Supporting Information for:

Disodium Diselenide in Colloidal Nanocrystals: Acting as an Anion Exchange Precursor, Metal Selenide Precursor, and Chalcogenide Ligand

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Experimental Details.

Materials.

Selenium, n-trioctylamine and sodium oleate were purchased from Strem Chemical Inc. $NaBH_4$ was purchased from Acros Organics. Toluene and hexane were purchased from J.T. Baker. Anhydrous ethanol, Pb acetate, oleic acid, 1-octadecene, bis(trimethylsilyl)phosphine, 1-dodecanethiol, oleylamine, Iron(Ⅲ) chloride hexahydrate, and silver nitrate were purchased from Sigma-Aldrich. All chemicals were used without further purification. All chemicals were used without further purification.

Synthesis of Na_2Se_2

Na_2Se_2 compound were synthesized using a previously reported method. 3g of selenium and 1g of $NaBH_4$ was loaded in a 250ml 3-neck-flask with vigorous stirring in ice bath. The mixture was degassed under vacuum at 50°C for 2h. The 100ml of anhydrous ethanol was added slowly to the 3-neck-flask under an N_2 atmosphere in ice bath. This mixture solution was heated to reflux temperature and then kept for 1.5 hr, and then the mixture was dried to remove the by-product under vacuum at 70°C for 4h.

Synthesis of nanoparticles

PbS nanoparticle : The PbS nanoparticles were prepared according to Jeong's report with slight modifications.[1] 0.237g of Pb acetate and 0.8ml of oleic acid was loaded in a 50ml 3-neck-flask with vigorous stirring, and then the mixture was degassed under vacuum at 110°C for 2h. To prepare sulfur precursor solution, 0.05ml of bis(trimethylsilyl)phosphine and 1 ml of 1-octadecene in vial were mixed at room temperature in nitrogen filled glove box. The sulfur precursor solution was quickly injected into the lead and surfactant solution at 150°C under nitrogen atmosphere, the mixture was stirred at 100°C for 1hr, and then cooled to room temperature. PbS nanparticles were precipitated from the reaction by adding ethanol and separated by centrifugation.

Ag nanoparticles : The Ag nanoparticles were synthesized by protocol of previous Osterloh's report.[2] The 20 mg of 1-dodecanethiol was dispersed in 50 ml of toluene, followed by heating of the solution to reflux. 50 mg silver acetate was dissolved in oleylamine. When toluene solution

was refluxed, Ag-oleylamie complex was swiftly injected into toluene solution. The color of solution was immediately changed to transparent yellow. The yellow solution gradually became darken. The Ag nanoparticles were aged for 12 hr at reflux temperature. Ag nanoparticles were larger and more uniform with time. After 12 hr, the solution was separated in four falcon tube. For precipitation of Ag nanoparticles, 40 ml of methanol was added in each tube. The tubes were centrifuged at 8000 rpm and supernatant was discarded. Whereas the precipitant was dispersed in anhydrous hexane or toluene.

FeO nanoparticles : The Iron oxide nanoparticles were prepared according to Hyeon's report.[3] To prepare iron-oleate complex, Iron(Ⅲ) chloride hexahydrate 1.08 g and sodium-oleate 3.65 g was solvated in solution containing 8 ml ethanol, 6 ml distilled water and, 14 ml hexane. This solution was heated to 70 °C and then kept for 4 hr. It turned into deep brown color. For washing of the complex, the lower layer was discarded and the same volume of distilled water was used to remove the remained reactant and ions. The prepared iron-oleate complex and oleic acid 0.57 g were dissolved in 20 ml of n-trioctylamine. The mixture was heated with constant heating ratio, 3.3°C per minute up to 365 ℃. It was kept at 365 ℃, for 30 min. After aging of the iron oxide nanoparticles, the solution was cooled down by ice bath and then precipitated by using ethanol three times, followed by centrifugation. The supernatant was discarded, whereas the precipitant was dispersed in anhydrous hexane or toluene.

Reaction of nanoparticles with Na_2Se_2

25mg of oleylamine-capping PbS nanoparticles and 3ml of hexane was loaded in a 20ml vial with vigorous stirring. A dropwise solution was prepared by dissolving 2mg of Na_2Se_2 in 3ml of Dimethylformamide. The Na_2Se_2 solution was added slowly to the NCs dissolved hexane solution under an N_2 atmosphere at room temperature. The NCs were precipitated from the reaction solution by adding buthanol and then separated by centrifugation. The NCs were redispersed in hexane

Characterization. The nanoparticles dispersed in hexane were spread on a copper grid and a silicon wafer for measurement using transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. TEM image and STEM-EDX were taken with a FEI Tecnai G2 F30 Super-Twin transmission electron microscope operating at 300 kV. SEM image and X-ray mapping data were obtained with a JSM-6700F field emission scanning electron microscope at 30 kV operating voltage, equipped with an INCA energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) patterns were taken using a Rigaku Ultima III diffractometer equipped with a rotating anode and Cu K_α radiation source ($\lambda = 0.15418$ nm).

