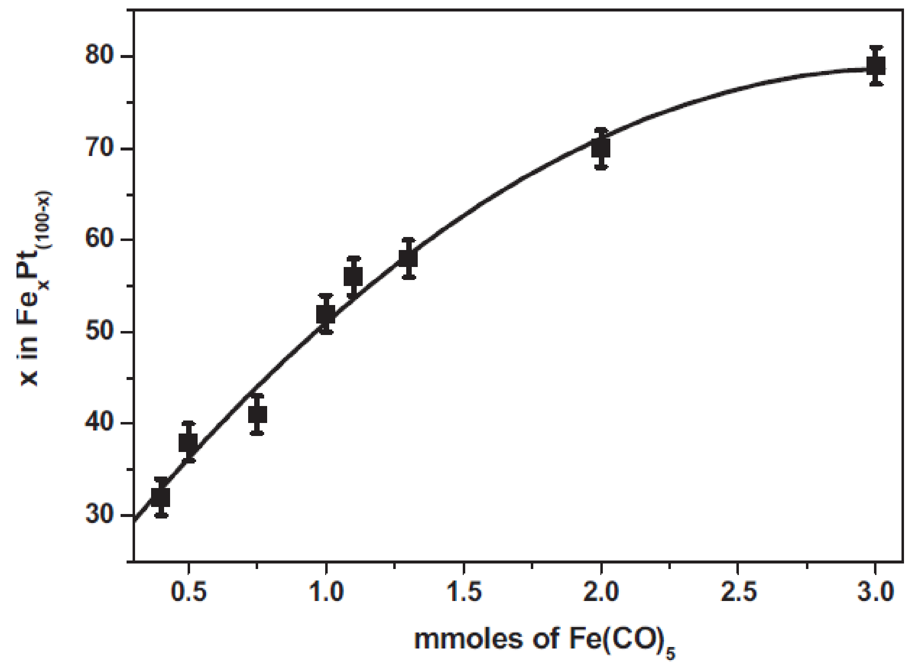


S. Sun, *Adv. Mater.* **2006**, 18, 393.

- **Composition is adjusted by controlling the molar ratio of iron carbonyl to the platinum salt.**

  Using dioctylether as solvent

- 3:2 molar ratio of $Fe(CO)_5$ to $Pt(acac)_2$ gave $Fe_{48}Pt_{52}$ particles,
- a 2:1 molar ratio yielded $Fe_{52}Pt_{48}$,
- 4:1 molar ratio produced $Fe_{70}Pt_{30}$



Sun and Murray, *Science* **2000**, 287, 1989.

Synthesis of Fe-Pt alloys Magnetic Nanoparticles

Controlled Synthesis of Monodisperse Nanoparticles Via Seed-mediated Growth process (Heterogeneous Nucleation)

- The FePt particle size can be tuned from 3 to 10 nm by first growing 3-nm monodisperse seed particles in situ and then adding more reagents to enlarge the existing seeds to the desired size.

Sun and Murray, *Science* **2000**, 287, 1989.

Synthesis of Fe-Pt alloys Magnetic Nanoparticles

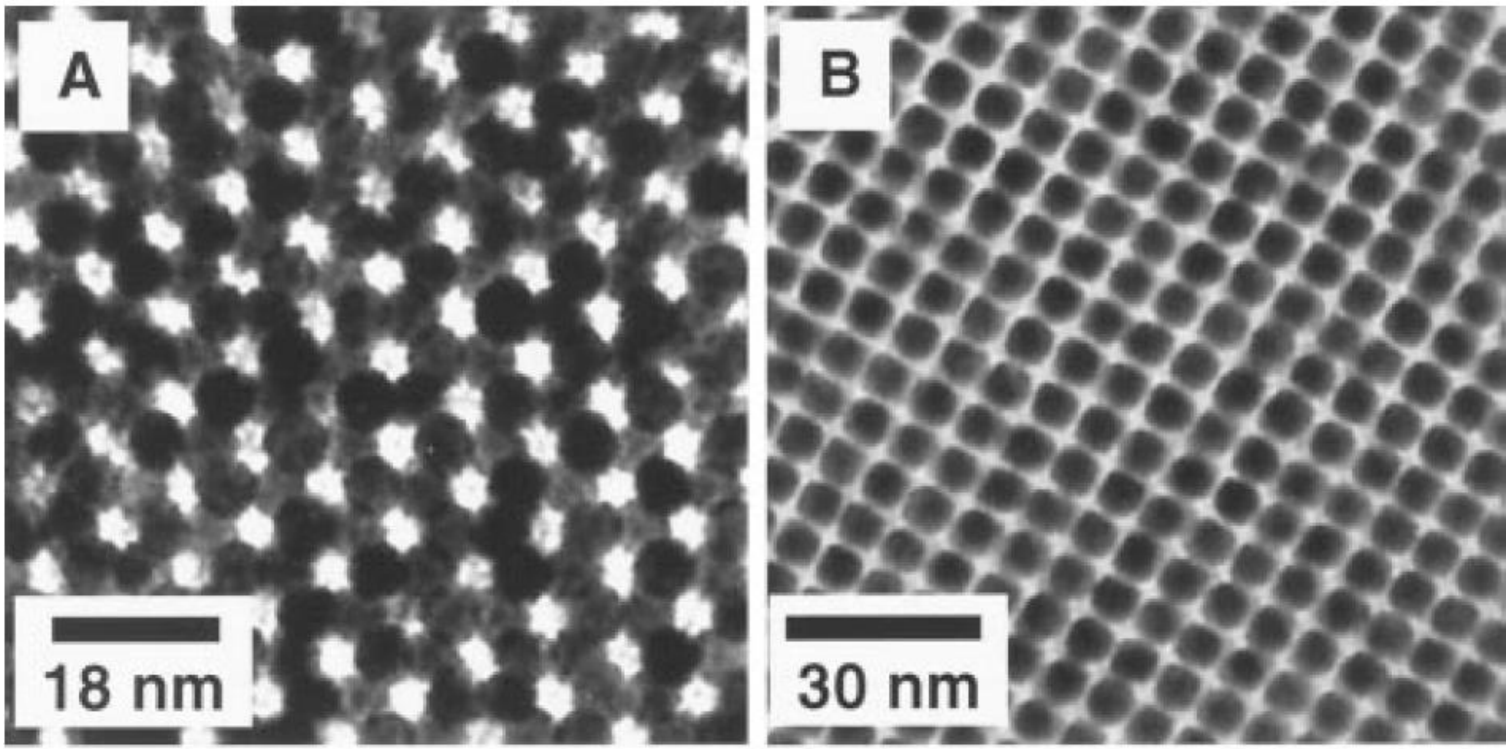
- Room temperature ligand exchange of these long-chain capping groups for shorter RCOOH/RNH_2 (R = dodecyl down to hexyl chains) allows the interparticle distance to be adjusted.
- With oleic group stabilization: hexagonal closed packing and Spacing between nanoparticles of ~ 4 nm
- With hexyl groups→ 1 nm spacing

Sun and Murray, *Science* **2000**, 287, 1989.

Synthesis of Fe-Pt alloys Magnetic Nanoparticles

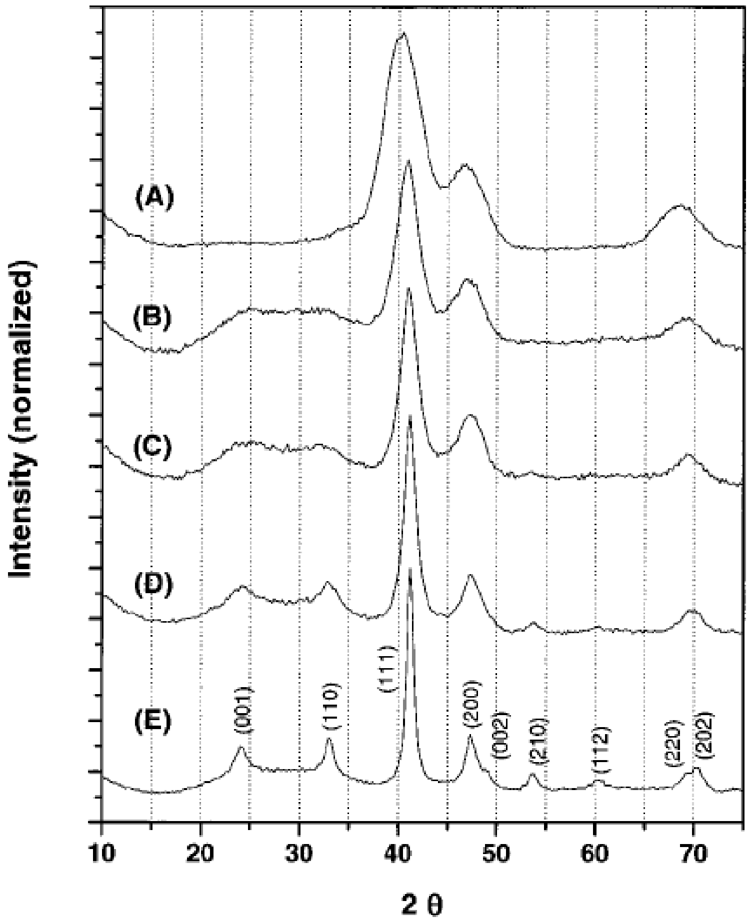
(A) TEM micrograph of a 3D assembly of 6-nm as-synthesized Fe50Pt50 particles.

(**B**) TEM of a 3D assembly of 6-nm Fe50Pt50 sample after replacing oleic acid/oleyl amine with hexanoic acid/hexylamine.



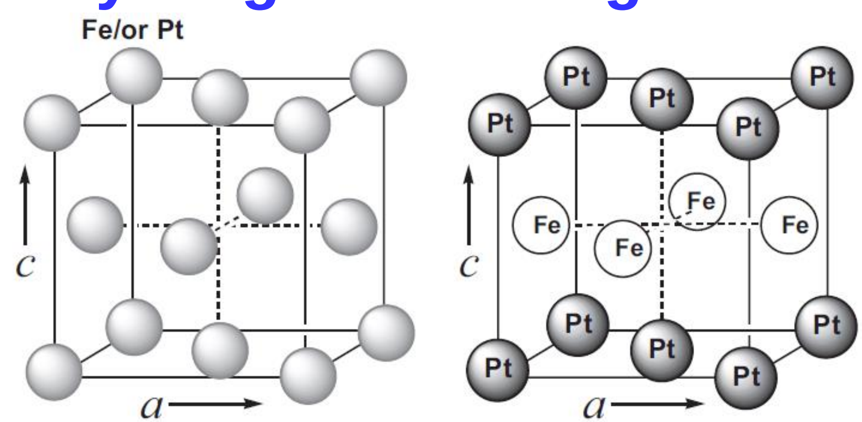
Synthesis of Fe-Pt alloys Magnetic Nanoparticles

XRD patterns (A) of as-synthesized 4-nm $Fe_{52}Pt_{48}$ particle assemblies and samples annealed under atmospheric N_2 gas for 30 min at temperatures of (B) 450ºC, (C) 500ºC, (D) 550ºC, and (E) 600ºC. The indexing for fct FePt reflections



1) As synthesized particles have fcc Structure (weakly magnetic),

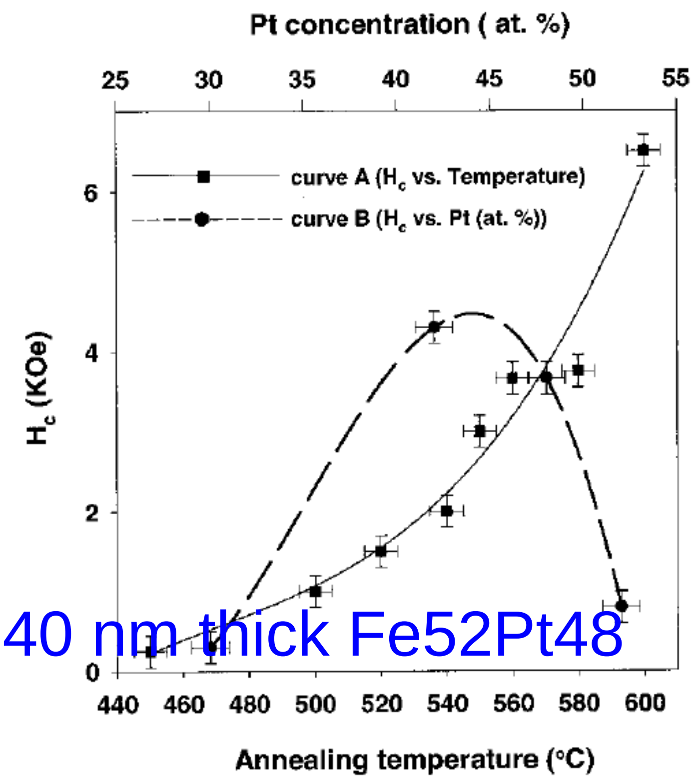
2) After annealing at 560 ºC, fct phase (highly magnetic) was generated, important for high areal density magnetic storage media.



Sun and Murray, *Science* **2000**, 287, 1989.

SQUID results of Fe-Pt Nanocrystals

Curve A shows the in-plane coercivity of a series of ;140-nm-thick, 4-nm $Fe_{52}Pt_{48}$ assemblies as a function of annealing temperature. Each sample is annealed for 30 min under 1 atm of N_2 gas.
Curve B indicates the composition-dependent coercivity of ;140-nm-thick FePt assemblies annealed at 560ºC for 30 min.



140 nm thick Fe52Pt48

As synthesized particles:

superparamagnetic at RT

and Blocking temp of 20-30K

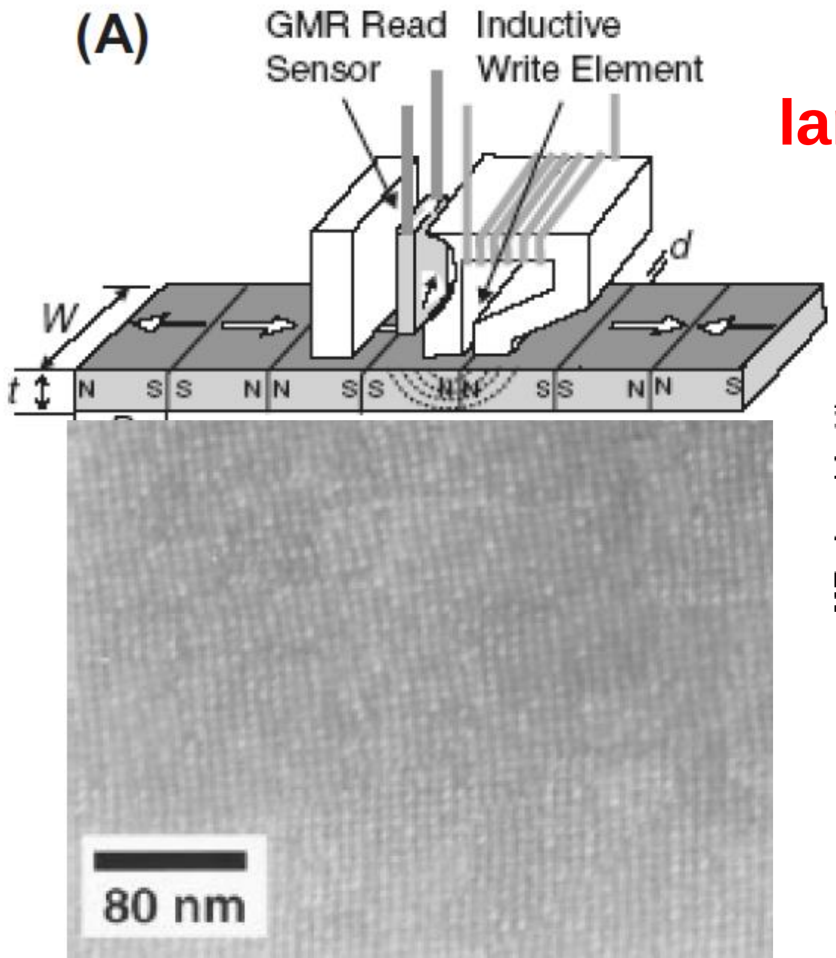
After annealing at 600C→ fct phase

RT ferromagnetic

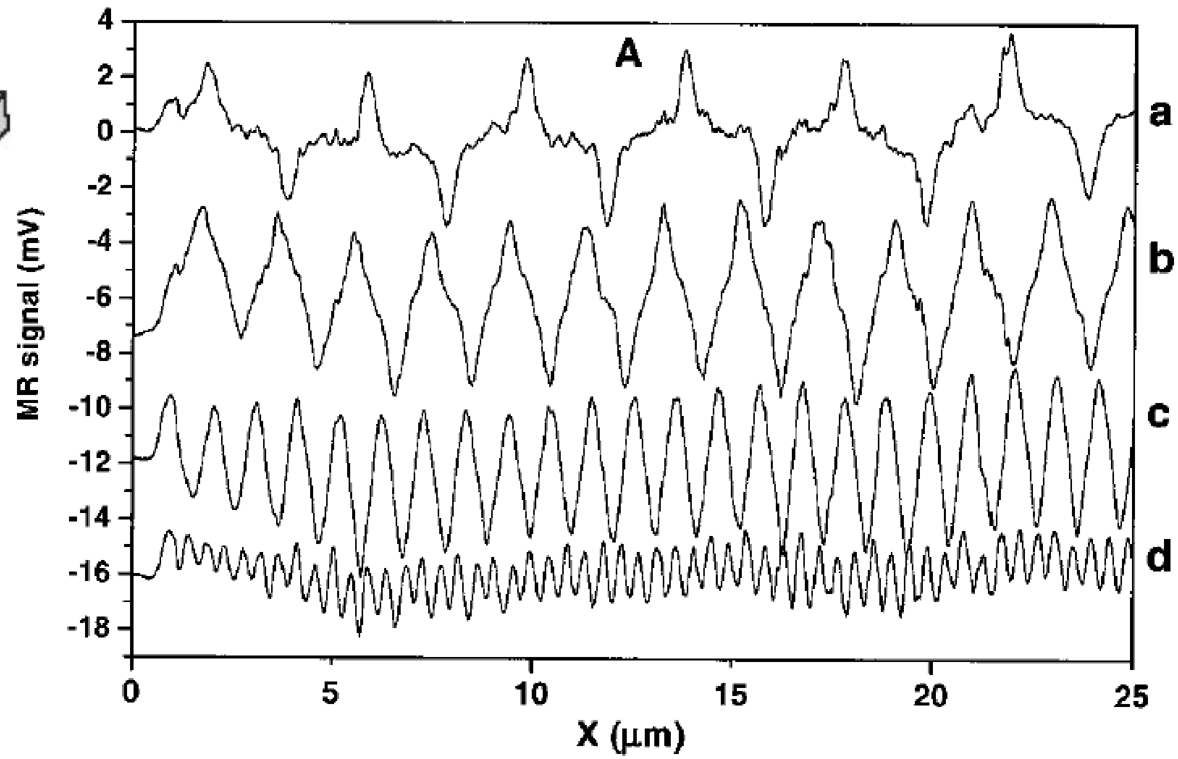
Sun and Murray, *Science* **2000**, 287, 1989.

