液相還元法によるNiCo合金ナノ粒子合成と　キャラクタリゼーション

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Applications of Ni-based nanoparticles

Highly Active Catalysts

Ni-based nanoparticles → various catalytic reactions

(Ni shows high ability to dissociate H_2 and successive hydrogenation)

Support and additive → promotion of catalytic activities

Magnetic properties

Excellent soft magnetic properties

control of the size, composition and crystalline structure

→important for their use in application field

magnetic sensors, magnetic refrigerant,

ferro-fluids and high density magnetic memories

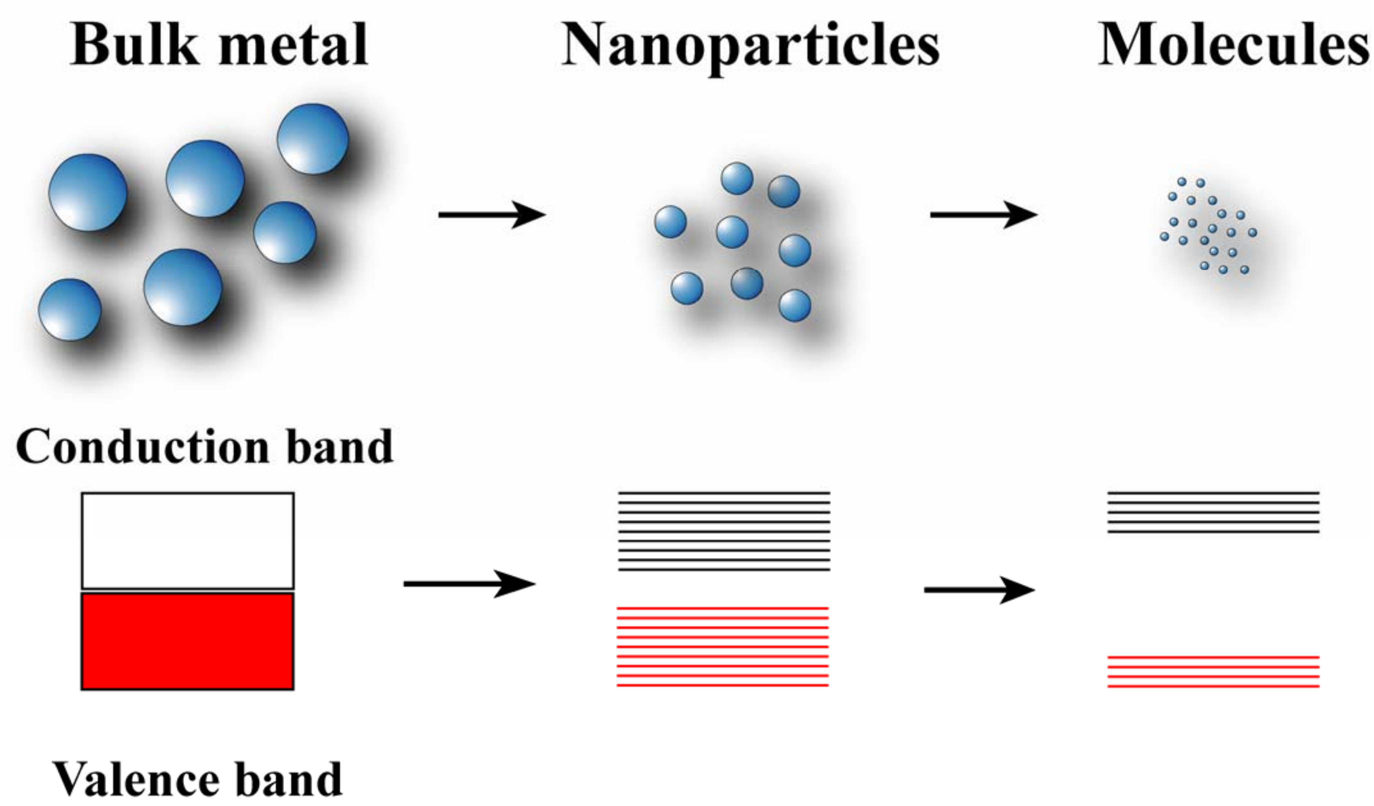
Conventional preparation methods

→substantial defects on the synthesis and the stabilization

It is important to develop the synthesis method of highly dispersed and highly stabilized Ni-based nanoparticles

