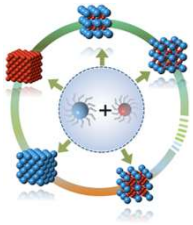
Synthesis and application of multi-functional binary nanoclusters

[1]Soo Jin Kwon, [2]Young Jin Kim, [2]Sang Uk Han, [3]Goo Reum Kim, [3]Man Soo Park

1. Department of Chemistry, Yonsei University, Seoul, Republic of Korea
2. Department of Chemical & Biomolecular Engineering, Yonsei University, Seoul, Republic of Korea
3. Center for Nanomedicine, Institute for Basic Science (IBS), Yonsei Advanced Science Institute, Yonsei University, Seoul, Republic of Korea

Introduction



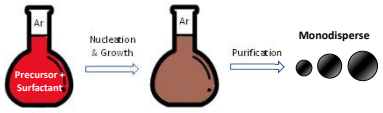
Magnetic nanoparticles (MNPs) and gold nanoparticles (GNPs) have potential for in-vivo biomedical applications due to low cytotoxicity and unique magnetic properties or optical properties.

Recent studies have focused on changing properties by tuning MNPs/GNPs sizes and assembling them into various kinds of structures for biomedical application . Therefore, we aimed to measure and control various properties of MNPs and GNPs by assembling them into nanoclusters.

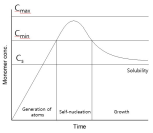
Our study devised synthesis methods for monodisperse building blocks of various sizes and nanoclusters by controlling synthetic conditions. We confirmed the relationship between particle size and magnetism or optical property in single building blocks. Also, we investigated how these properties differ in single nanoparticles and unary nanoclusters. Finally, we found out that binary supercrystals can be formed by mixing different building blocks.

Experimental Methods

1. Synthesis of building blocks

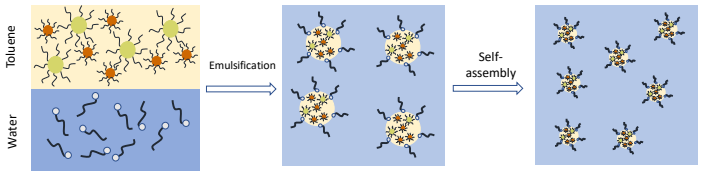


[Nucleation-Growth Mechanism]



2. Synthesis of nanoclusters (Oil-in-water emulsification)

: Unary & Binary nanoclusters

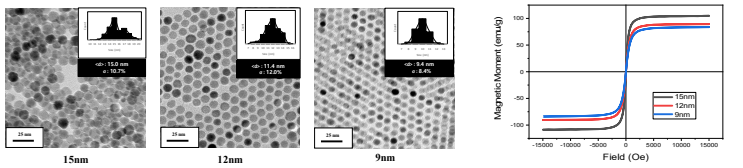


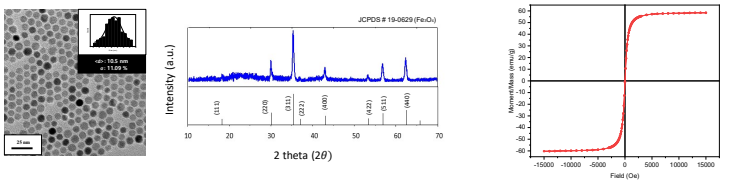
Oil-in-water emulsion : oil phase (toluene) + water phase (deionized water&sodium dodecyl sulfate)

Results

1. Building Blocks (MNPs, GNPs)

(a) MNPs





(b) GNPs

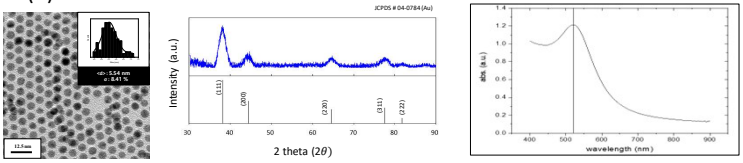
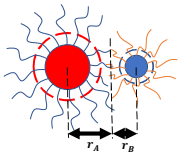


Fig 1. Measurement of morphological, physical, optical, and crystallographic properties of MNPs and GNPs. (a) Transmission Electron Microscope(TEM) image, XRD, VSM results of MNPs, (b) Transmission Electron Microscope(TEM) image, and XRD, UV-Vis(peak at 518nm) spectrum of GNPs.

