Nanoparticle Research at UW-Oshkosh: Practical Ways to make Useful Materials

Charles P. Gibson
Department of Chemistry,UW Oshkosh

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Nanoparticle research at UWO: Background

(1) Nanoparticle research at UWO began in 1992.

(2) At the time, there were few good methods for making nanoparticles. (Synthetic challenge.)

(3) In particular, there was no practical method for making Fe, Co, and Ni nanoparticles.

(4) Fe, Co, and Ni are ferromagnetic. There might be important practical uses of these materials.

(5) Initial goals were to develop practical syntheses of nanoscale iron, cobalt, and nickel.

Strategy: metal cation reduction in aqueous solution.

(1) The approach is well established for noble metals

$$Pt^{2+}\,(aq) + 2e^{-} \rightarrow Pt\,(ns)$$

(2) The $2e^{-}$ are supplied by a reducing agent, such as hydrogen, hydrazine, etc.

(2) Processing conditions need to be "just so", otherwise large particles form.

(3) Only seems to work for noble metals. (Not for base metals like Fe, Co, and Ni.)

Noble metals vs. base metals.

(1) Noble metal cations are easy to reduce.

	Potentials (acidic)
Pt^{2+} (aq) + $2e^-$ → Pt (ns)	+1.18V
½ N_2H_4 → 2 H^+ + ½ N_2 + $2e^-$	+0.23V
Pt^{2+} + ½ N_2H_4 → Pt (ns) + ½ N_2 + 2 H^+	+1.41 V

(2) Base metal cations are normally quite difficult to reduce.

Co^{2+} (aq) + $2e^-$ → Co (ns)	-0.28V
½ N_2H_4 → 2 H^+ + ½ N_2 + $2e^-$	+0.23V
Co^{2+} + ½ N_2H_4 → Co (ns) + ½ N_2 + 2 H^+	-0.05 V

A stronger reducing agent is needed.

(1) But not too strong (e.g. Na). Otherwise it will react with water.

(2) Avoid reducing agents that give undesired byproducts (e.g. borohydrides)

(3) How about hydrazine under basic conditions!

$\frac{1}{2}\, N_2H_4 \rightarrow 2\, H^+ + \frac{1}{2}\, N_2 + 2e^-$	+0.23V (acidic)
$\frac{1}{2}\, N_2H_4 + 2\, OH^- \rightarrow 2\, H_2O + \frac{1}{2}\, N_2 + 2e^-$	+1.16 V (basic)

(4) Base metals are normally insoluble in basic solutions.

$$M^{2+} + 2\, OH^- \rightarrow M(OH)_2 \text{ (solid)}$$

(5) Except when the concentration of base is very high.

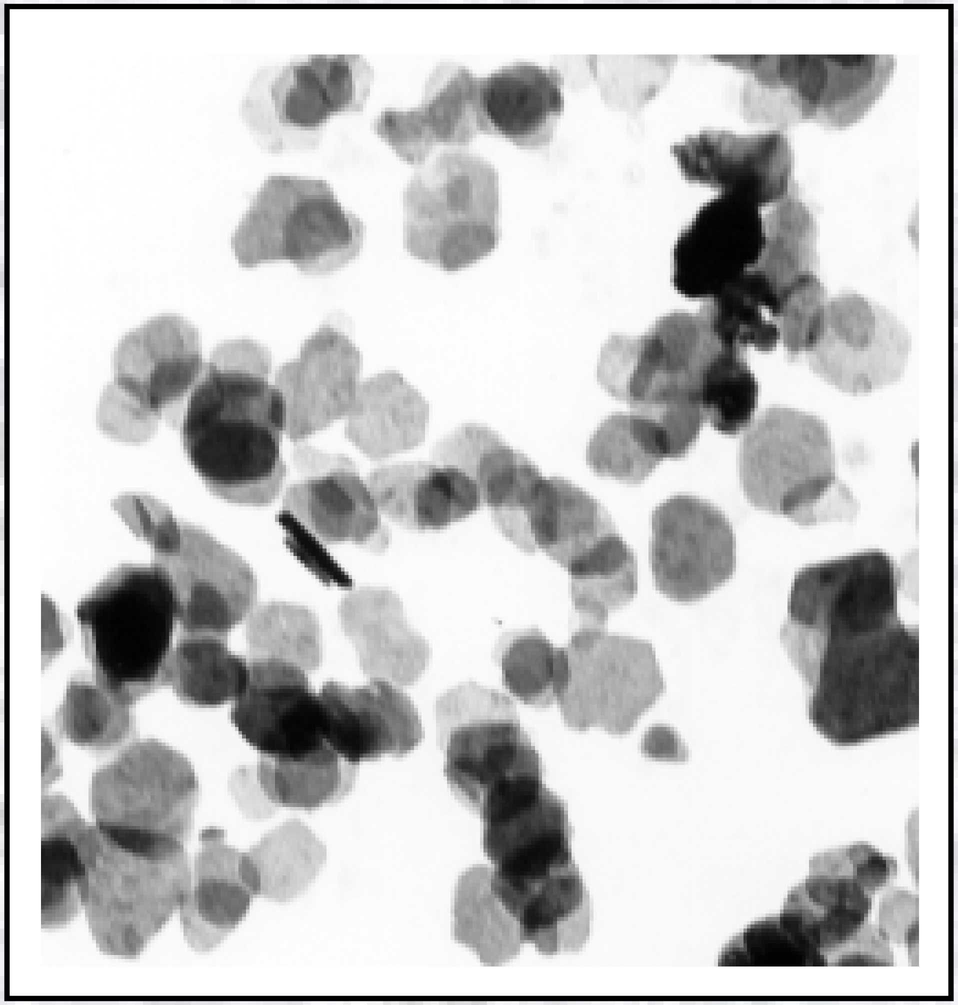
$$M^{2+} + n\, OH^- \rightarrow M(OH)_2 \text{ (solid)} \rightarrow M(OH)_4^{2-} \text{ (aq)}$$