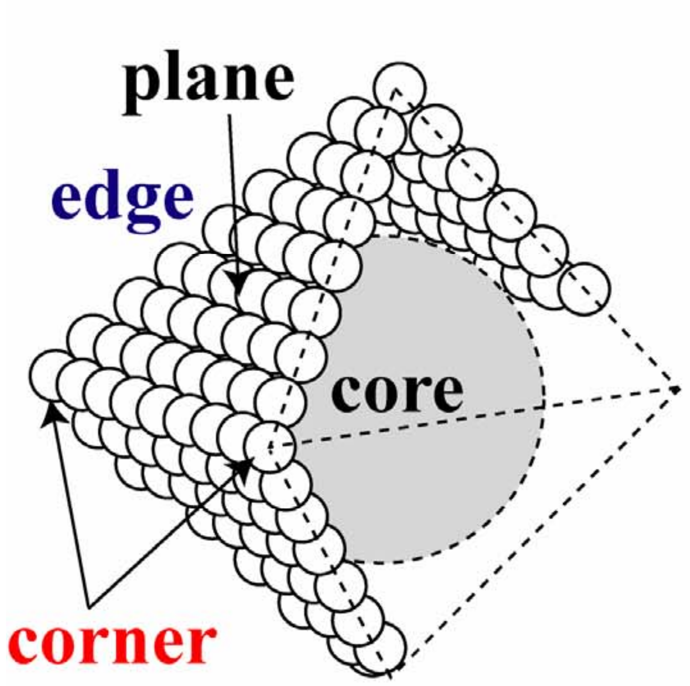
Background

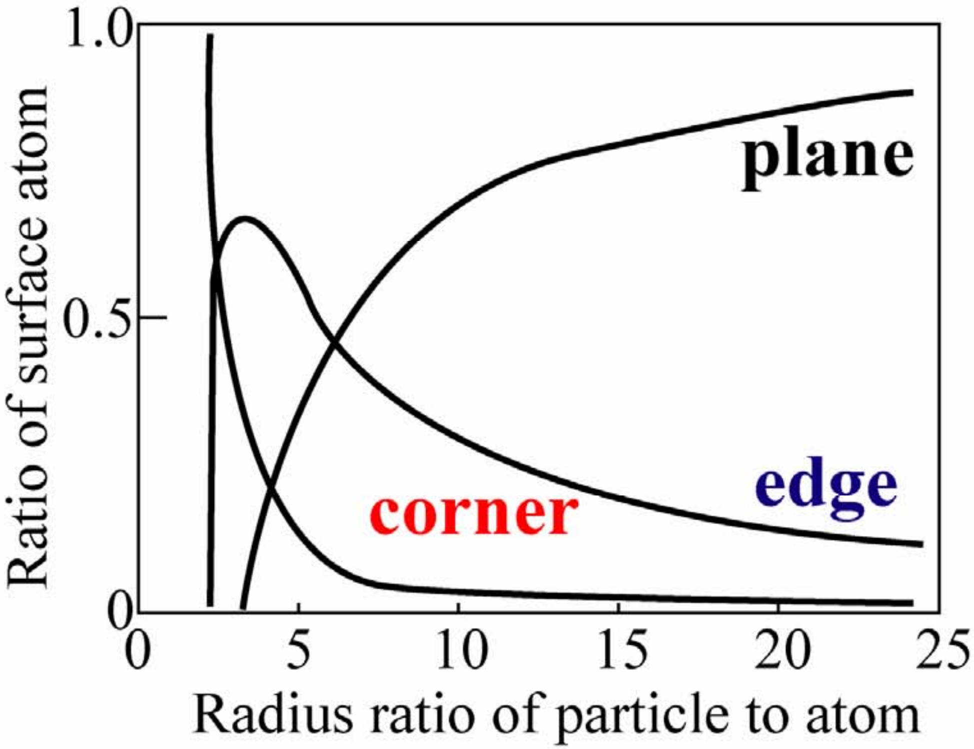
Quantum Size Effect



properties → size, shape, chemical composition

Nanoparticles ➡ 0.5 -100 nm ➡ High surface energy





The ratio of the atoms located on the surface against the total number of the atoms in the one particle