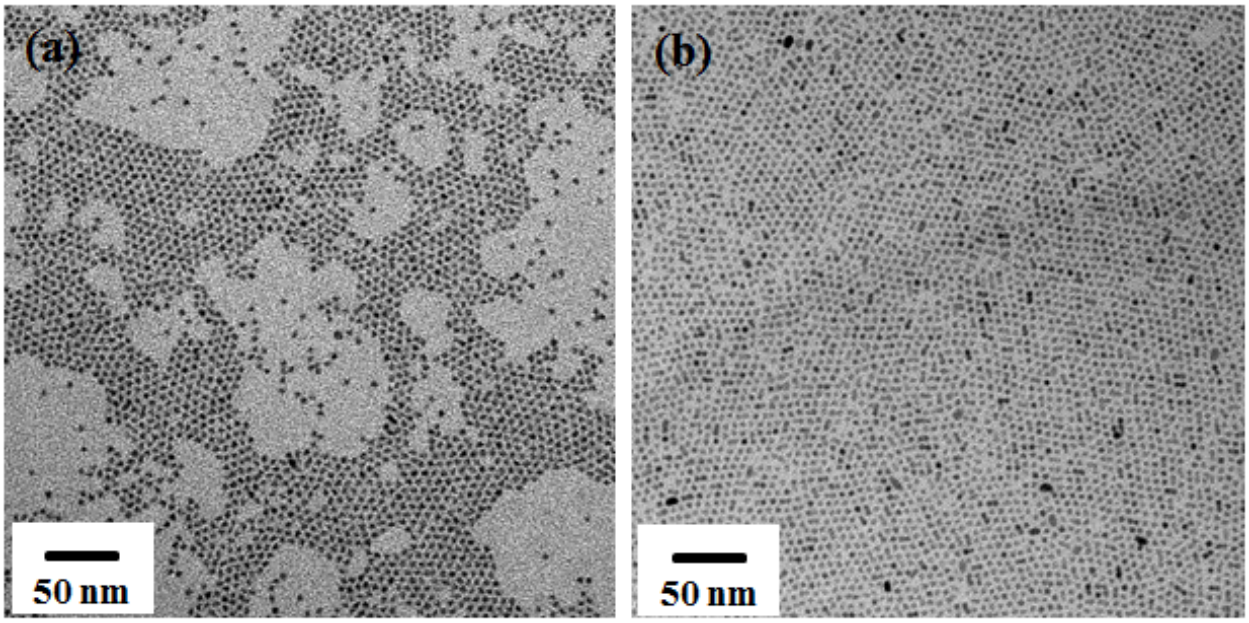


Figure S1. Low magnification Transmission electron microscopy (TEM) images of (a) bare PbS, (b) PbS-Na_2Se_2 molar ratio 4 : 1.

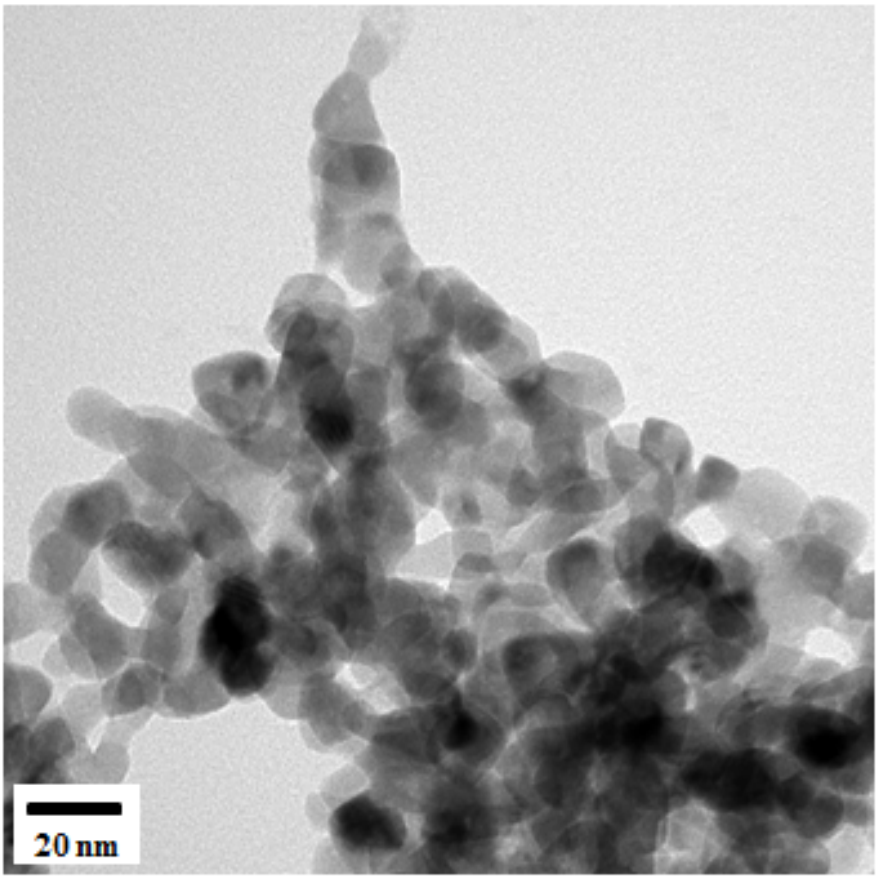


Figure S2. TEM image of PbS-Na_2Se_2 molar ratio 1 : 4.