Reaction are thermodynamically allowed, but there is no reaction under ambient conditions. (Activation barrier).

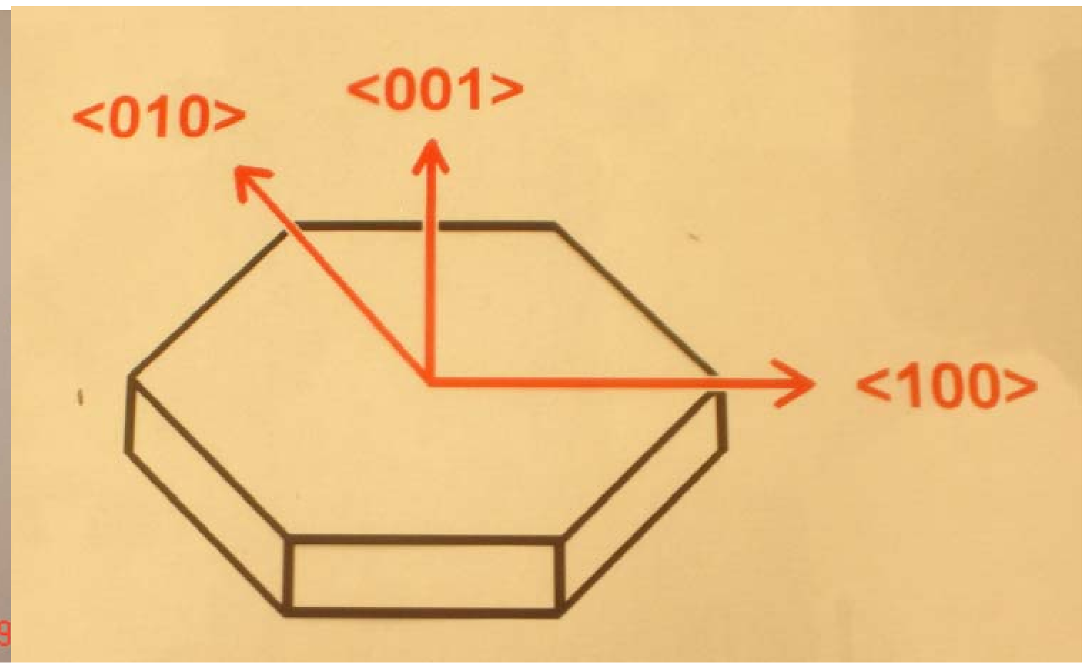
- **High-intensity ultrasound creates pressure waves in the solution, which provide the needed energy.**

- **Ultrasound also creates hydrodynamic shear forces, which help keep particles small (ideally, <100 nm).**