nanoparticles > bulk materials

Synthesis methods of nanoparticles

Vapor phase method

advantage → high purity

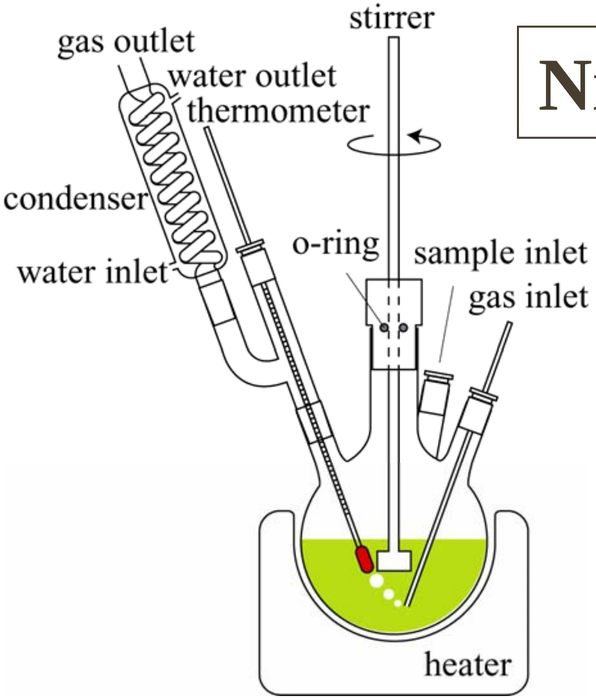
disadvantage → difficult, large scale system

Liquid phase method

advantage → easy (directly obtained from various precursor compounds soluble in specific solvent)

disadvantage → aggregation, oxidation

Our previous studies



Schematic drawing
of the reaction vessel

$Ni(AA)_2$+$Zn(AA)_2$ 2-propanol 40ml

AA=$CH_3COCHCOCH_3$

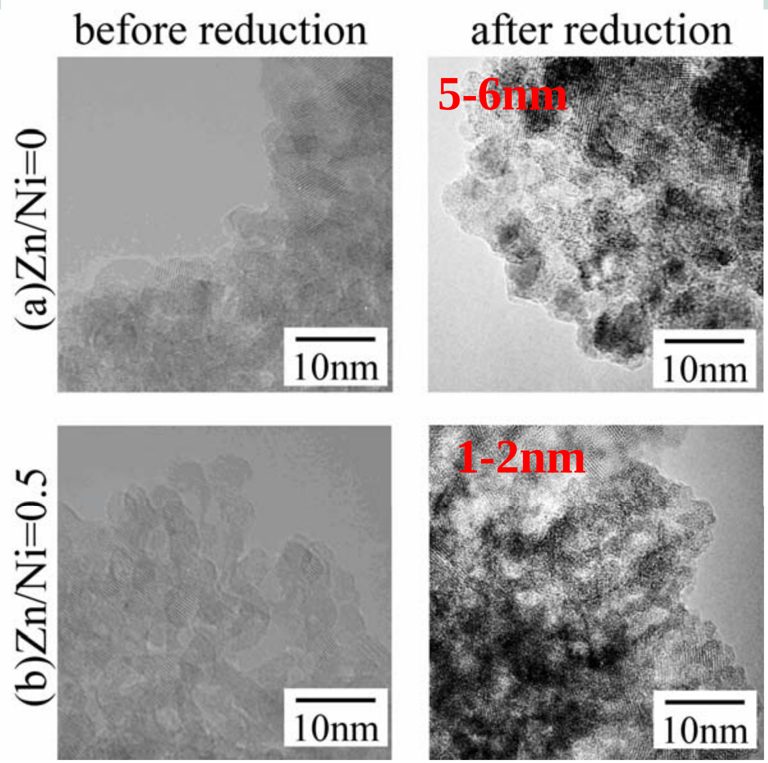
N_2 gas flow (30min, 82℃)

10ml of 1.0×10^{-1} mol/l $NaBH_4$

$$Ni^{2+} + BH_4^- \rightarrow Ni + B^{3+} + 2H_2$$

Ni-based nanoparticles

Our previous studies



Valence

Ni → metallic (surface :oxide)

Zn, B → oxide

Effect of Zn and TiO_2

Zn addition→ restrict the growth

TiO_2 → stabilize the particle

×NiZn "alloy" nanoparticles

Alloy nanoparticle synthesis

- We have never succeeded in the preparation of Alloy nanoparticles by Liquid-phase reduction method.