Demonstration of > terabit/in^2 magnetic storage media

Magneto-resistive (MR) read-back signals from written bit transitions in a 120-nm-thick assembly of 4-nm-diameter $Fe_{48}Pt_{52}$ nanocrystals. The individual line scans reveal magnetization reversal transitions at linear densities of (a) 500, (b) 1040, (c) 2140, and (d) 5000 fc/mm.



Recording densities about 10 times larger than the CoCr-based alloy media



Direct Synthesis of Monodisperse Magnetite Nanocrystals from Controlled Thermolysis of Fe-Oleate Complex Without Size Sorting Process (HEAT-UP PROCESS)

The monodisperse iron ferrite nanocrystals were produced from the thermal decomposition of an iron-oleate complex, which was synthesized from a reaction between $Fe(CO)_5$ and oleic acid at ~ 100 ^oC, followed by the controlled chemical oxidation using trimethylamine *N*-oxide as a mild oxidant.

T. Hyeon *et al. J. Am. Chem. Soc.* 2001, 123, 12798

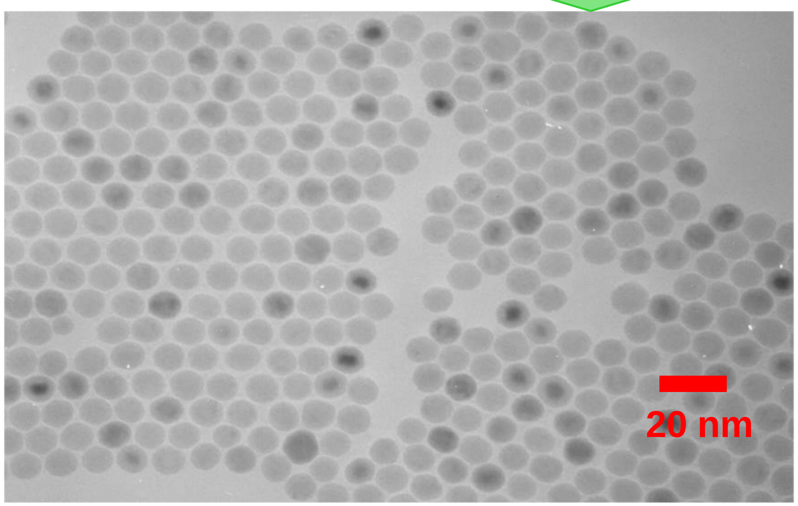
Heat-up Process:

Direct Synthesis of Monodisperse 11 nm Magnetite Nanocrystals Without Size Sorting Process by Heating Fe-Oleate Complex to 320^{o}C followed by aging for 10 min

T. Hyeon *et al.* *J. Am. Chem. Soc.* 2001, 123, 12798

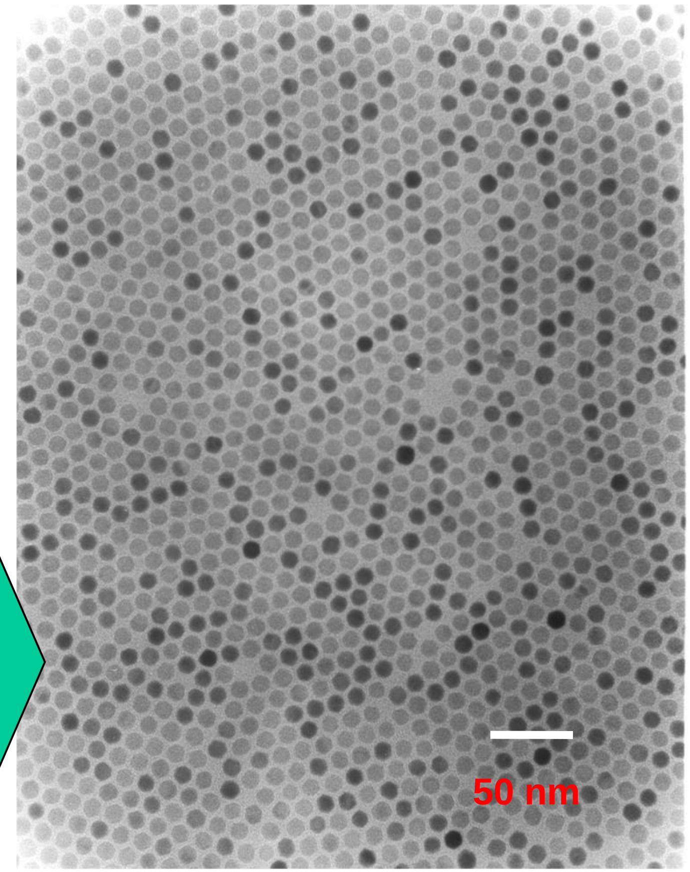
Heat-up Process to produce Uniform Fe_3O_4 Nanocrystals by slowing heating Fe-oleate complex to 320 °C

Slowly heating Fe-oleate complex
from R.T. to 320 °C
followed by Aging for ~ 10 min



11 nm Fe nanoparticles

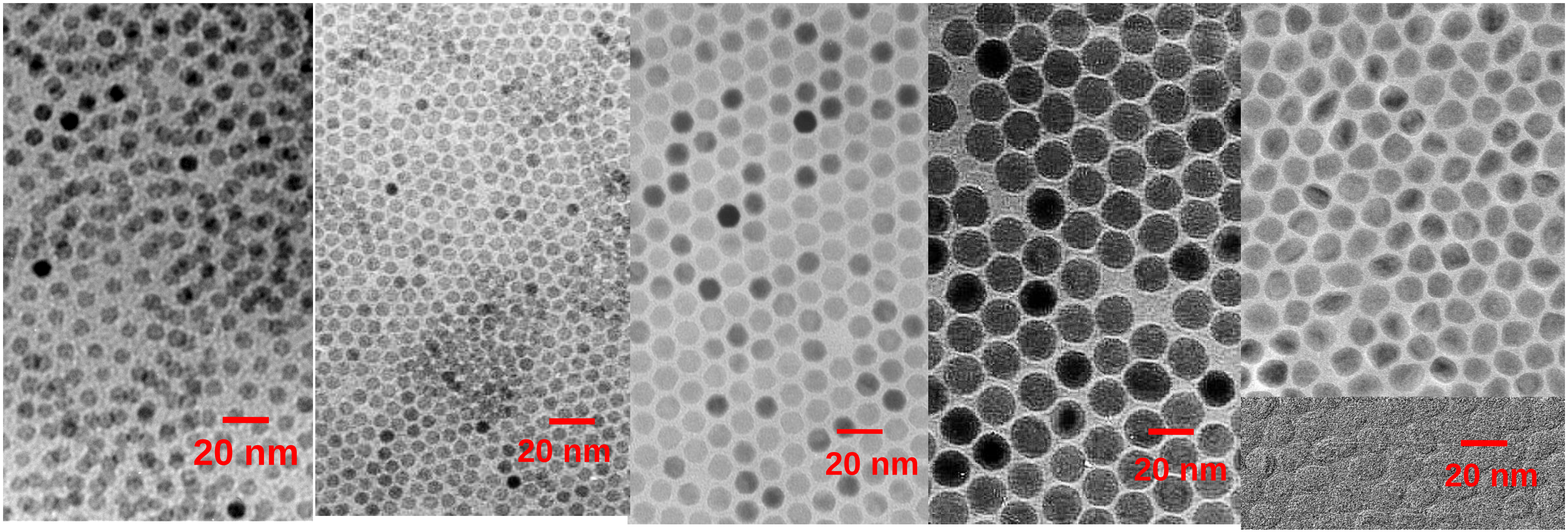
Controlled
Mild chemical
Oxidation
Using Me_3NO



11 nm Iron oxide
Nanocrystals

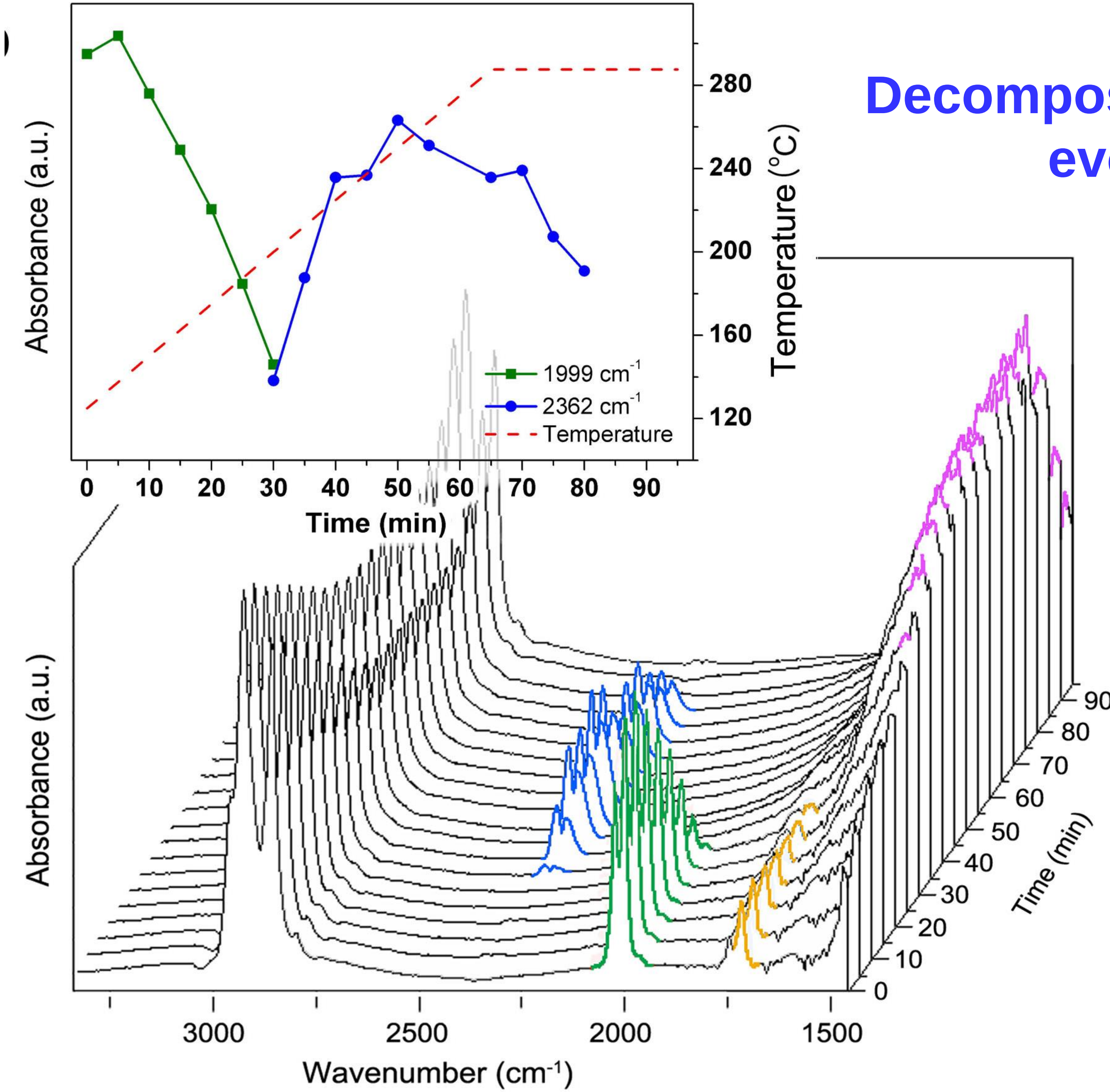
Size-controlled Synthesis of Monodisperse Iron Oxide Nanocrystals without a Size Selection Process!!!

4 nm 8 nm 11 nm 13 nm 20 nm



Particle size was controlled by varying experimental conditions such as ratios of $Fe(CO)_5$ and Oleic acid.

T. Hyeon *et al. J. Am. Chem. Soc.* **2001**, 123, 12798.



Decomposition of $Fe(CO)_5$ with evolution of CO_2

↓

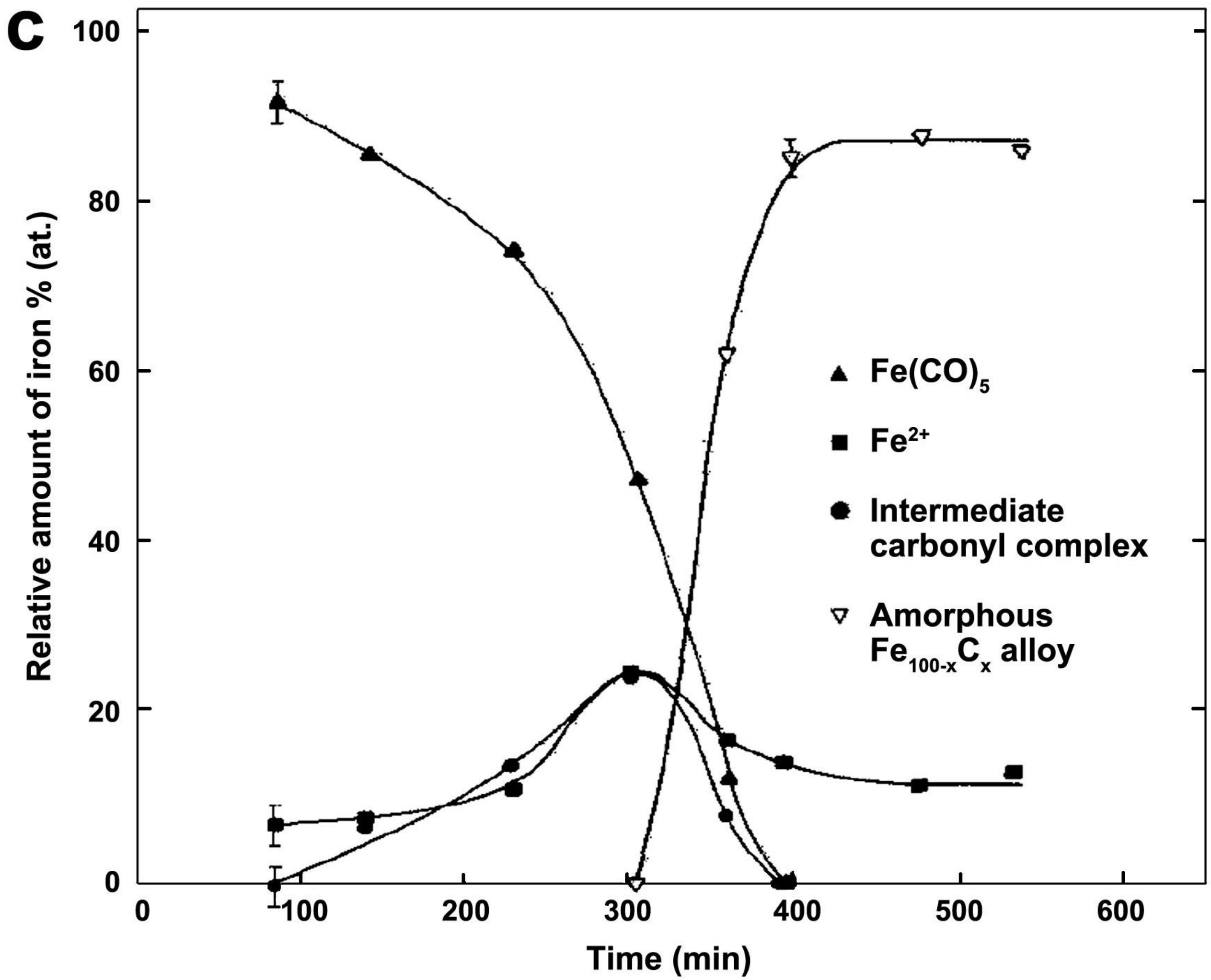
Reaction with oleic acid to generate Fe-Oleate complex (intermediate species)

↓

Further thermolysis to generate Fe-O clusters (monmers)

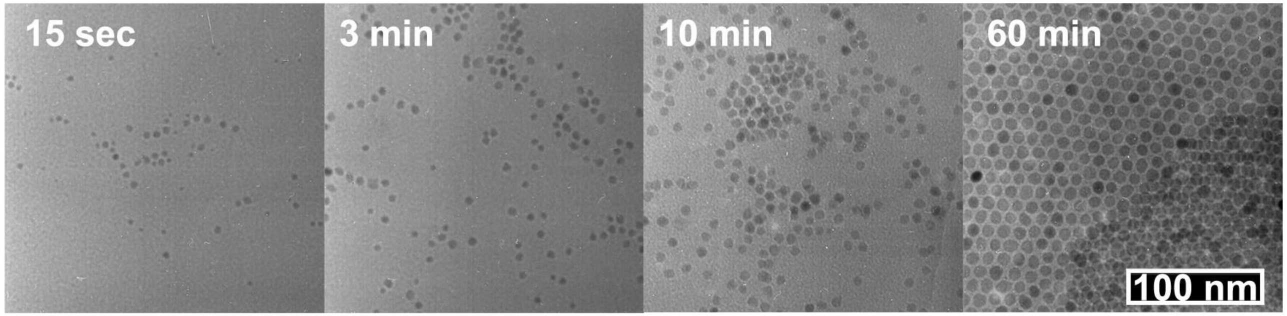
Soon Gu Kwon and Taeghwan Hyeon, *Acc. Chem. Res.* **2008**, 41, 1696-1709.