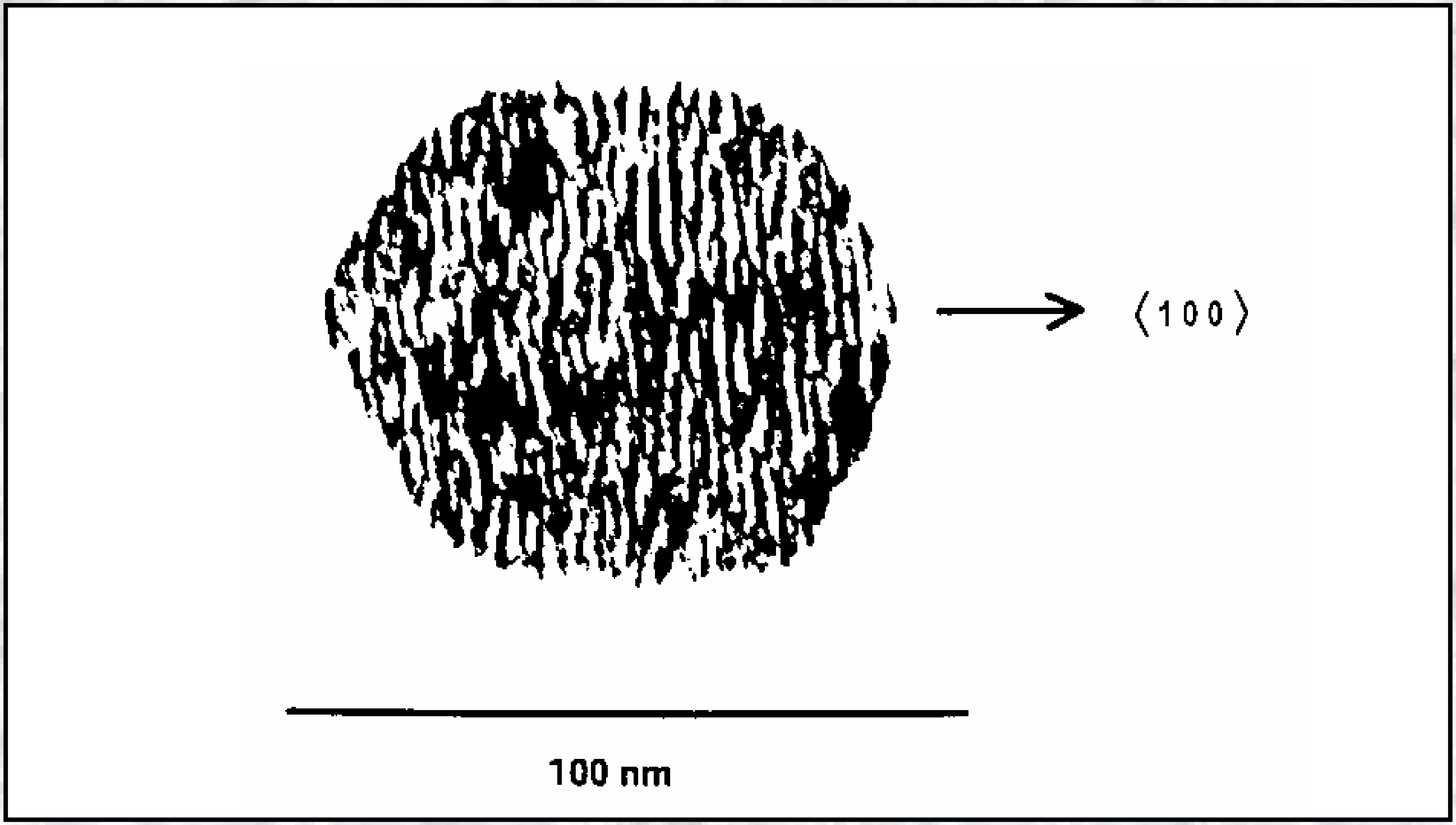
The strategy was successful! Cobalt nanoclusters were produced in ca. 100 % yield!