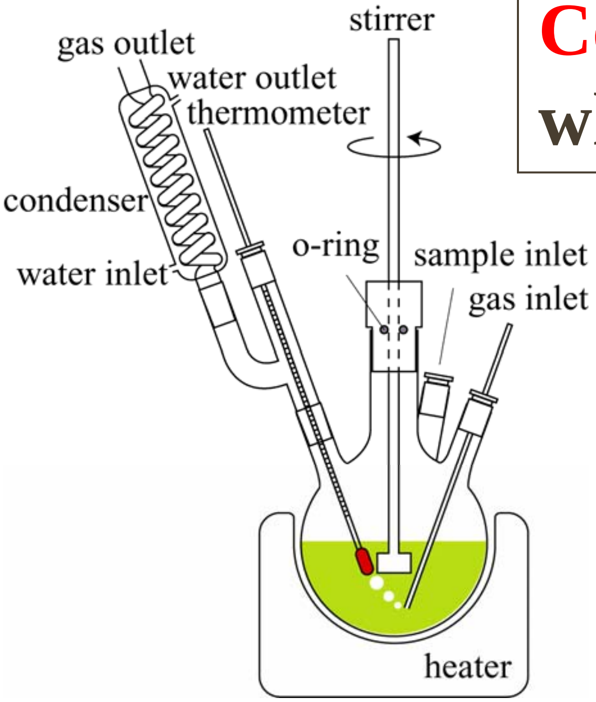
- Liquid-phase reduction method
  - Ni-Zn nanoparticles
  - Ni = metal, Zn = oxide, B = oxide as impurity

Objective

Synthesis of the CoNi "alloy" nanoparticles

- ***Development of the synthesis procedure***
- ***Characterization of synthesized materials***
- ***Growth mechanism of nanoparticles***

Synthesis procedure



Schematic drawing
of the reaction vessel

$Ni(AA)_2$+$Co(AA)_2$ 2-propanol 40ml
Co:Ni=0:2, 1:2, 2:2, 2:1and 2:0
where "2" denotes $2.5x10^{-4}$mol

AA=$CH_3COCHCOCH_3$

N_2 gas flow (30min, 82℃)