2. Supercrystal self-assembly

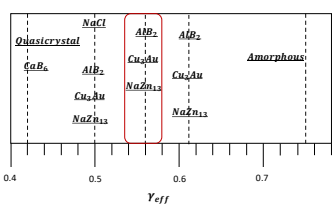
(a)



$$r = R(1 + 3L/R)^{1/3}$$

$$\gamma_{eff} = \frac{r_B}{r_A}$$

(b)



(c) Emulsion stability depending on surfactant

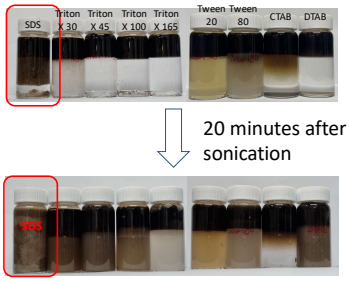


Fig 2. (a) Definition of key geometric parameters of soft sphere model(OPM), R defines inorganic radius of particle, γ_{eff} defines effective particle radius, L defines the length of surface ligand, (b) chart showing various binary supercrystal depending on γ_{eff}, (c) emulsion stability of various kinds of surfactants (SDS, CTAB, DTAB, Tween(20,80,) Triton X(30, 45, 100, 165)

3. Unary nanoclusters (MNCs, GNCs)

(a) MNCs

(b) GNCs

* =518nm

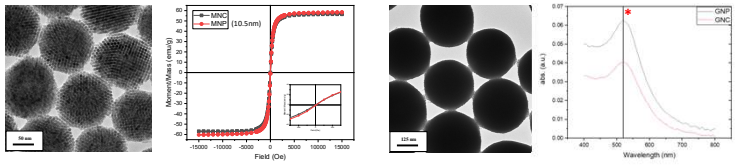


Fig 3. Measurement of morphological, physical, and optical properties of MNCs and GNCs. (a) Transmission Electron Microscope(TEM) image, and VSM of MNCs, (b) Transmission Electron Microscope(TEM) image, and UV-Vis spectrum of GNCs.

4. Binary supercrystals (AlB_2)

(a)

(b)

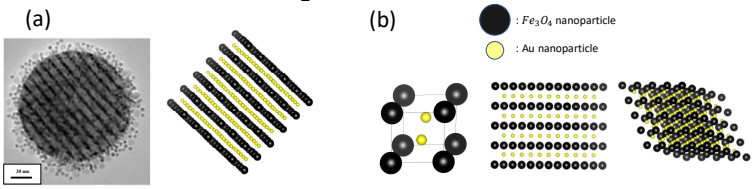


Fig 4. Characterization of AlB_2-type Fe_3O_4-Au binary supercrystals. (a) Transmission Electron Microscopy (TEM) image of a AlB_2-type SCs along its [011] direction and corresponding projection of AlB_2 structure, (b) projection of unit cell, [120], [12$\bar{4}$] direction of AlB_2-type SCs

Conclusion & Further Study

Three types of experiments are conducted for synthesizing and observing the properties of monodisperse building blocks(MNPs, GNPs), nanoclusters and ways to control them.

In the first experiment, XRD patterns of MNPs showed their inverse spinel structure and it was confirmed that M_s was proportional to the size of MNPs. Also, XRD patterns of GNPs revealed that it has face-centered-cubic (fcc) structure and UV-Vis spectrum of GNPs showed absorption peak at 518nm.

The second experiment discovered that it is possible to assemble nanoparticles into nanoclusters by oil-in-water emulsion. Comparing MNPs and MNCs, they showed similar magnetization curve, which showed that even after assembling, MNCs were still superparamagnetic. Also, it was discovered that GNPs and GNCs revealed same wavelength of UV-Vis absorption peak.

The final experiment showed that binary supercrystals can be formed using the same method as the unary clusters. After comparing the TEM image with corresponding projection, we concluded that we synthesized our target structure, AlB_2.

In the future, we plan to search for experimental conditions to improve the yield. Since iron oxide and gold nanoparticles have prospects in hyperthermia and bio-imaging, we will assemble building blocks into three dimensional binary supercrystals with different concentration ratio to compare interactions and multifunctional properties of different structures such as $NaZn_{13}$, Cu_3Au.

Reference

Talapin et al, *J. Am. Chem. Soc.* **2019**, *141*, 5728-5740
Murray et al, *Nature*, **2010**, *466*, 474-477
Qiao, Zhu et al, *J. Am. Chem. Soc.* **2018**, *140*, 9095-9098
Angang Dong et al, *J. Am. Chem. Soc.* **2018**, *140*, 15038-15047
J. Cheon et al., *Nano Today* **2017**, *13*, 61-76