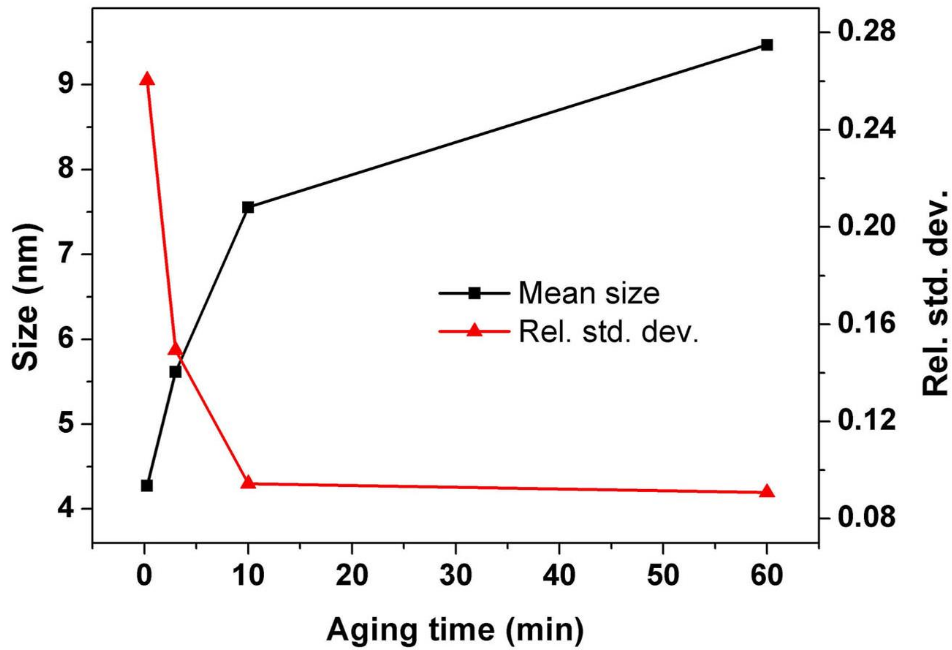
Stabilization of intermediate iron complexes delays nucleation process and, consequently, these intermediate species accumulate in the solution.



Soon Gu Kwon and Taeghwan Hyeon, *Acc. Chem. Res.* **2008**, 41, 1696-1709.

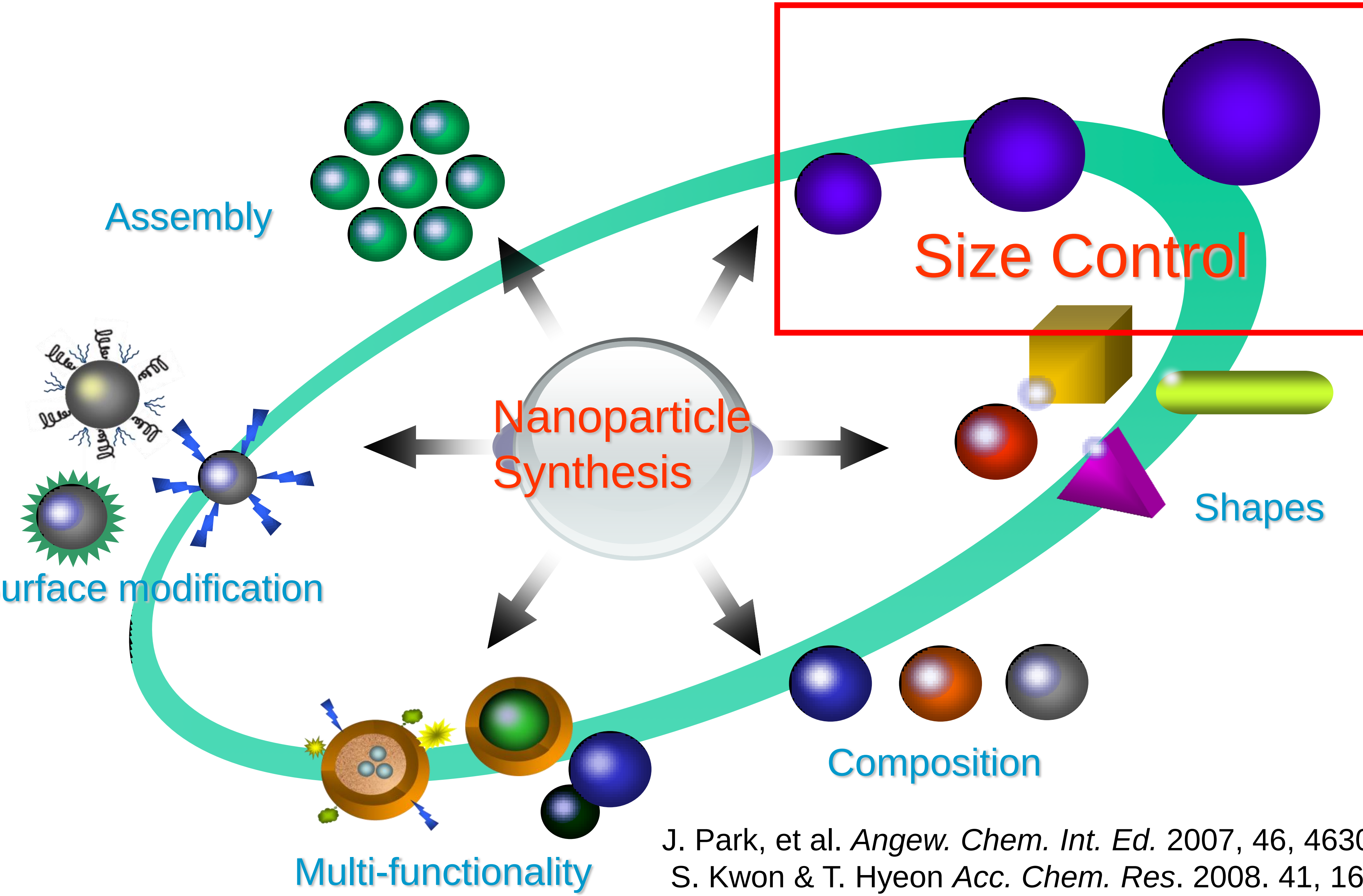
Following the intermediate step, nucleation start suddenly. Temporal change of nanoparticle size distribution was almost terminated within 10 min after nucleation, during which mean size increase and decrease of σ_r occurred simultaneously.





Soon Gu Kwon and Taeghwan Hyeon, *Acc. Chem. Res.* **2008**, 41, 1696-1709.

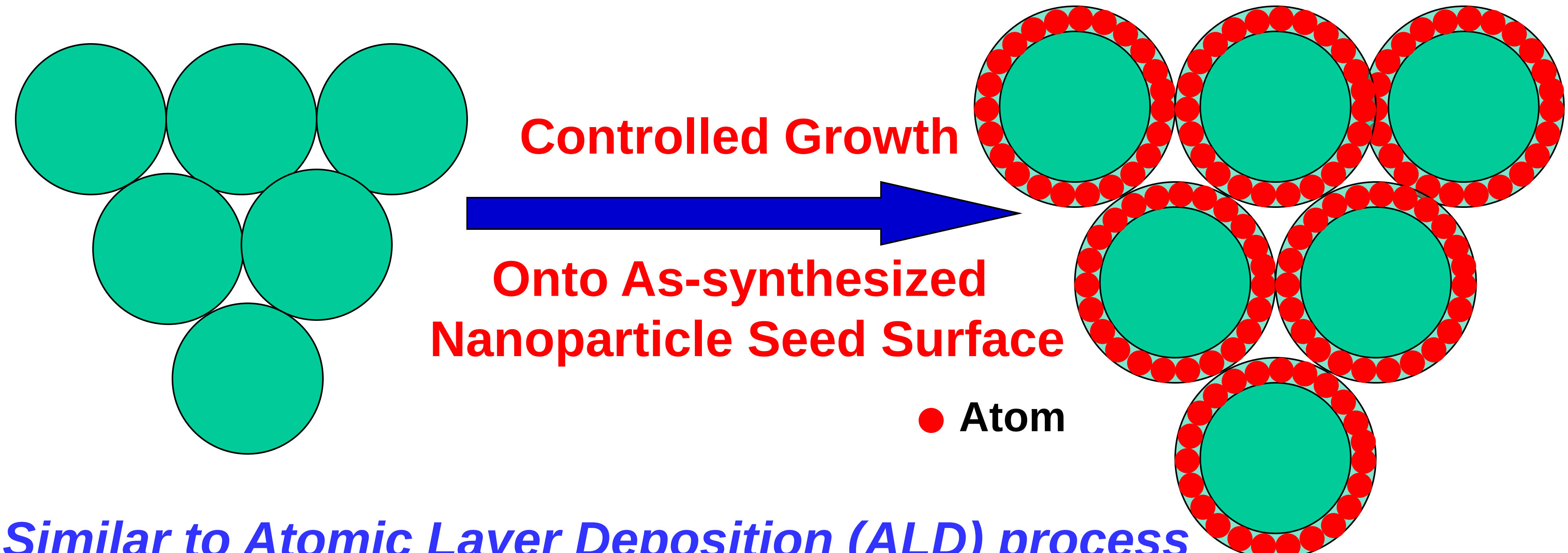
Key Issues in Nanocrystal Synthesis



J. Park, et al. *Angew. Chem. Int. Ed.* 2007, 46, 4630
S. Kwon & T. Hyeon *Acc. Chem. Res*. 2008. 41, 1696.

1-nm-level-diameter Controlled Synthesis of Monodisperse Magnetite Nanoparticles without a Size Selection Process

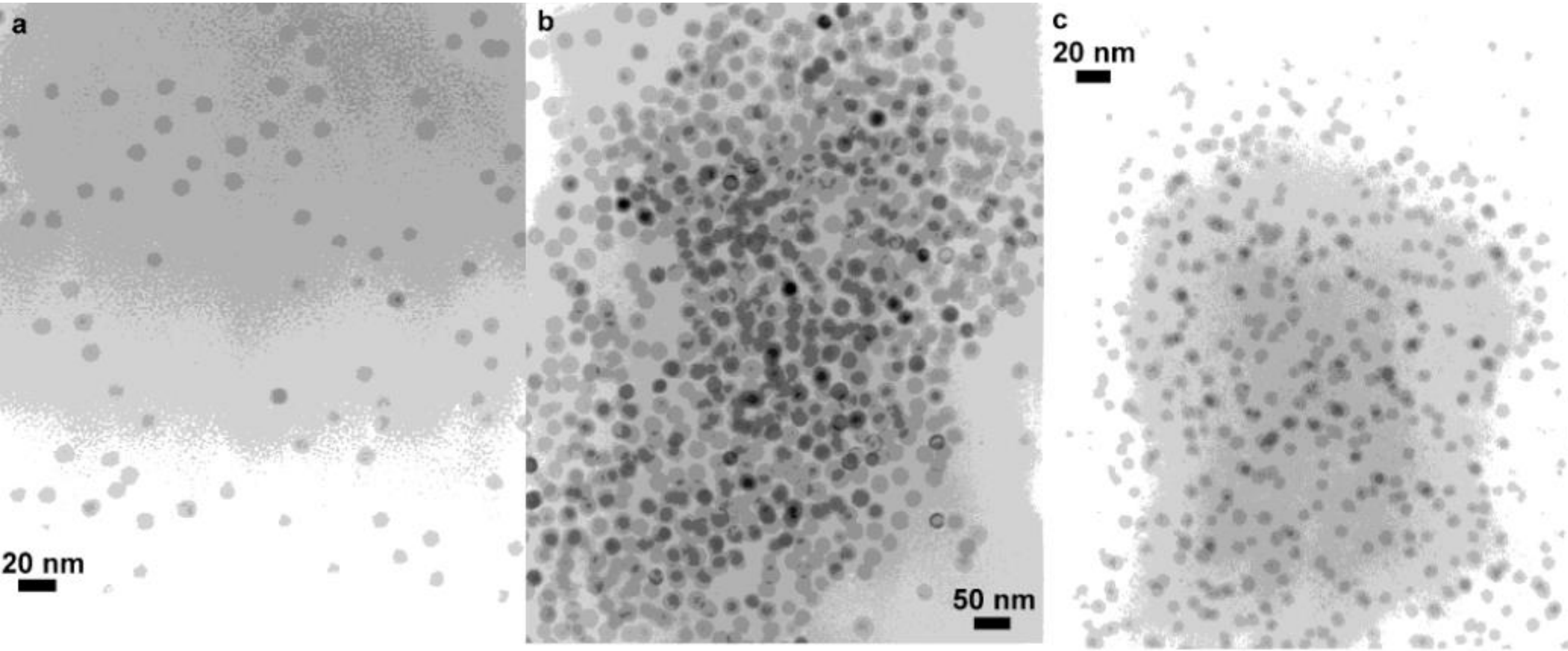
Controlled Synthesis of Monodisperse Nanoparticles via Seed-mediated Growth process (Heterogeneous Nucleation)



Similar to Atomic Layer Deposition (ALD) process

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

Heterogeneous Seeded Growth to Synthesize Monodisperse Nanoparticles of Bi, Sn, In using Au_{101} cluster seeds



W. E. Buhro, *J. Am. Chem. Soc.* **2001,** *123*, 9198.

Also See Finke *et al*, *J. Am. Chem. Soc.* **1997,** *119*, 10382.

Monodisperse 9 nm nanoparticles from controlled growth of 8 nm nanoparticles with Fe-oleate complex

Addition of Separately-prepared Fe-oleate complex into 8 nm sized monodisperse Fe nanoparticles

↓

Aging of the mixture at 350 ºC

↓

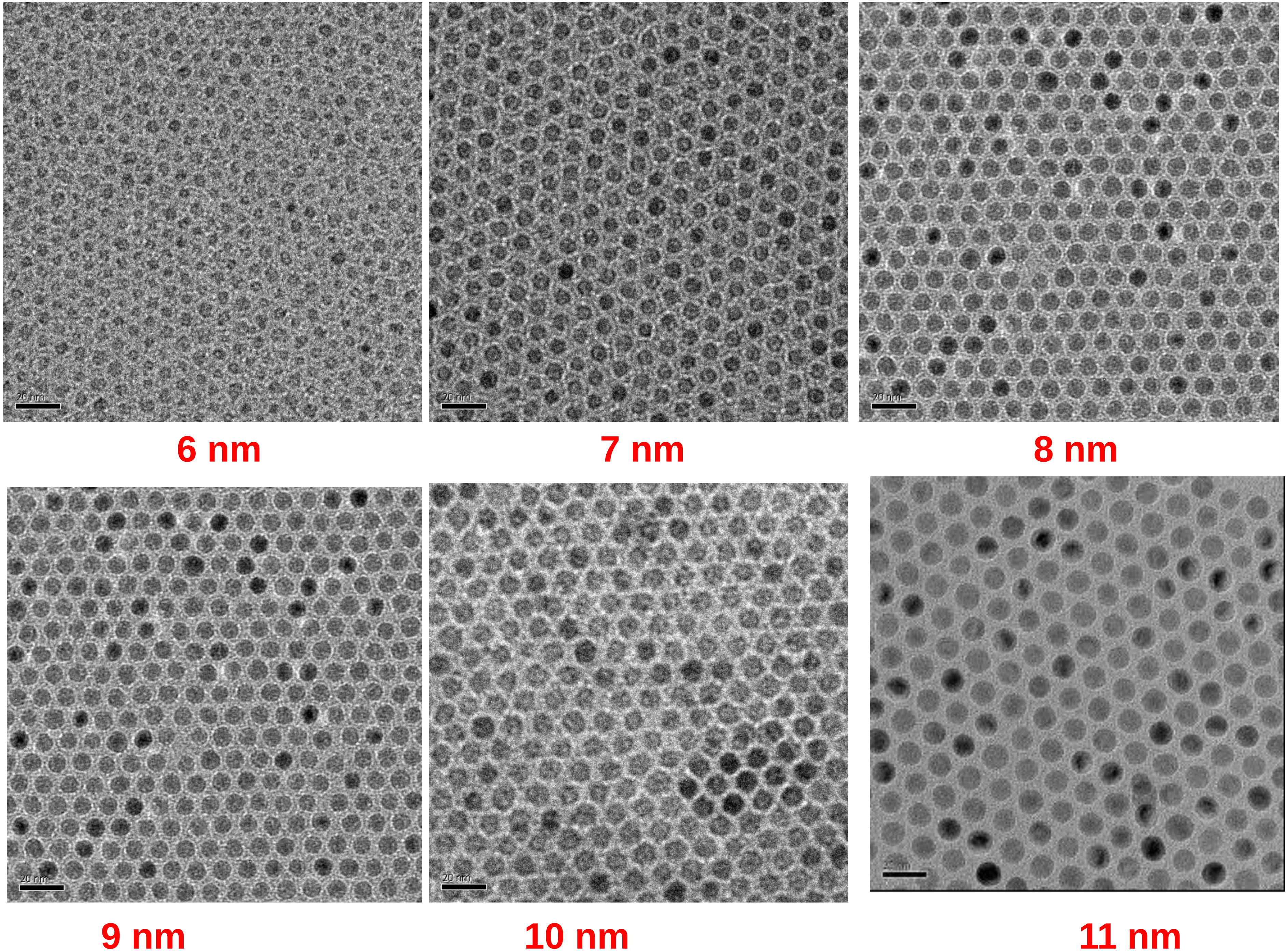
Synthesis of monodisperse 9 nm Fe nanoparticles