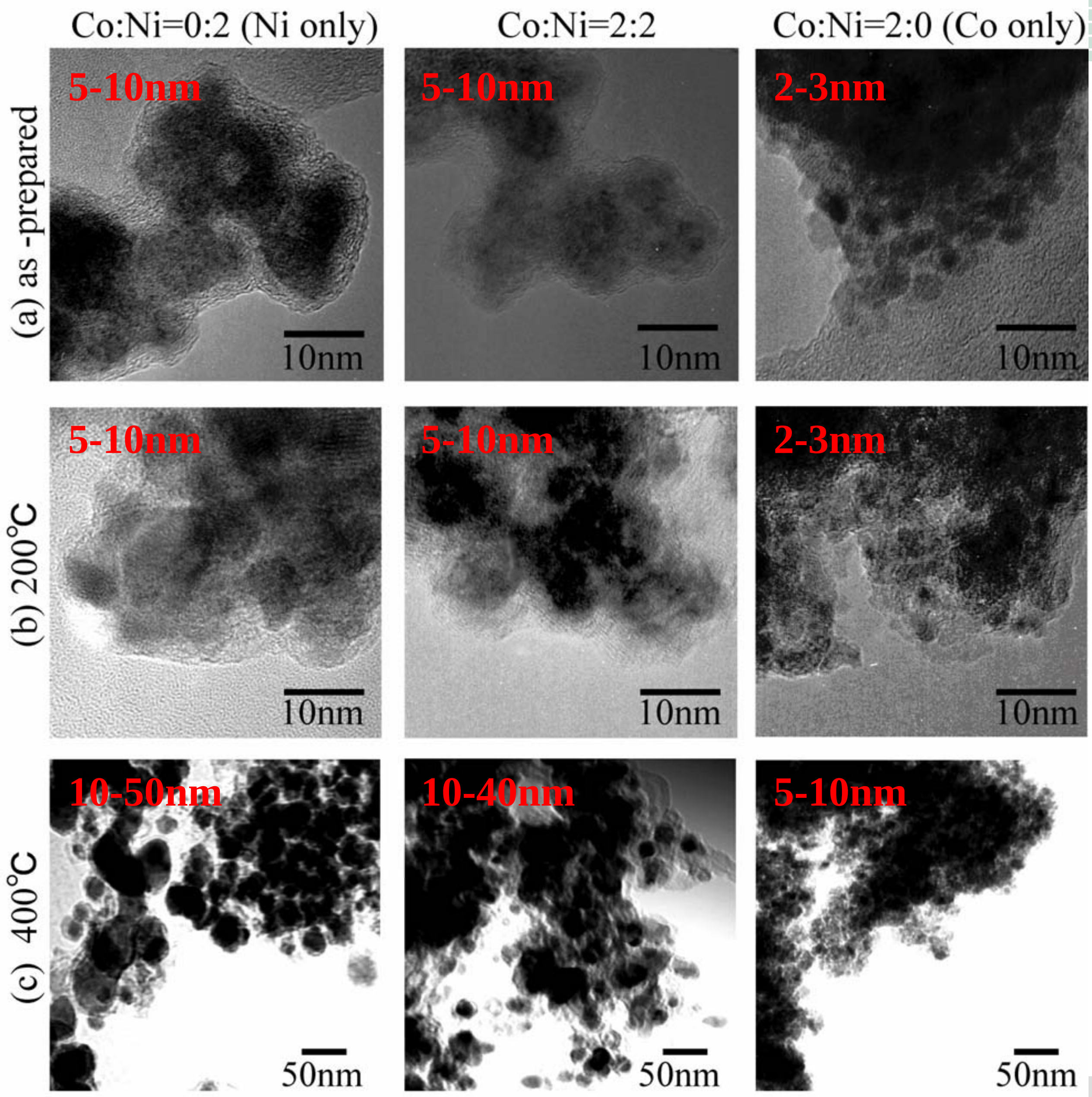
10ml of $1.0x10^{-1}$ mol/l $NaBH_4$

$Ni^{2+} + Co^{2+} + BH_4^- \rightarrow NiCo + B^{3+} + 2H_2$

Synthesized materials

Heat treatment : 200℃～ 400℃