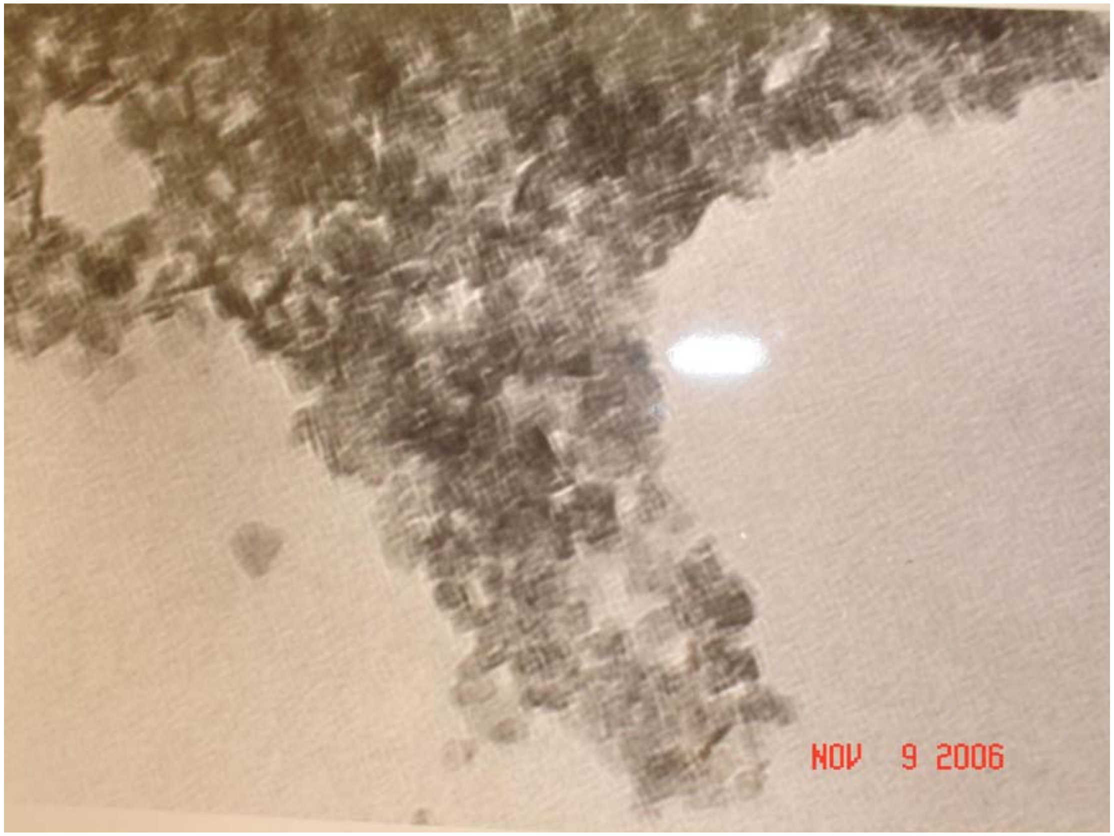
The Co particles are single hcp nanocrystals.



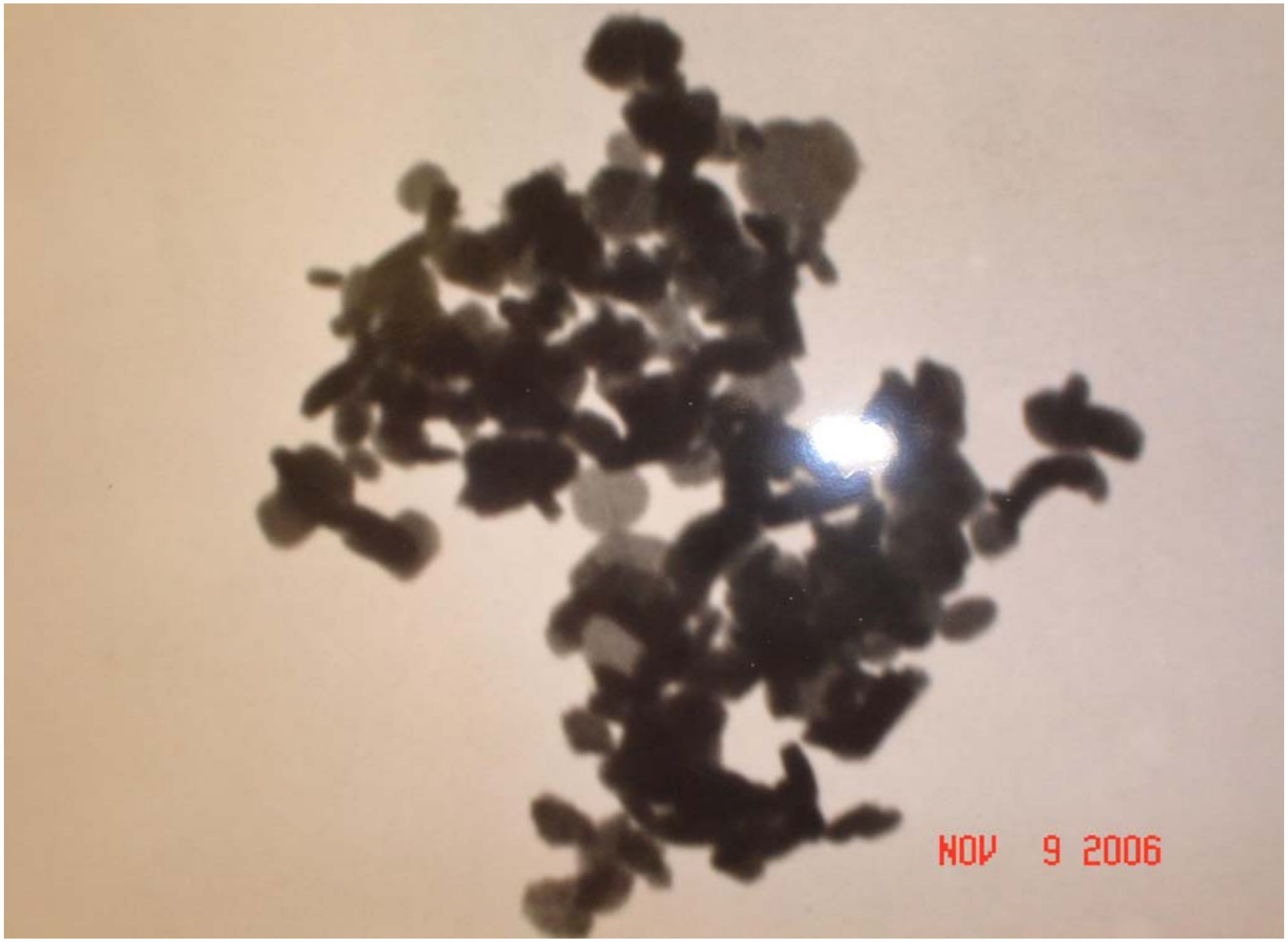
They are also single magnetic domain particles.