↓

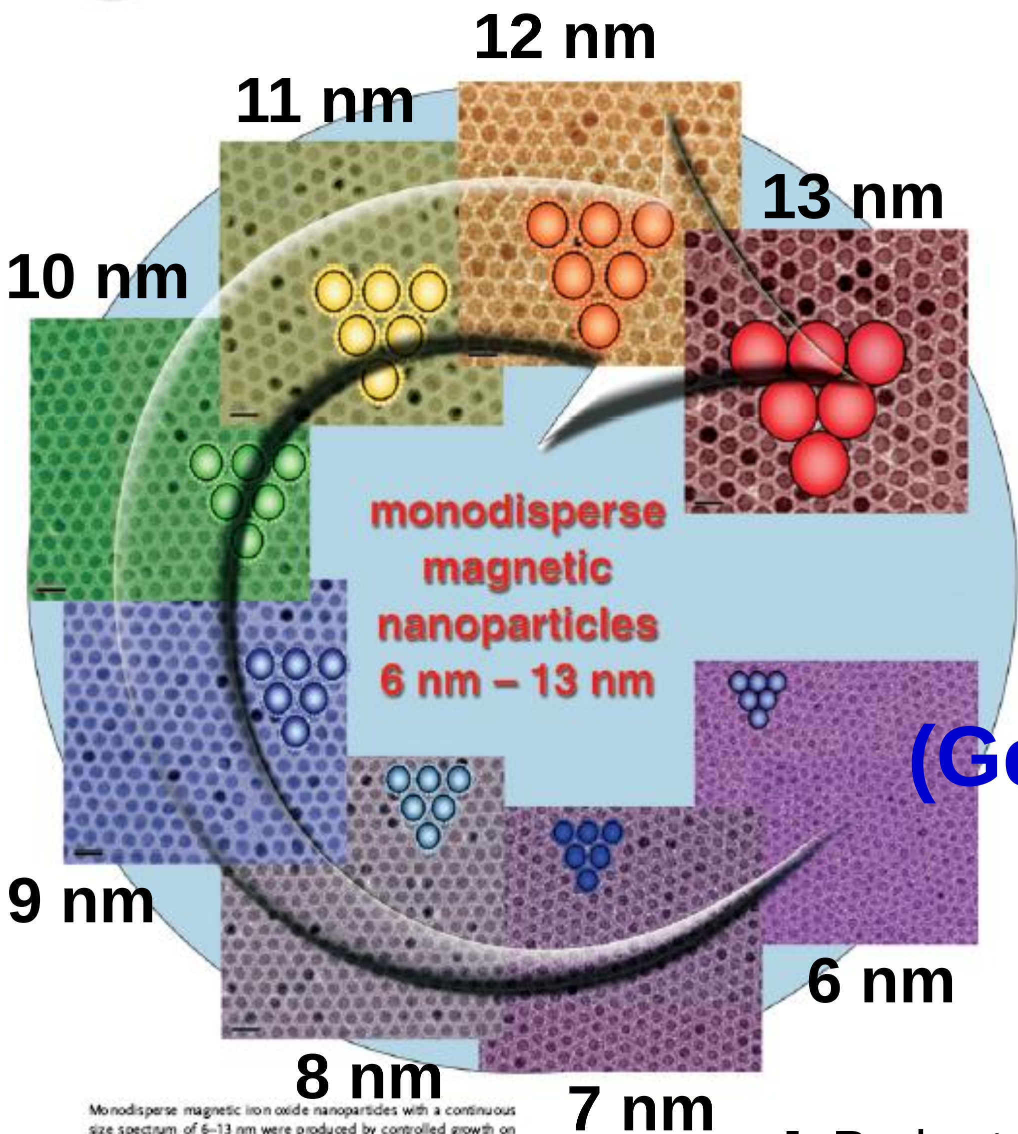
Chemical Oxidation

↓

9 nm monodisperse Iron Oxide Nanocrystals


6 nm
7 nm
8 nm
9 nm
10 nm
11 nm

Communications



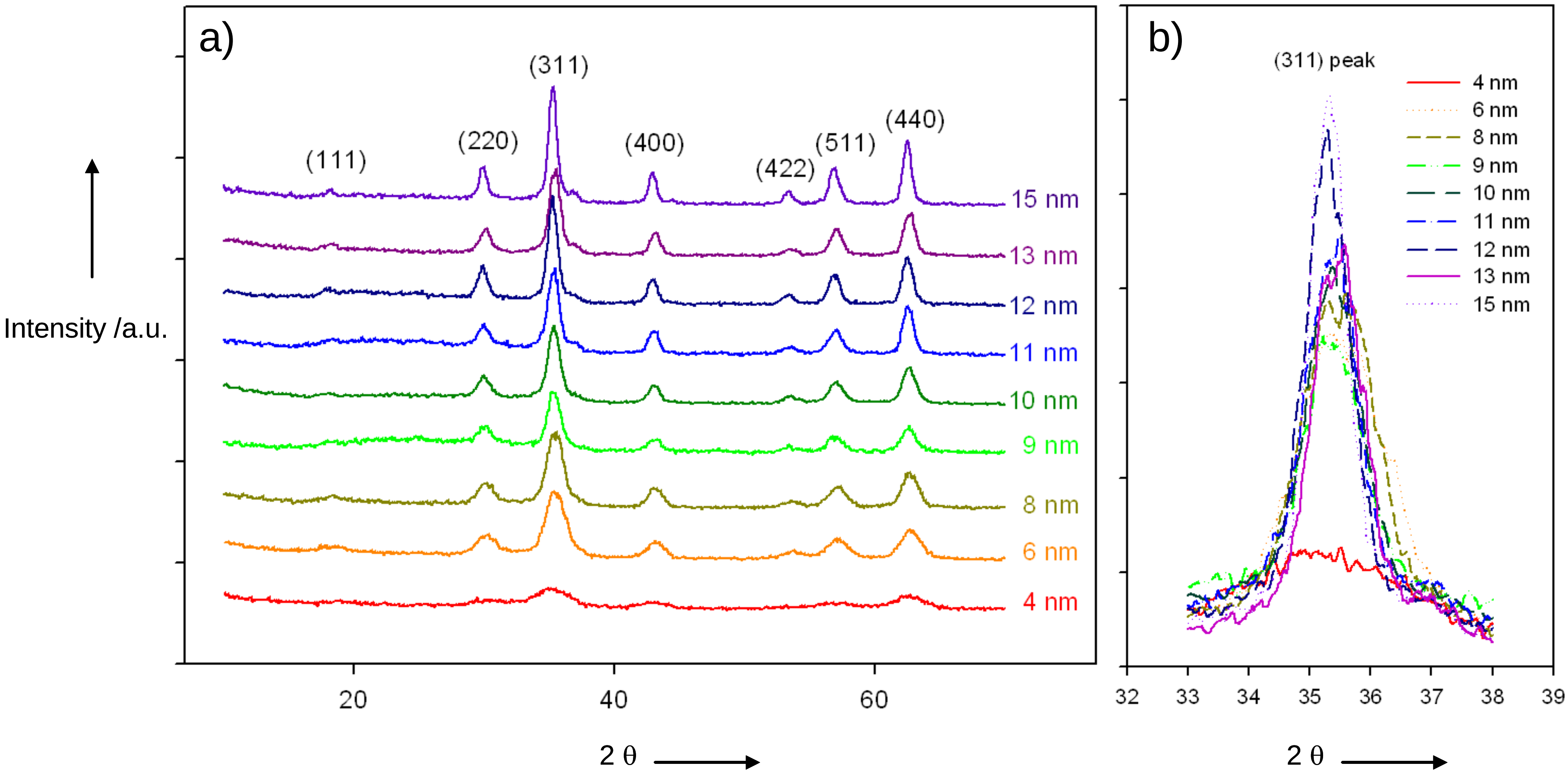
Monodisperse magnetic iron oxide nanoparticles with a continuous size spectrum of 6–13 nm were produced by controlled growth on previously synthesized monodisperse nanoparticle seeds. The detailed synthetic procedure and characterization is described in the communication by T. Hyeon et al. on the following pages.

Frontipiece article for Communications in Angew. Chem. (German Chemical Society)

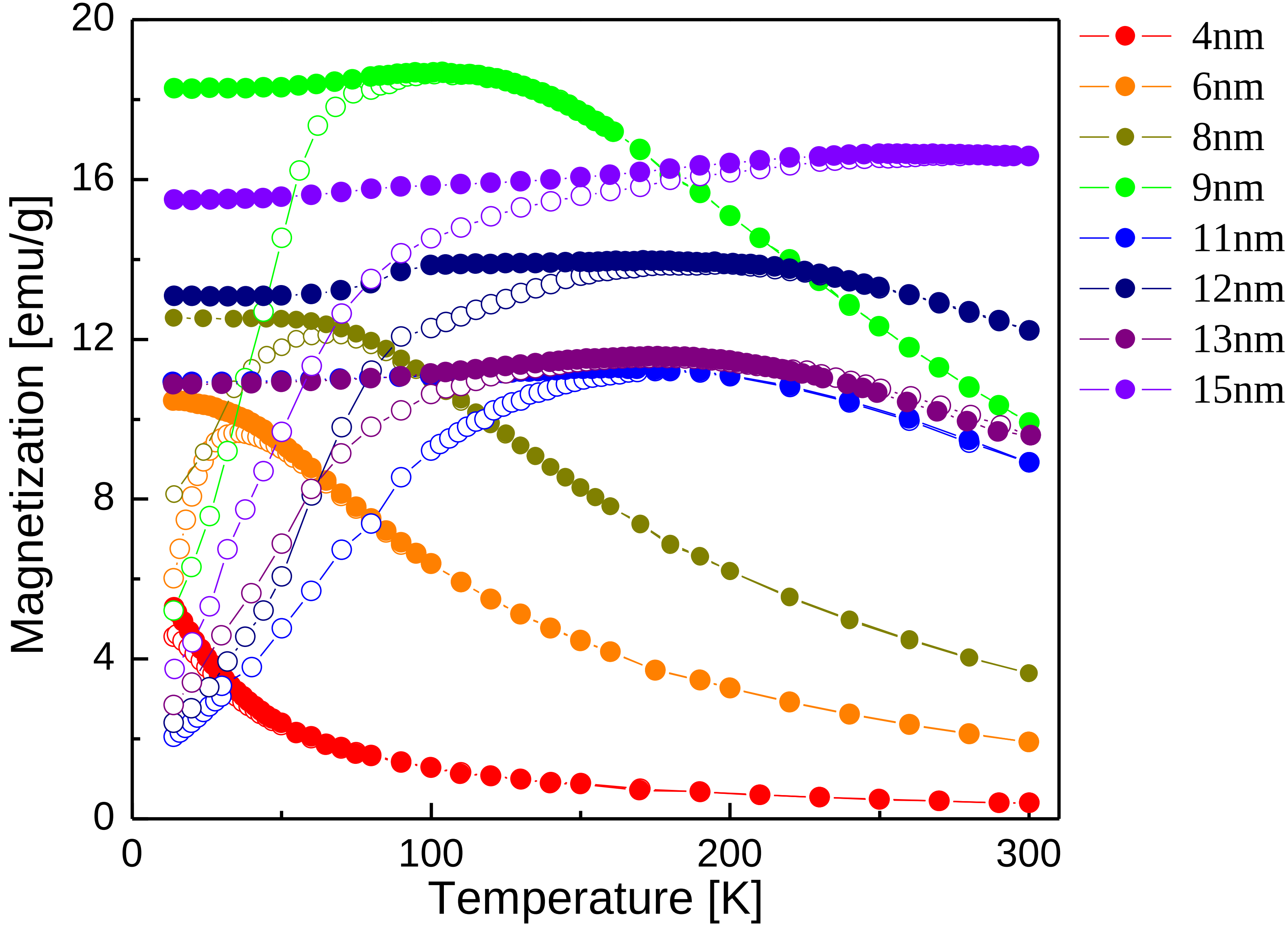
J. Park *et al.*, *Angew. Chem. Int. Ed*. **2005**, 44, 2872.

  DOI: 10.1002/anie.200461665 Angew. Chem. Int. Ed. 2005, 44, 2872 – 2877

XRD Patterns of Iron Oxide Nanocrystals



Temperature dependence of magnetization measured after zero-field cooling (ZFC) and field cooling (FC) using 100 Oe

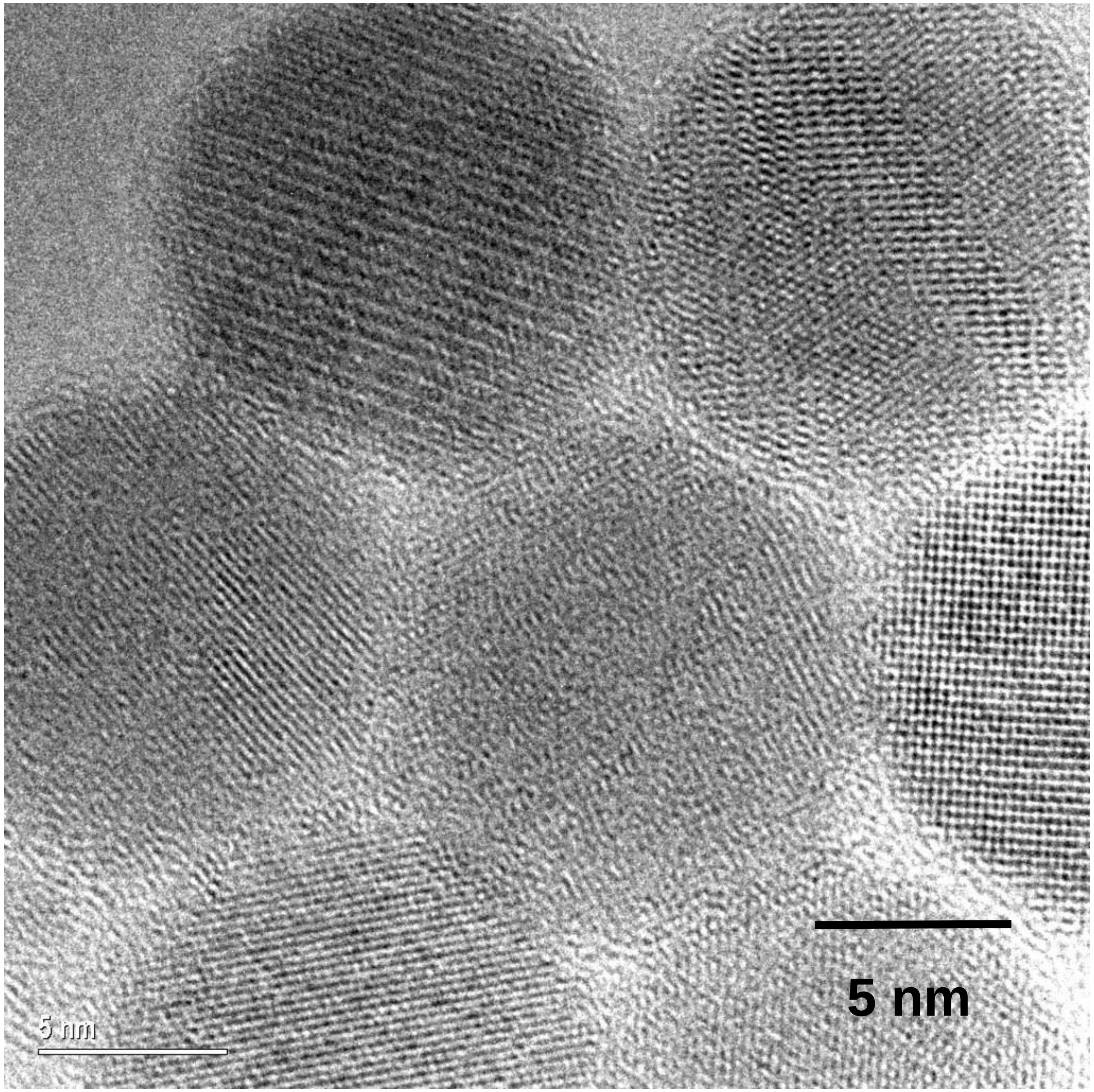


Key Issues in Nanoparticle Synthesis

- **Size uniformity (monodisperse)**
- **Particle Size Control**
- **Crystal structure Characterization**
- Shapes: Nanorods, Nanowires and More
- Large-scale Synthesis via Simple, Inexpensive routes