HR-TEM images of as-prepared and heated particles

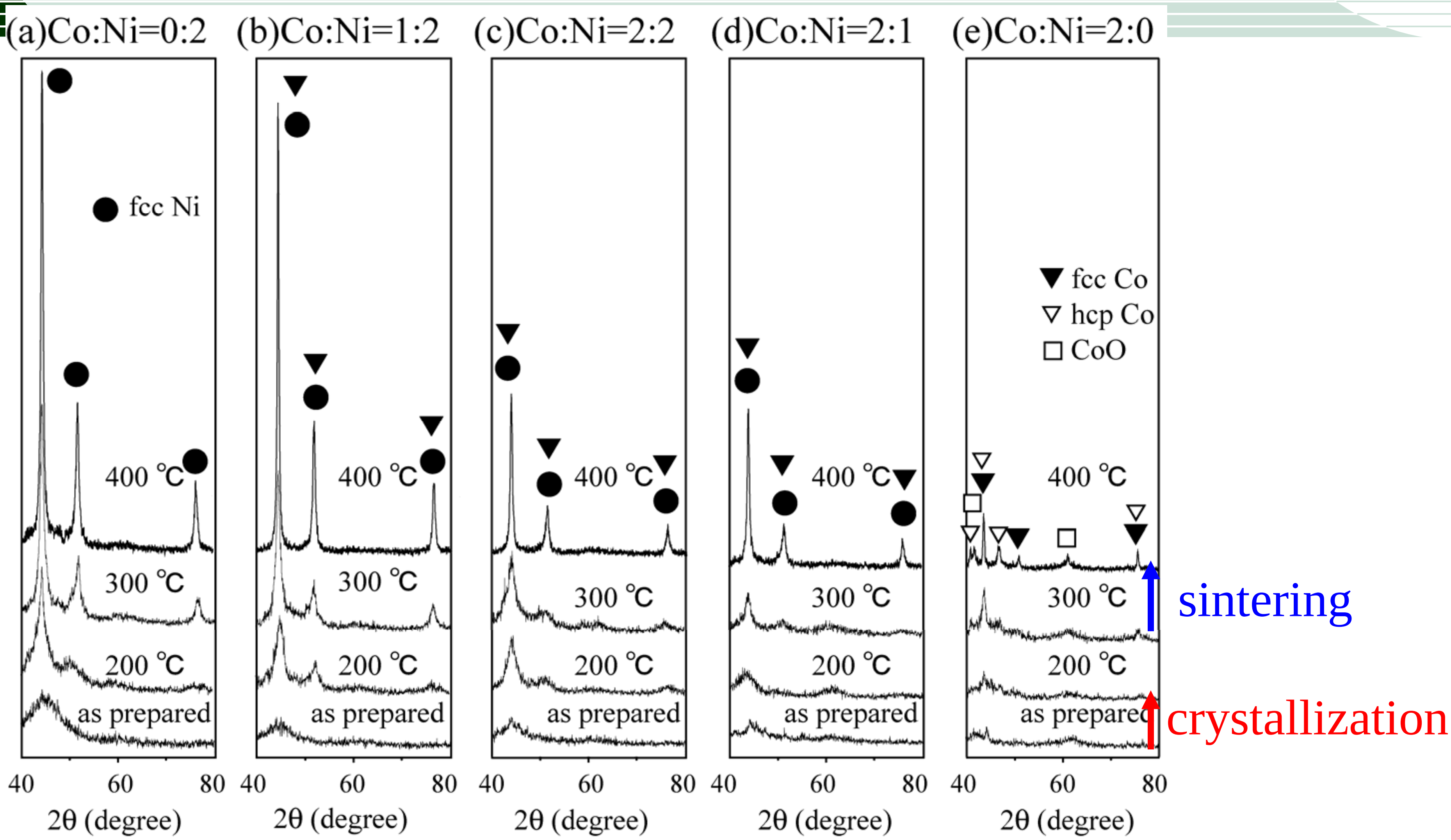


Particle size

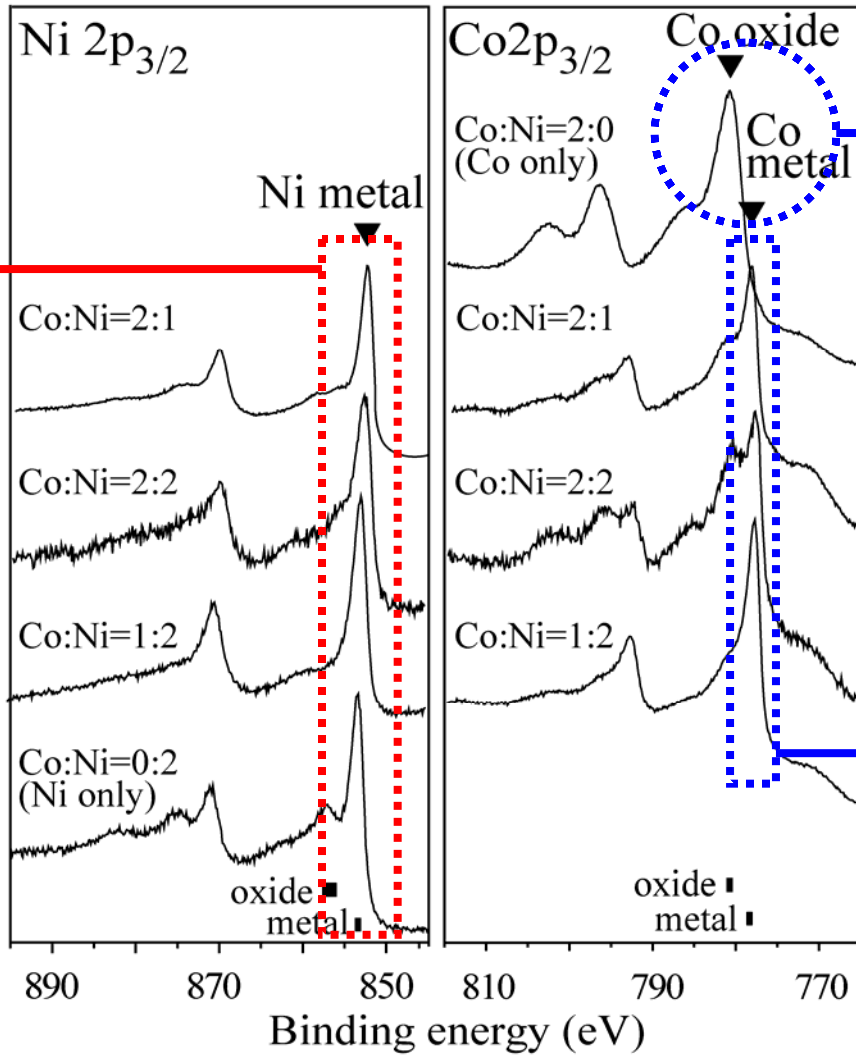
almost same (200℃)

increased (400℃)