The process also works with Ni.



And with Fe



Potential end uses were identified. Anisometric Co nanoparticles were evaluated in these uses.

(1) Magnetic Properties (D Leslie-Pelecky – U. Nebraska).

+ Useful magnetic properties.

- No clear advantage over conventional materials.

(2) MRI contrast agents (Kathy Putzer – UWO).

+ Useful as a T_2 contrast agent.

+ Nice compliment to established T_2 contrast agent.

- Toxicity of Co has not been established.

(3) Cemented carbides (Sarah Kieper - UWO)

? Can be used to make nanograined Co/WC

? Nanograined Co/WC will have superior properties

Potential end uses…

(4) **Magnetic susceptors for microwave cooking (Scott Omachinski – UWO).**

+ Superior in many ways to conventional susceptors.
+ No temperature ramping
+ Differential heating possible.
+ Can be applied lithographically.

Provisional Patent Application !

- Competing with established technology.
- Established technology is good enough for popcorn.
- High development costs.

No follow-up patent.

Potential end uses…

(5) Powder metallurgy (Mike Faley, Greg Potratz – UWO).

+ Ansiotropic particles can be compacted and heated to form metal object *at relatively low temperature*.

+ The resulting metal object contains anisotropic grains, which are oriented in the same direction (nanotexturing). This can provide improved properties.

+ Desirable, but no known examples.

New composition of matter - nanotextured metal objects

US Patent 6,036,061, 24 October 2000

This research project led directly to two patents:

(1) A new composition of matter – anisometric metal nanoparticles.
(US Patent 6,156,428, 5 December 2000.)

(2) A new composition of matter – nanostructured metal objects made via powder metallurgy.)
(US Patent 6,036,061, 24 October 2000)

Opportunities for collaboration…

(1) We have developed a useful process for making anisometric nanoparticles of the base metals Fe, Co, Ni, (and also Cu). We have investigated some of the potential end uses of these materials, but further development is limited but lack of time, expertise, and/or resources.

(2) We welcome collaboration that will result in the development of practical uses of these materials.

(3) At this point, the Fe, Co and Ni syntheses has been scaled up to give 10's of grams of materials. Further scale up has been limited by the size of the sonicator we have available. Scale up to kg's probably needed to develop practical uses. (Cu synthesis already scaled up.)

(4) The most promising practical use may be nanophase cemented carbides (WC/Co), possibly incorporating carbon nanotubes to improve toughness.

(5) Medical applications? Imaging? Targeting cancer cells?

Other projects and opportunities for collaboration…

(1) We developed an energetic material that produces nanoscale metal oxides – possible burn rate enhancer. Applications: rocket propellants (DoD, NASA).

(2) We developed a novel microwave synthesis of BN nano/microtubes. Applications?

(3) We are interested in investigating the use of nanoparticles in the treatment of wood with the goal of improving properties (e.g., fire resistance, elasticity). Preliminary experiments conducted, results are promising.

(4) We developed a new high yield, scalable synthesis of nanoscale ZnS and CdS. Applications: phosphors (DoE, industry); IR optics (DoD, industry)