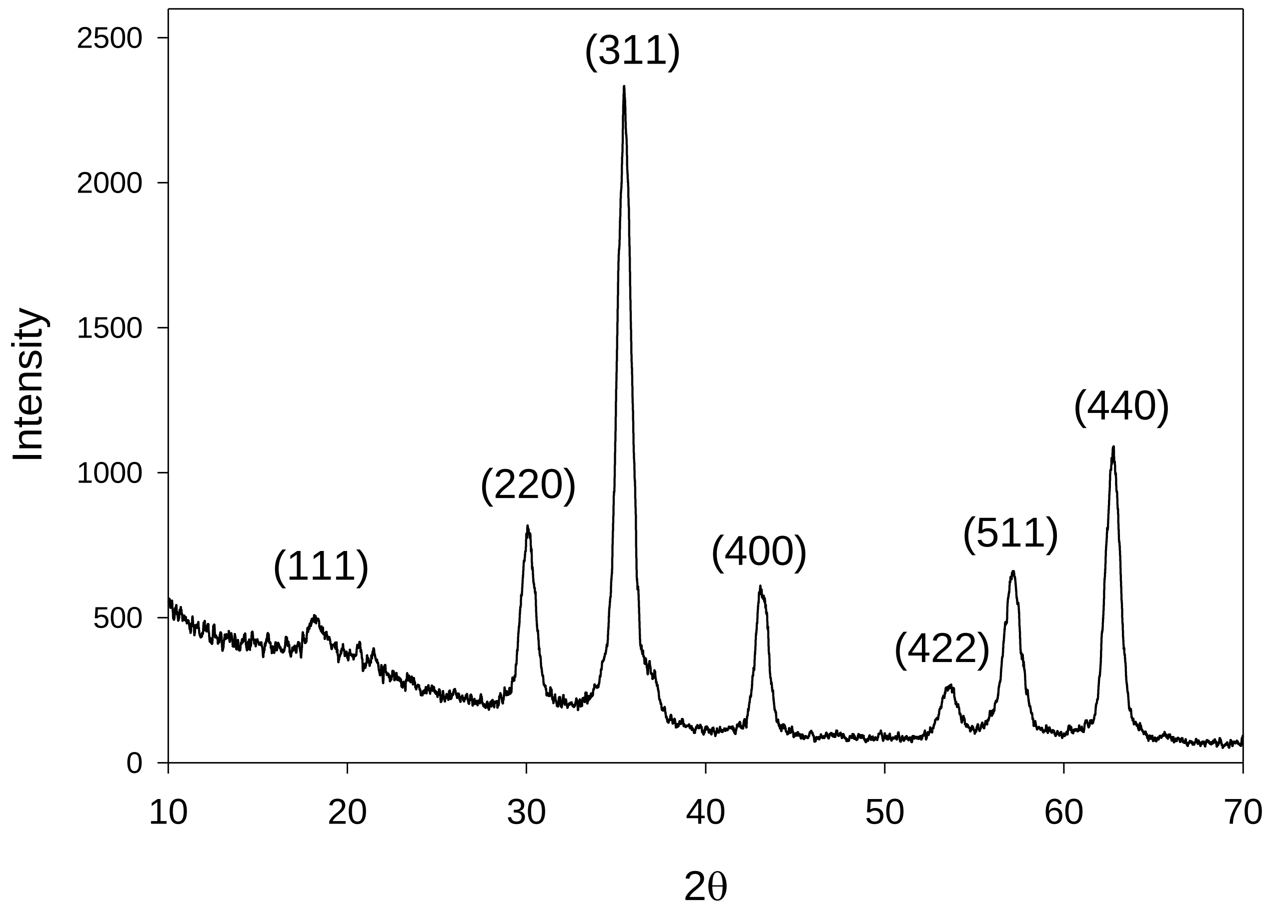
T. Hyeon, *Chem. Comm. (Feature Article)*, **2003**, 927

HRTEM image of 11 nm Iron oxide nanocrystals



Each nanocrystallite is highly crystalline, showing lattice pattern

XRD of 11 nm Iron Oxide Nanocrystals



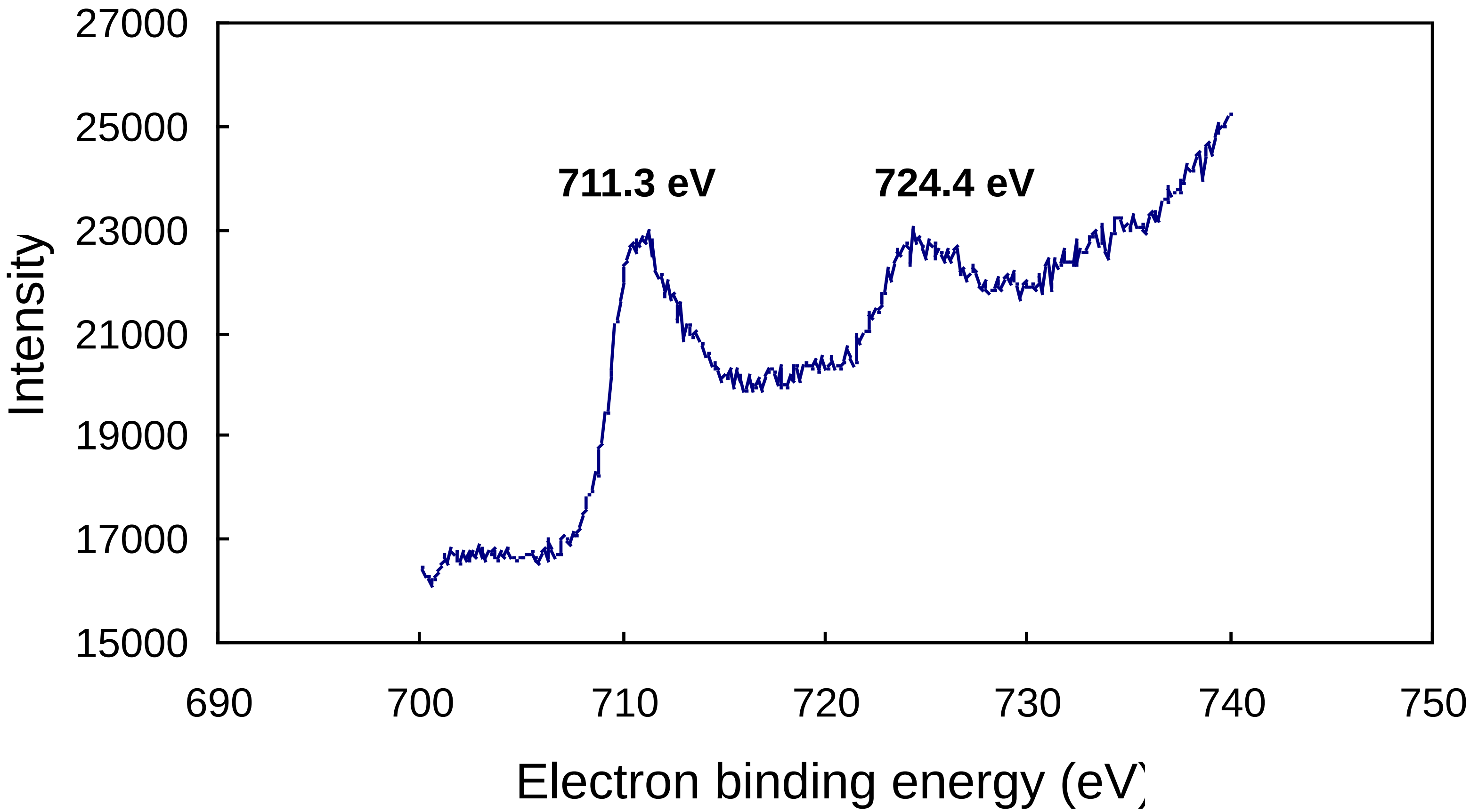
The Nanoparticles are highly crystalline.

Are they Maghemite (γ-Fe_2O_3) or Magnetite (Fe_3O_4)?

Maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) exhibit very similar XRD pattern.

Our Nanoparticles	γ-Fe_2O_3 (Maghemite)	Fe_3O_4 (Magnetite)
2.52	2.518	2.532
2.95	2.953	2.967
2.11	2.089	2.099
1.70	1.705	1.715
1.60	1.607	1.616
1.47	1.476	1.485
1.27	1.273	1.281

We reported the nanoparticles as Maghemite (γ-Fe_2O_3) based on the following XPS data.



The positions of the Fe($2p_{3/2}$) and Fe($2p_{1/2}$) peaks are 711.3 and 724.4 eV, which are in good agreement with the values reported for *γ-Fe_2O_3*.

But the assignment was turned out to be wrong!

XPS is not useful tool to characterize nanoparticles →

INSTEAD,

We started using X-ray absorption spectroscopy (XAS)

Combined with Magnetic Circular Dichroism (MCD) for

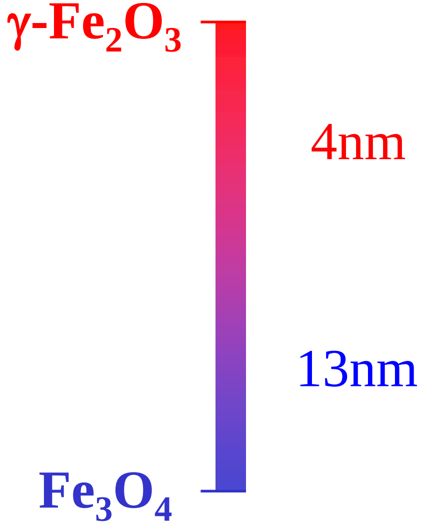
the Structure characterization of Iron oxide nanoparticles.

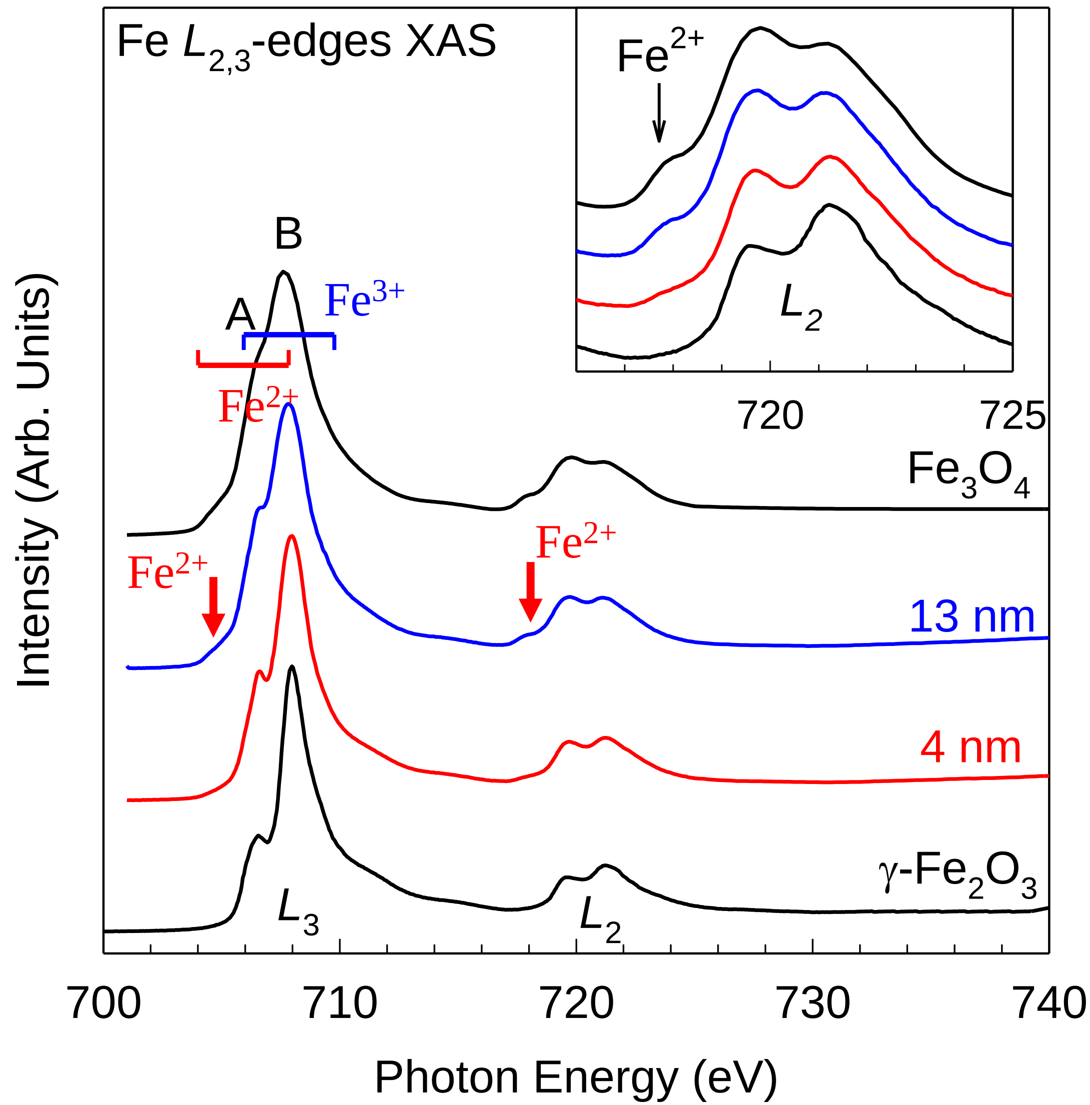
In collaboration with Prof. Jae Hoon Park at POSTECH&PLS

$L_{2,3}$-edge XAS of Spinel Iron-oxide Nanoparticles

Spectra of the nano-particles are Neither pure γ-Fe_2O_3 nor pure Fe_3O_4 but mixtures of γ-Fe_2O_3 and Fe_3O_4.

More Fe^{2+} in the 13 nm than in the 4 nm.



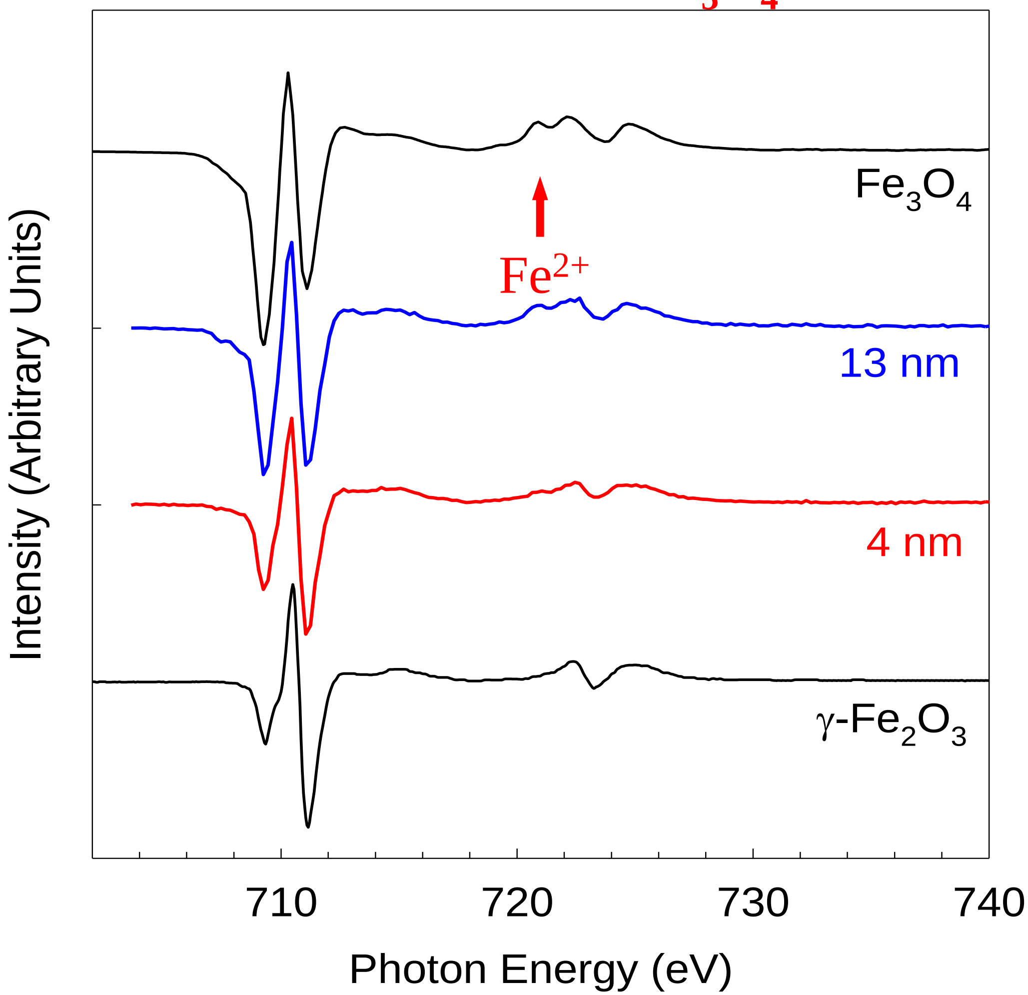


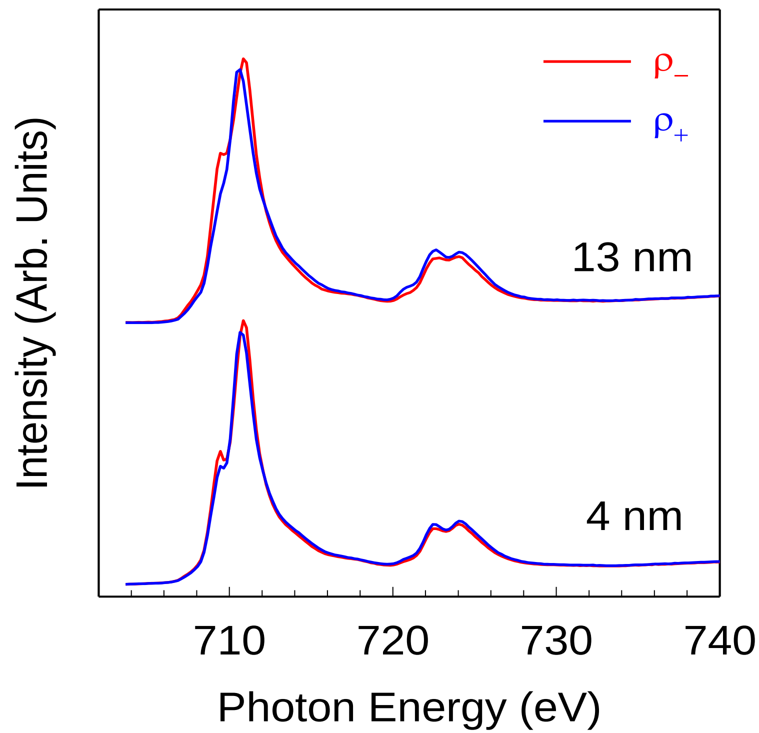
L_{23}-edge XMCD of Iron Oxide Nanoparticles

- Typical Ferrimagnetic behavior.