XRD profiles of as-prepared and heated particles



ESCA analysis of as-prepared CoNi nanoparticles



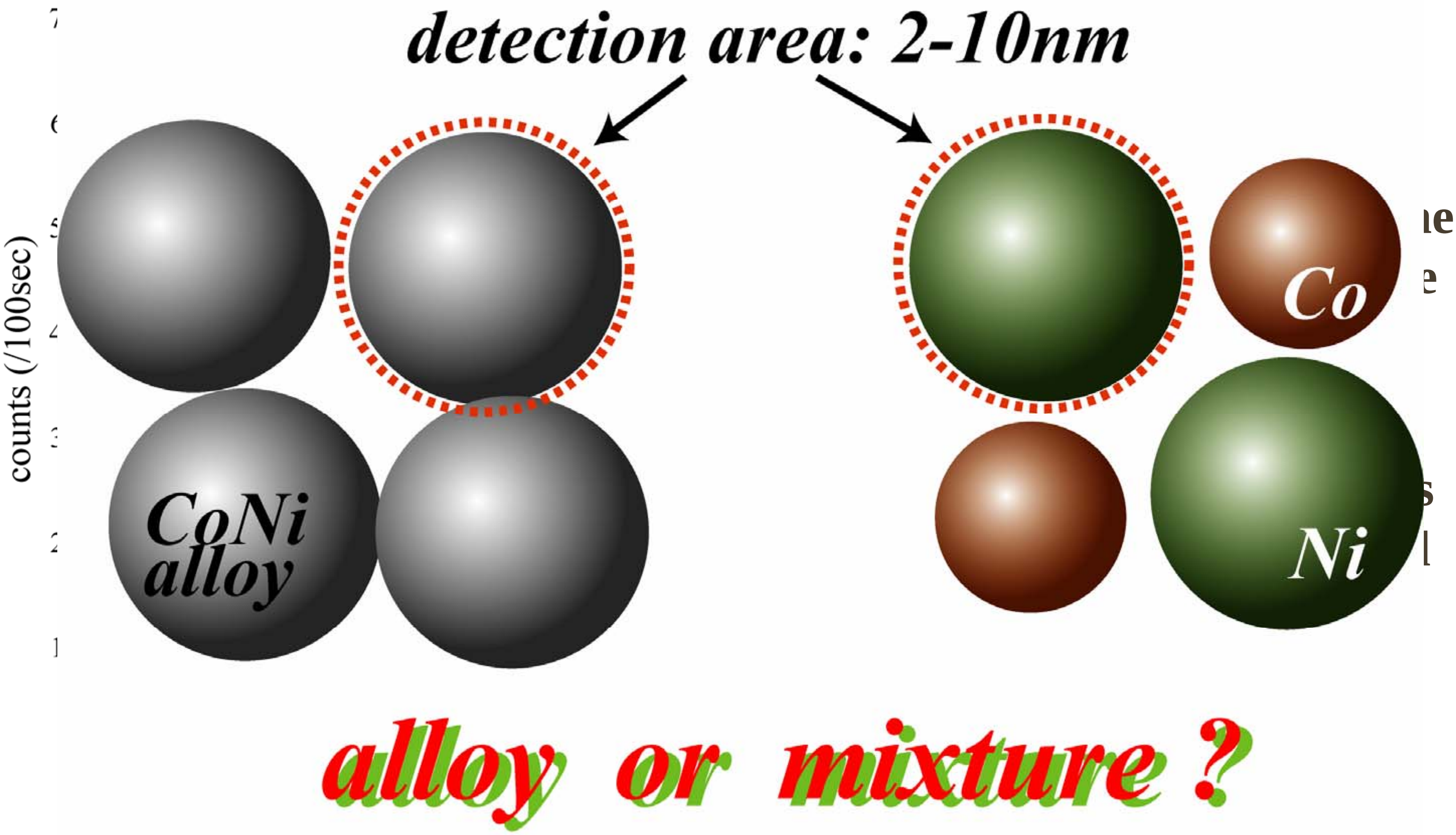
Ni →metallic

+ XRD results

Co →metallic

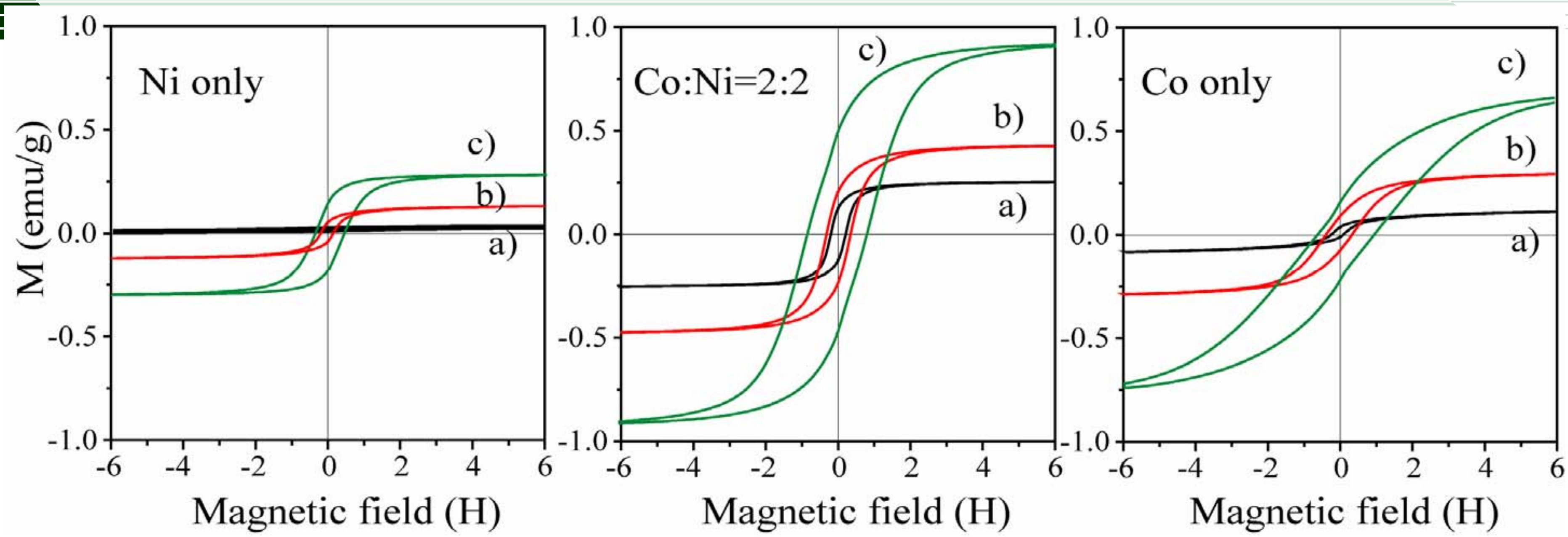
EDS analysis of CoNi nanoparticles

concentration of each metal detected from one nanoparticle



→CoNi alloy nanoparticles

Magnetic properties of CoNi alloy nanoparticles



(a) as-prepared

(b) Heat treated at 200℃

(c) Heat treated at 400℃

Magnetic properties of CoNi alloy nanoparticles

→ 44.9 emu g^{-1} after crystallization (200℃, 5-10nm)

→ 100.0 emu g^{-1} after sintering (400℃, 10-40nm)

Conclusion

(1) Particles size: 5-10 nm (Co:Ni=0:2-2:2), 2-3 nm (Co:Ni=2:0)

(2) Ni and Co → metallic, co-existed in one nanoparticle

→CoNi "alloy" nanoparticles

(3) Magnetic properties of CoNi alloy nanoparticles

→ 44.9 emu g^{-1} after crystallization (200℃, 5-10nm)

→ 100.0 emu g^{-1} after sintering (400℃, 10-40nm)

(Growth mechanism (reduction rate, activation energy) was also introduced in the paper)