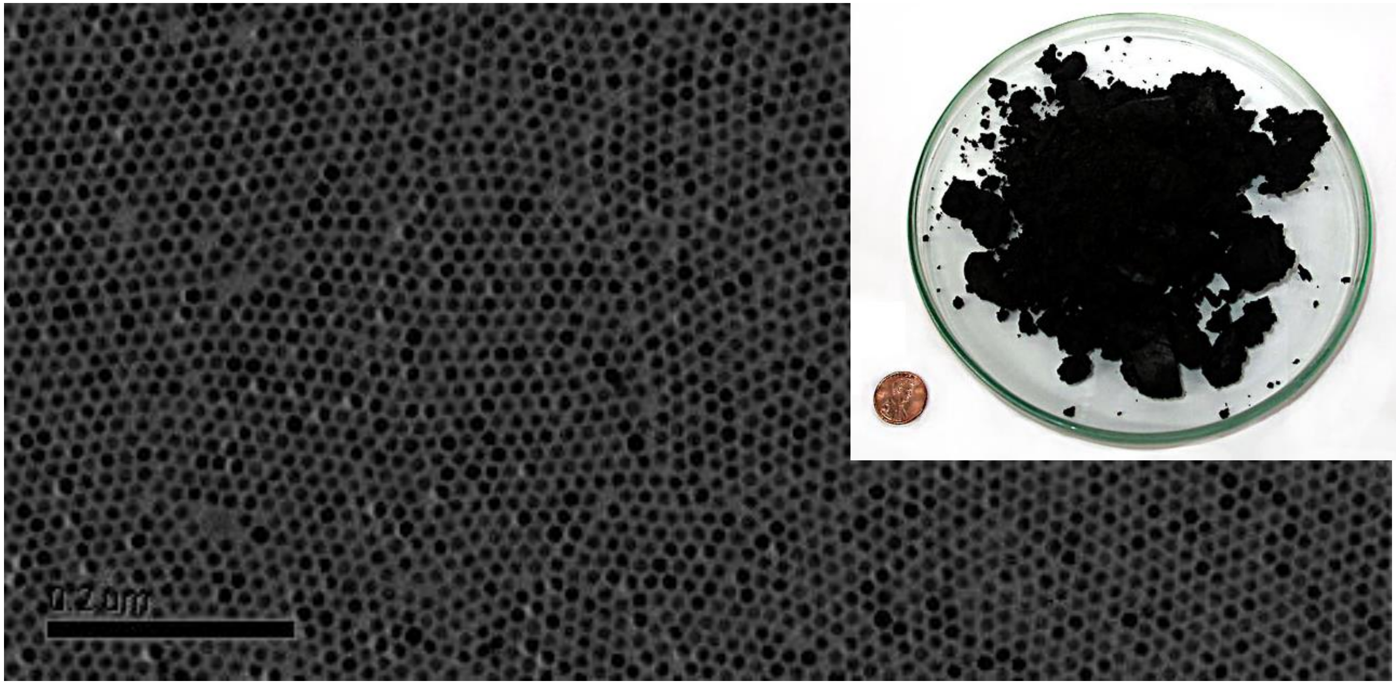
XMCD of 4 nm similar to γ-Fe_2O_3

XMCD of 13 nm similar to Fe_3O_4





Ultra-large-Scale Synthesis of Uniform-sized Nanoparticles

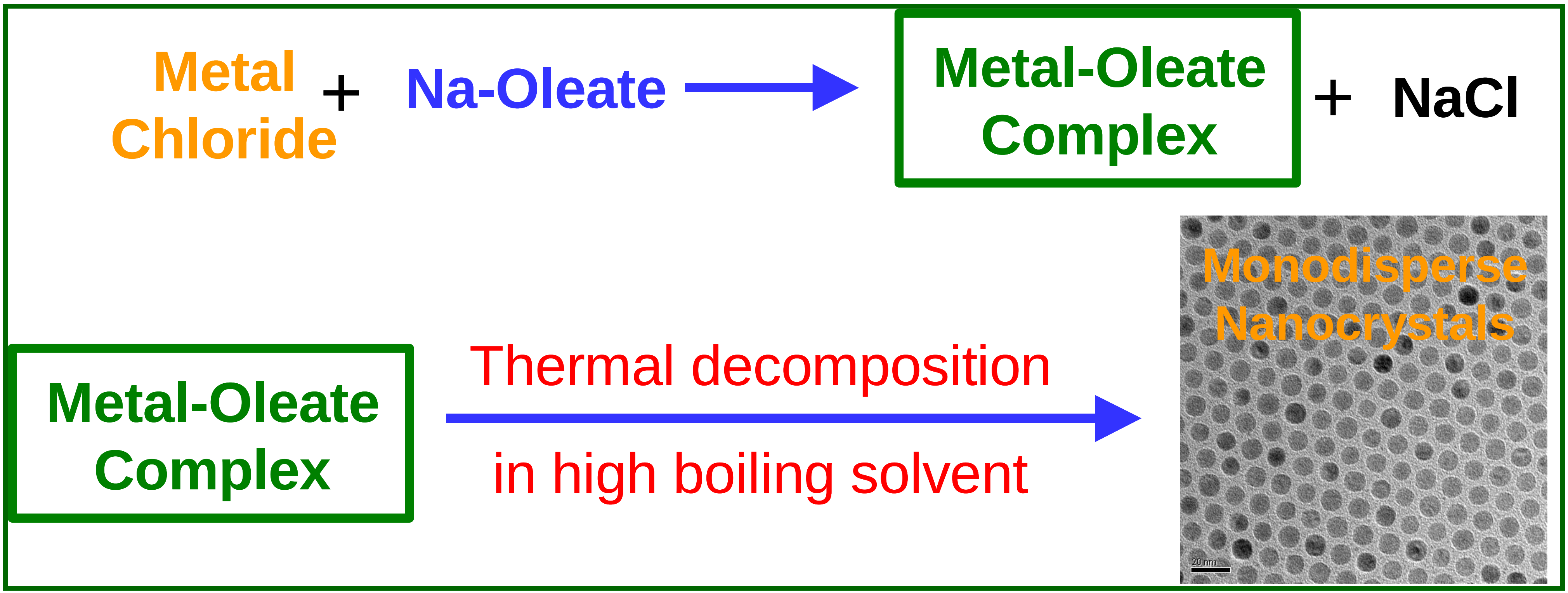


1) Large-scale Synthesis: 40 grams using 1 L reactor
2) Simple and Environmentally-Friendly process
3) Inexpensive using Hydrated Metal chlorides

J. Park *et al., Nature Mater*. **2004**, 3, 891.

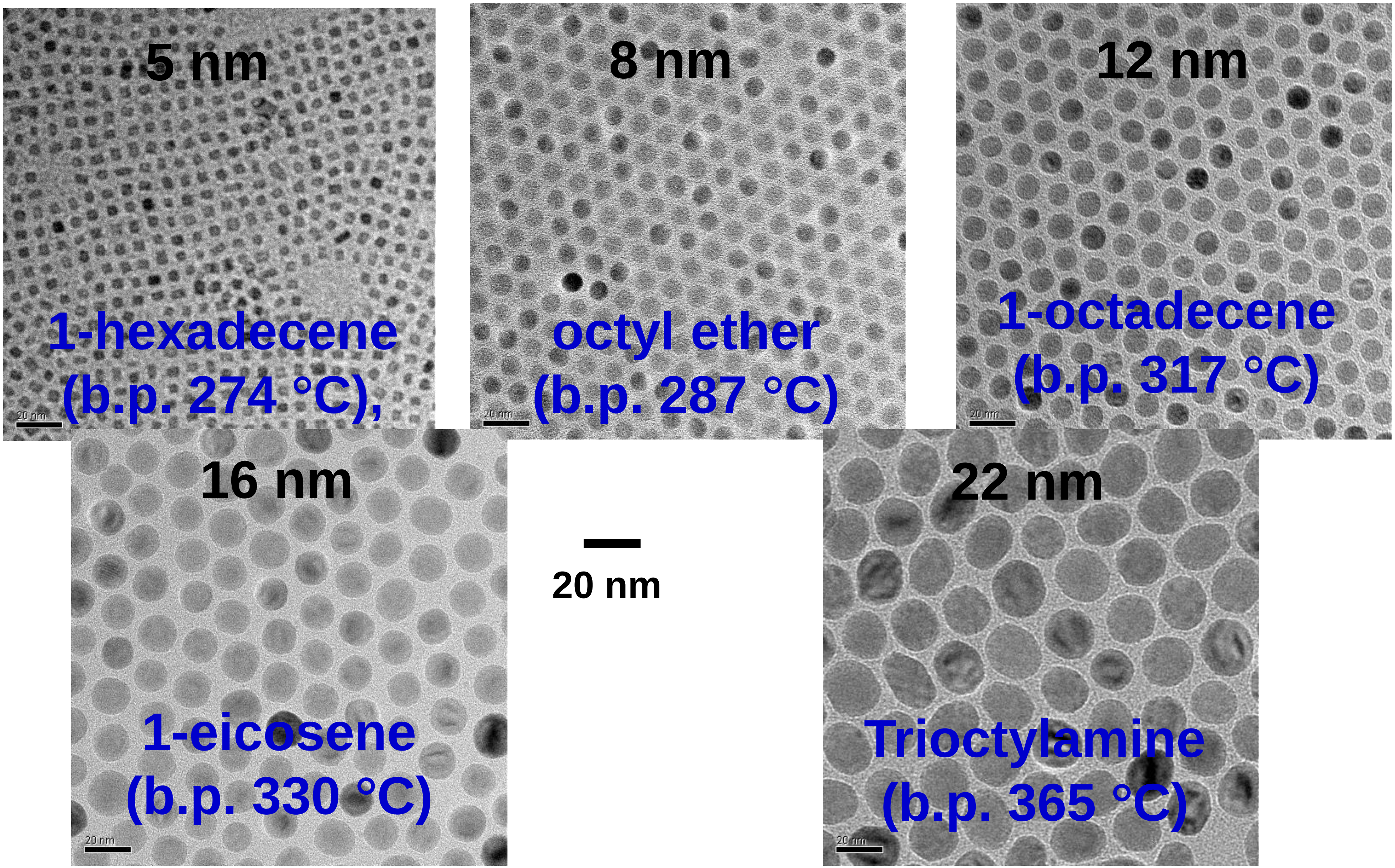
• Iron-oleate complex were prepared by reacting inexpensive and environmentally friendly compounds, namely hydrated iron chloride and sodium oleate.

• The synthesized iron-oleate complex was added to an appropriate high boiling point solvent, and slowly heated to ~ 300 °C to produce the nanocrystals.

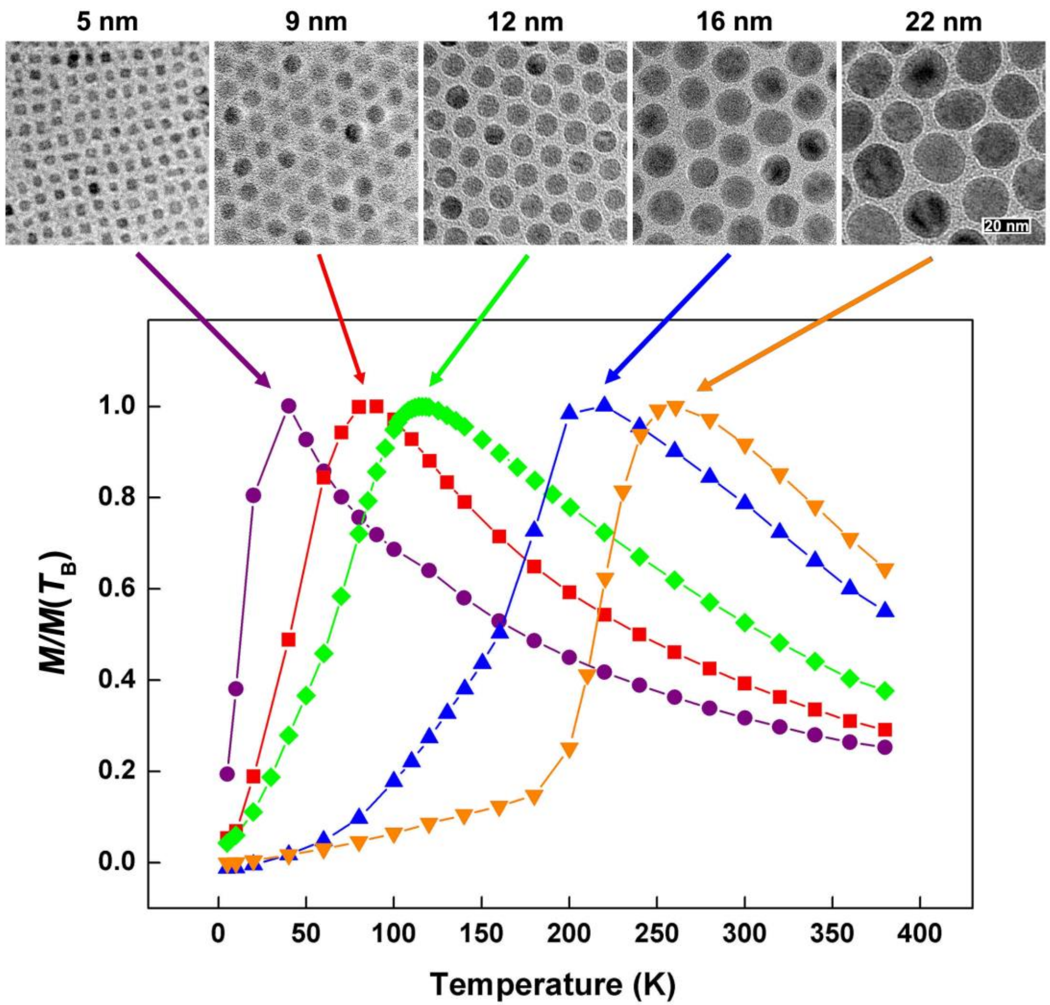


J. Park *et al.*, *Nature Mater*. **2004**, 3, 891.

Particle sizes can be easily controlled by varying the solvents.



Magnetization (*M*) vs. Temperature of iron oxide nanoparticles



1) Temperature dependence of magnetization measured after zero-field cooling (ZFC) using 100 Oe.

2) All of our nanocrystals show superparamagnetic behavior at high temperatures.

3) However, upon cooling, the zero-field cooled magnetization begins to drop and deviate from the field-cooled magnetization at blocking temperature, T_B. It is located at 40 K for the 5 nm sample, and T_B increases continuously as the diameter of the nanocrystals increases: for example, the blocking temperature increases to 260 K for the 22 nm sized nanocrystals.

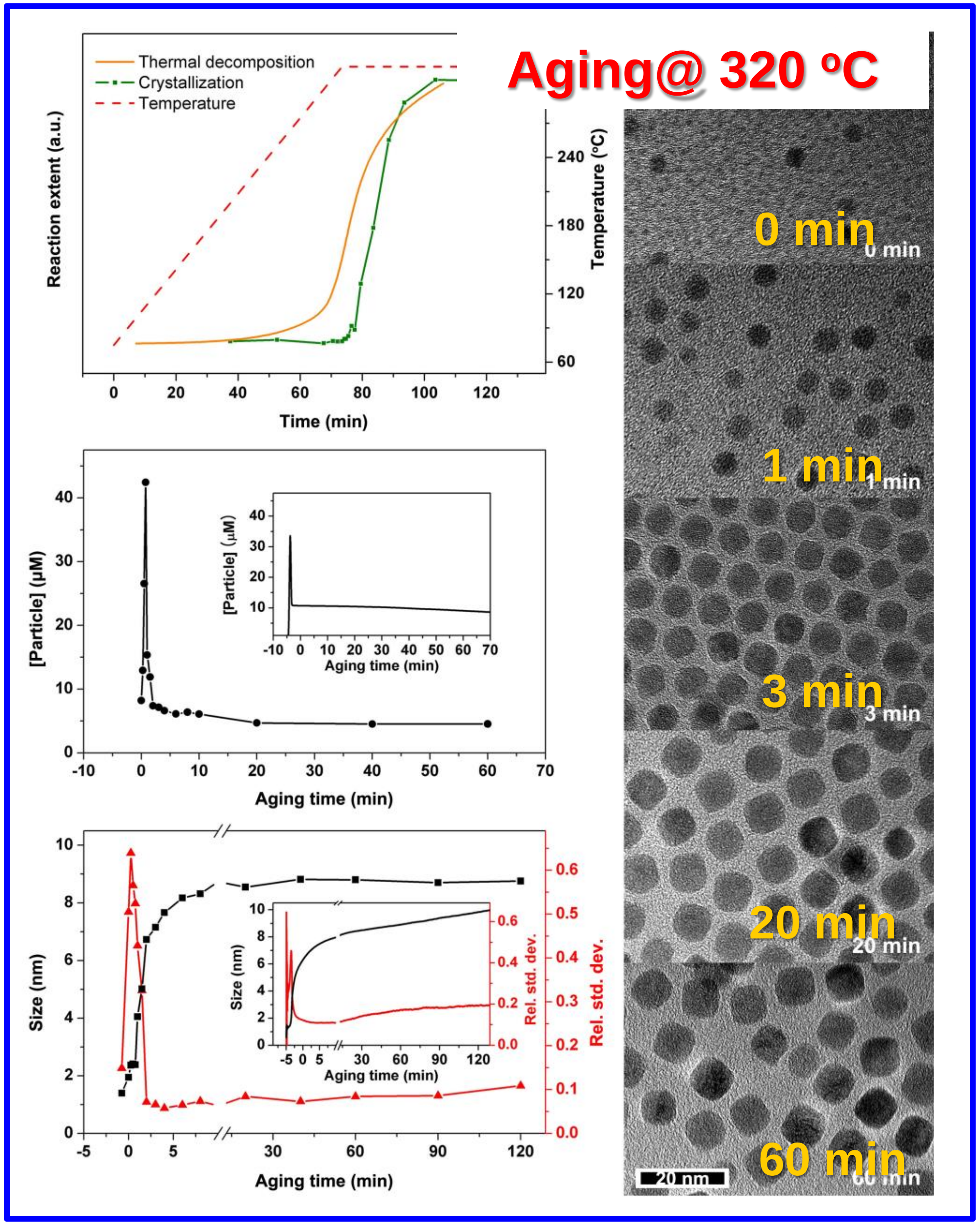
How did it happen ?

(Formation Mechanism for Uniform Nanoparticles)

How were these uniform-sized nanoparticles produced

via “very simple” heat-up of Fe-Oleate complex?

Growth Mechanism of Monodisperse Iron Oxide Nanocrystals by "Heating-up" Process using TEM, TG-MS, Electrochem. & in-situ SQUID



1) 10 min Lag between thermalysis of iron-oleate complex and nanoparticle formation → Formation & accumulation of monomers (polyoxo-clusters?)

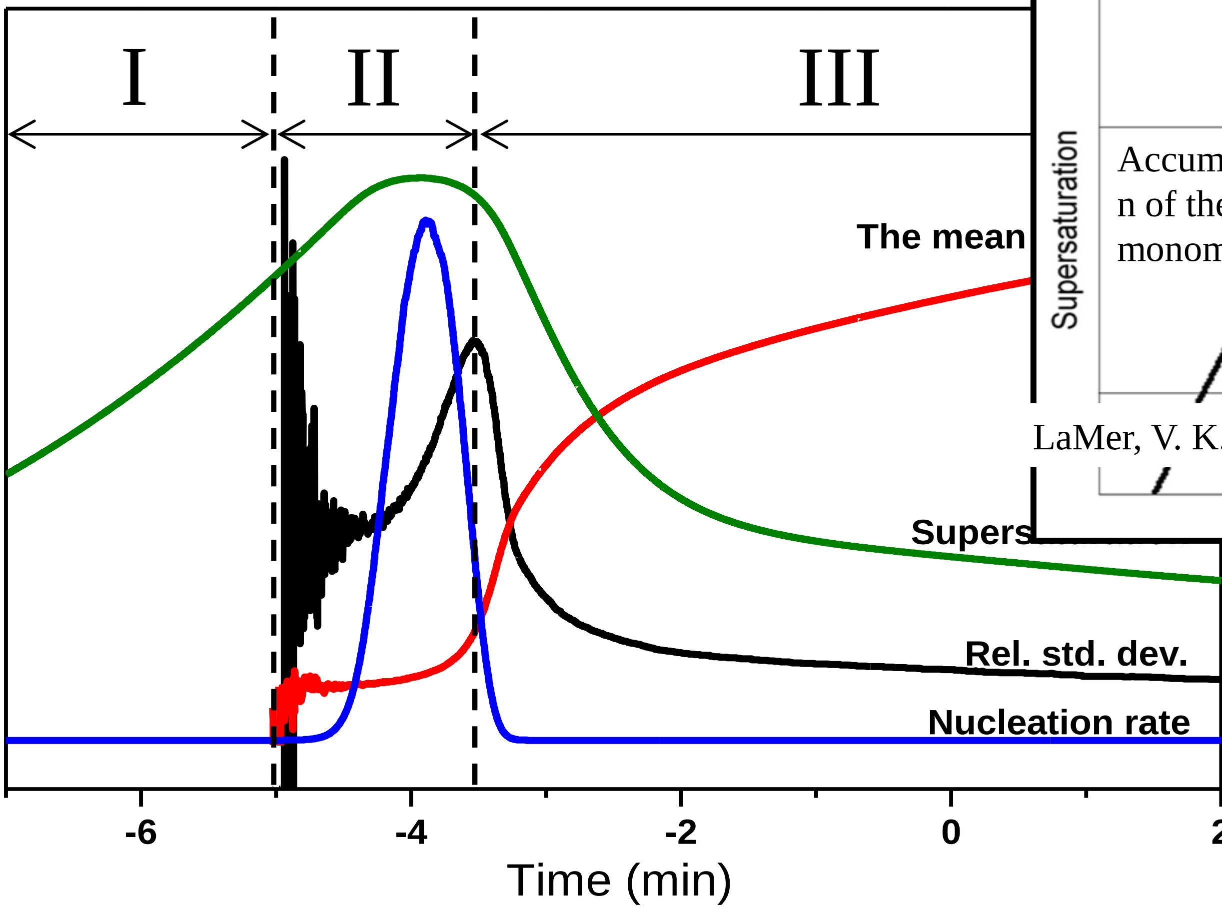
2) Burst of nucleation occurs at 320 °C, 0 min.

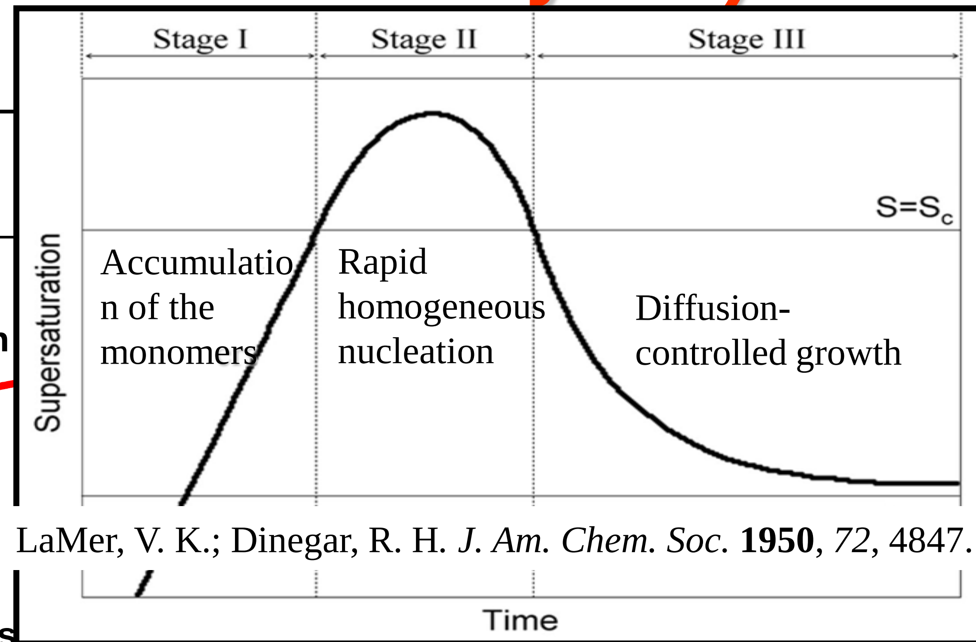
3) Rapid particle size increase along with size distribution narrowing within 4 min aging.

S. G. Kwon & T. Hyeon, *J. Am. Chem. Soc*. **2007**, 129, 12571.

How did it happen? (LaMer vs. Kwon&Hyeon)

S. G. Kwon et al., *J. Am. Chem. Soc*. **2007**, 129, 12571.





LaMer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4847.

Sudden increase in nanocrystal concentration (burst of nucleation) is followed by rapid narrowing of size distribution (size focusing), which is well explained by LaMer model.

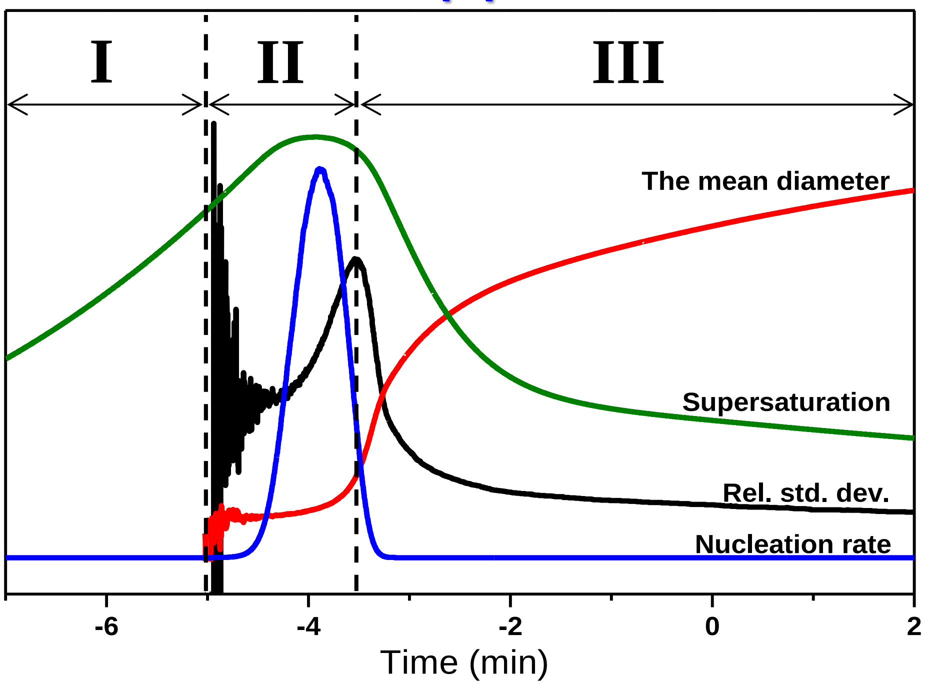
Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.

Talapin, D. V.; Rogach, A. L.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2001**, *105*, 12278; *J. Am. Chem. Soc.* **2002**, *124*, 5782.

Seemingly very different processes (Heat-up vs. Hot-injection)

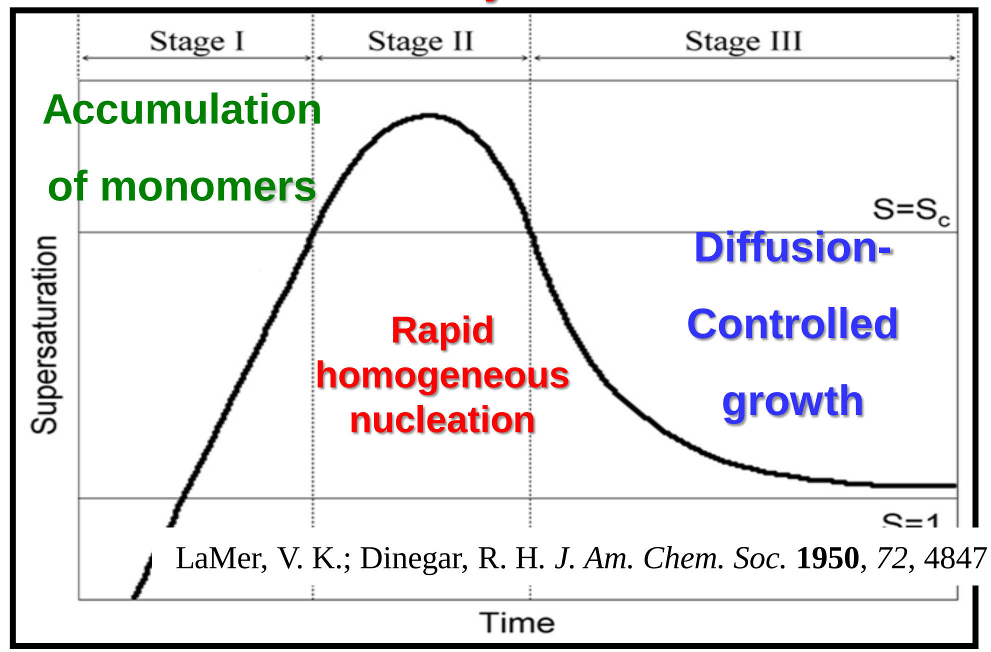
→ But very similar LaMer mechanim works for both processes.

Iron oxide nanocrystal formation via Heat-up process



S. G. Kwon *et al*. *J. Am. Chem. Soc*. **2007**, 129, 12571.

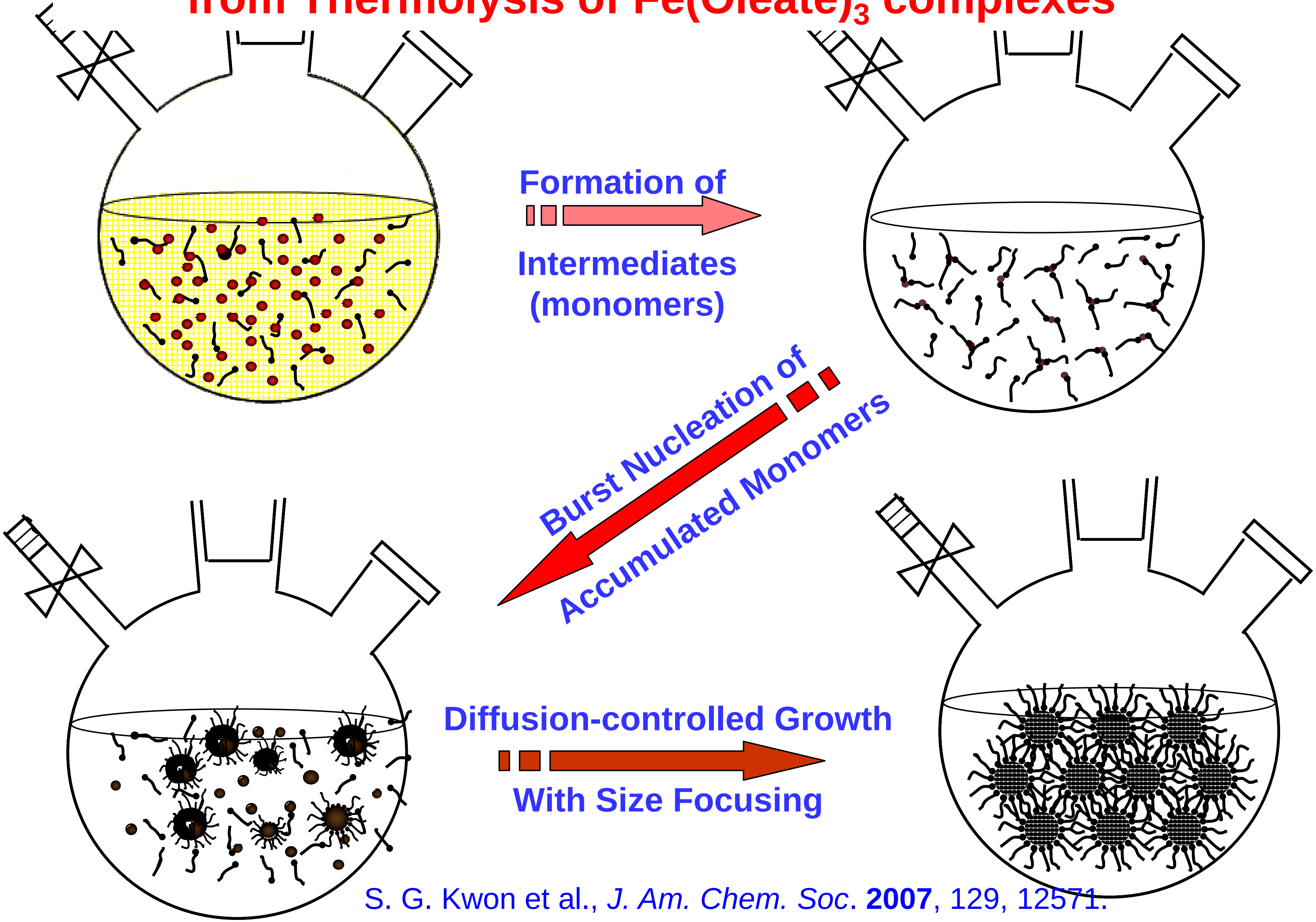
CdSe Nanocrystal formation via Hot-injection method



Peng, X.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.
Talapin, D. V.; Weller, H. *J. Am. Chem. Soc.* **2002**, *124*, 5782

LaMer mechanism for monodisperse particles (Burst of nucleation followed by diffusion-controlled growth) works in both "Heat-up" & "Hot-injection" processes

Proposed Mechanism for Monodisperse Nanoparticles from Thermolysis of $Fe(Oleate)_3$ complexes



S. G. Kwon et al., *J. Am. Chem. Soc*. **2007**, 129, 12571.

> 1 kg of 11 nm Fe_3O_4 Nanocrystals

AUGUST 24, 2009
C&EN
CHEMICAL & ENGINEERING NEWS

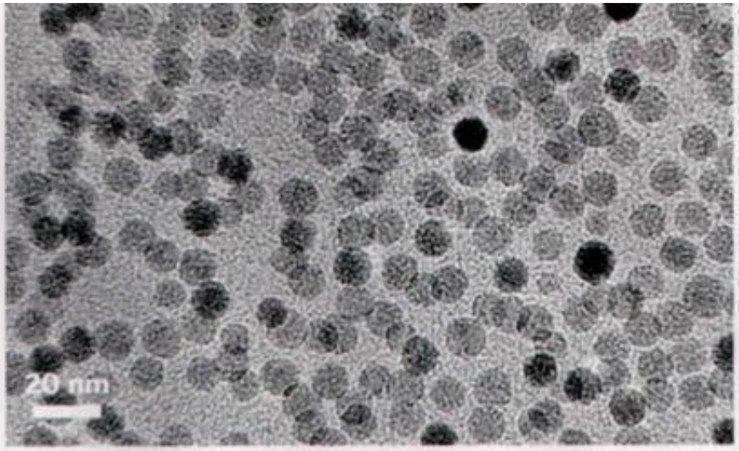
Chem. & Eng. News, August 24, 2009

SCIENCE & TECHNOLOGY CONCENTRATES

http://pubs.acs.org/cen/news/87/i34/8734news10.html

NANOCRYSTALS BY THE KILOGRAM

Kilogram-scale batches of uniform-sized nanocrystals can be prepared via a simple synthesis procedure, according to researchers in South Korea. The availability of a low-cost method for making bulk quantities of monodisperse (single-sized) nanocrystals may speed up development of nanotechnology applications. Several methods for preparing monodisperse nanocrystals have already been reported, but typically those methods yield gram quantities of product and require size-sorting steps. Taeghwan Hyeon, a professor of chemical engineering at Seoul National University, reported that his research group, in collaboration with Wan-Jae Myeong and coworkers at Hanwha Chemical, also in Seoul, have synthesized kilogram-scale batches of uniformly sized 11-nm-diameter magnetite (Fe_3O_4) crystals via a procedure they developed. The method, which takes less than seven hours to complete and does not require size-sorting steps, calls for reacting a surfactant with hydrated iron chloride, an inexpensive reagent, and then heating the complex [illegible] Scaling the synthesis even further may be particularly useful for applications in data storage, medical imaging, and magnetically directed drug delivery.—MJ



TAEGHWAN HYEON/SEOUL NATIO

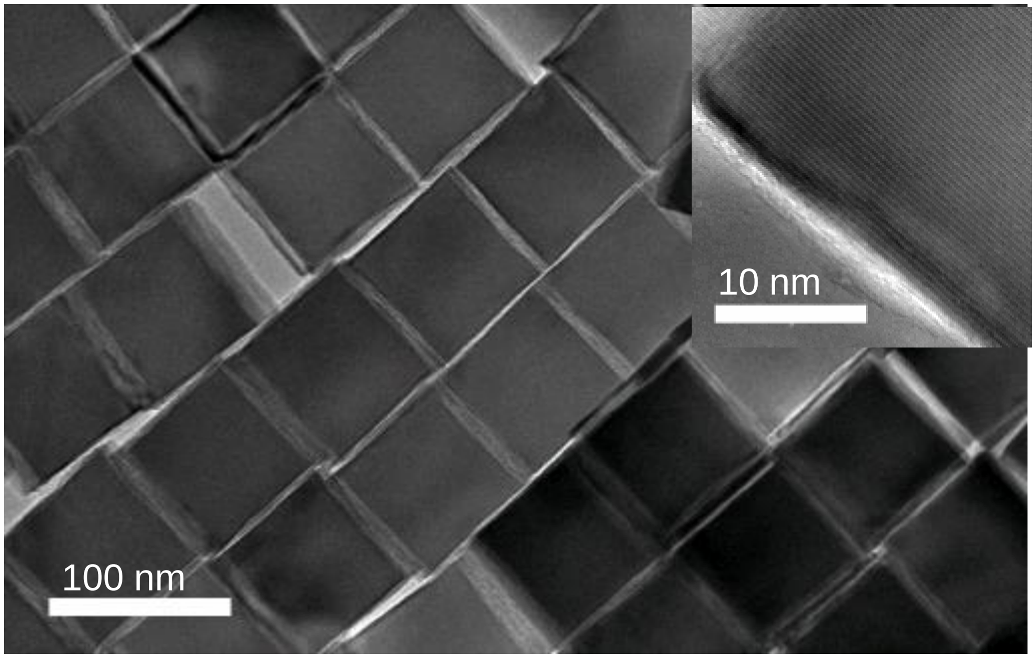
TEM analysis shows that these Fe_3O_4 (magnetite) crystals, which were made via a kilogram-scale preparation method, are highly uniform in size and shape.

Hanwha Chemicals Co.

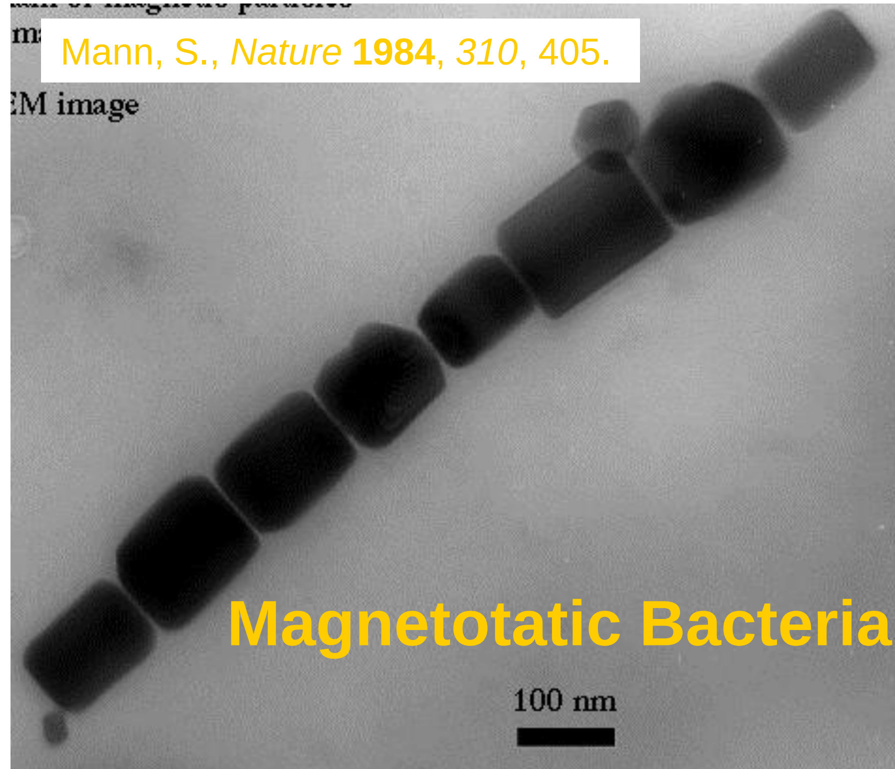
- Pilot Plant of 100ℓ reactor

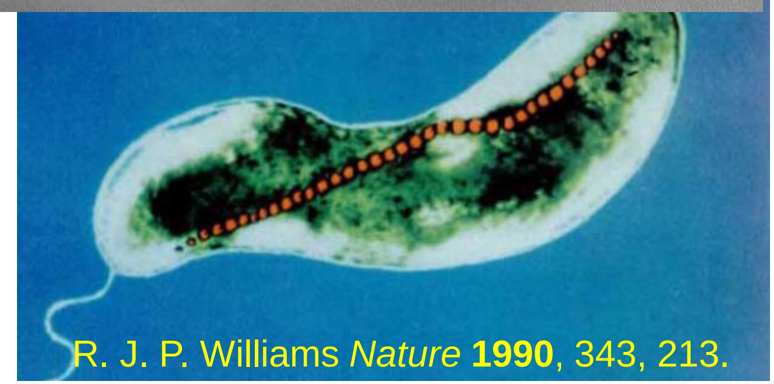
- kg/batch for < 7 hour

Artificial Magnetosomes: New MRI Contrast using 80-nm-sized Fe_3O_4 nanocubes



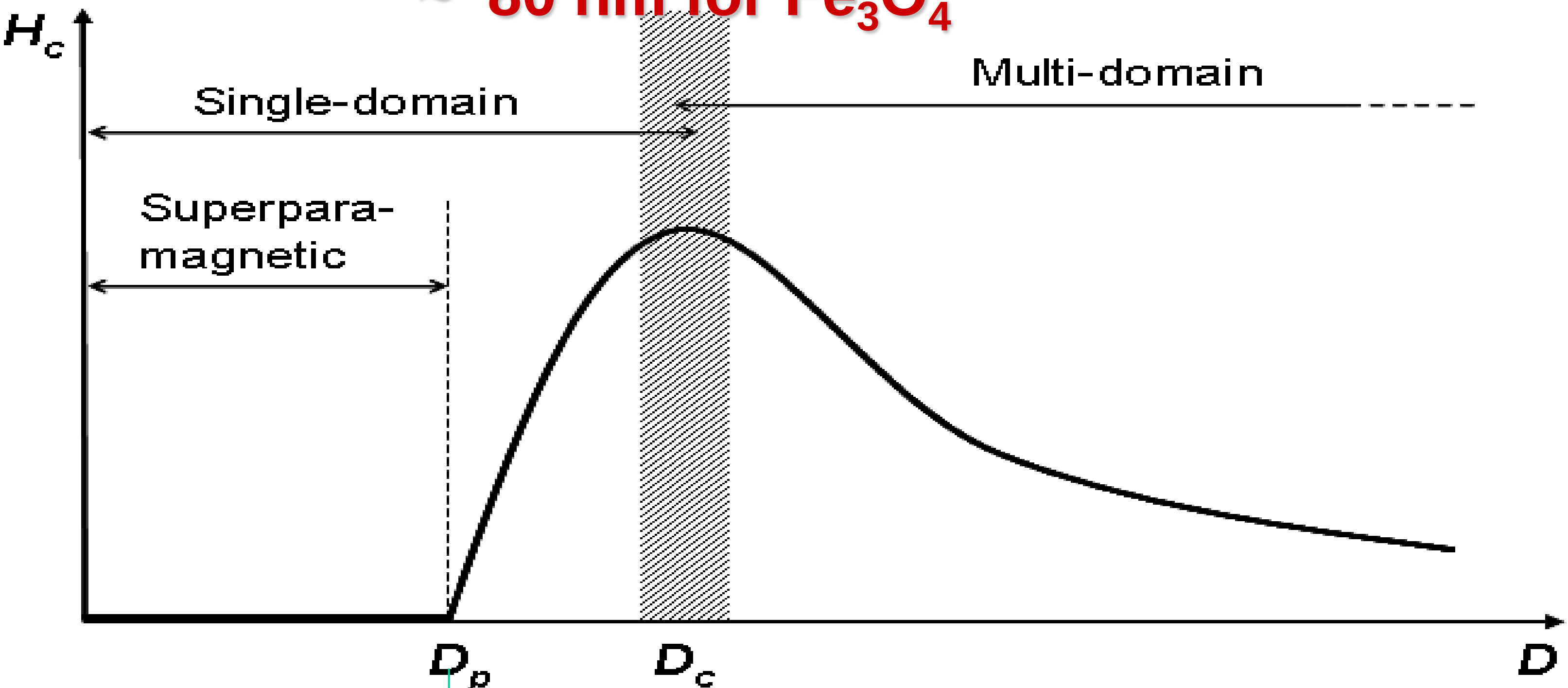
Dokyoon Kim et al., *J. Am. Chem. Soc.* **2009**, 131, 454



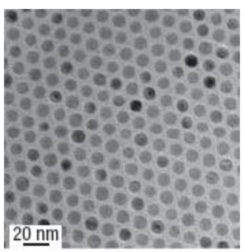


Size dependent magnetic properties

~ 80 nm for Fe_3O_4

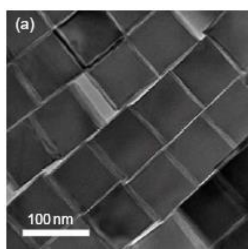


11 nm



T. Hyeon,
Nat. Mater. 2004

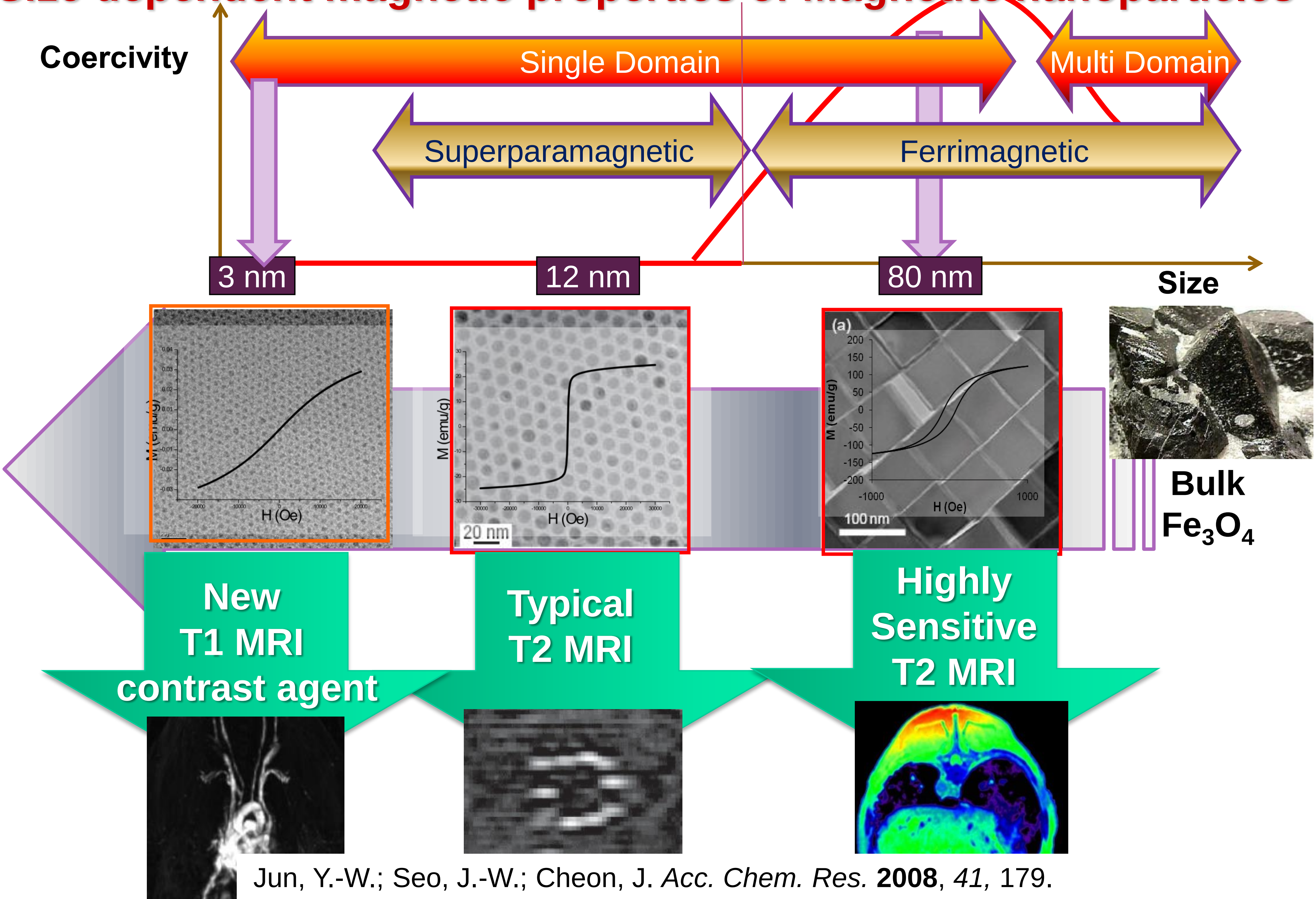
80 nm



T. Hyeon,
JACS 2009

Bulk
Fe_3O_4

Size dependent magnetic properties of Magnetite nanoparticles



Jun, Y.-W.; Seo, J.-W.; Cheon, J. *Acc. Chem. Res.* **2008**, *41*, 179.