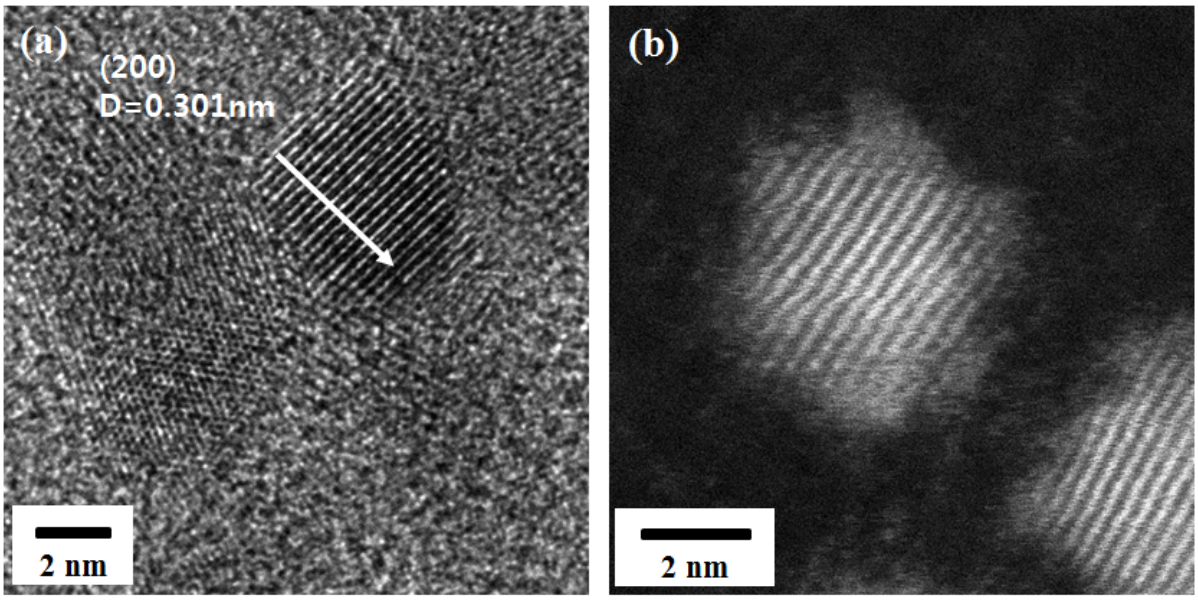
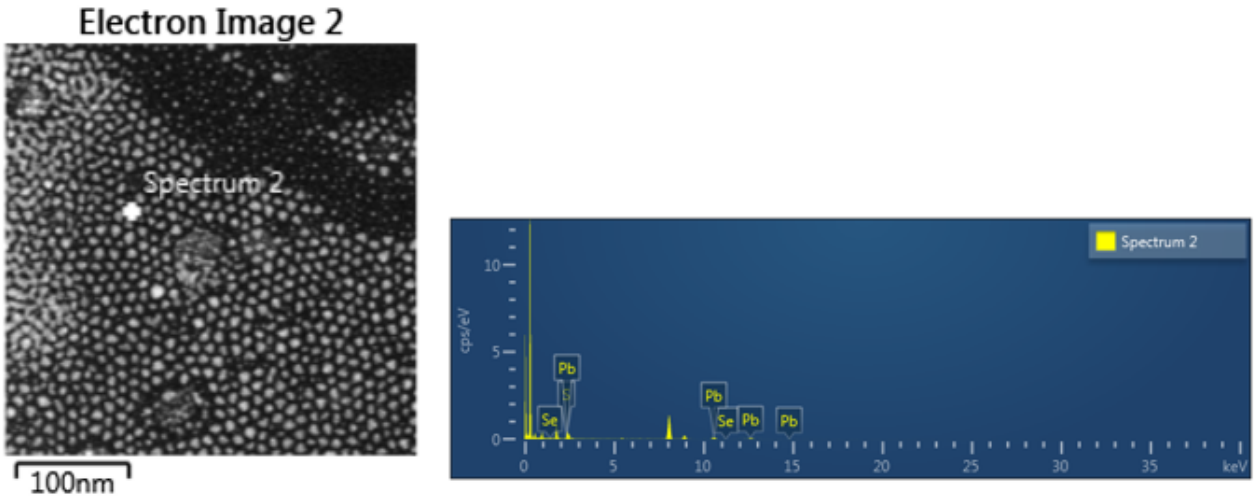


Figure S3. HR-TEM images of (a) with the distance between the lattice planes and HR-STEM image of (b) PbS-Na_2Se_2 molar ratio 4 : 1.



Element	Line Type	k factor	Absorption Correction	Wt%	Wt% Sigma	Atomic %
S	K series	0.95908	1.00	2.83	1.72	15.53
Se	K series	2.09255	1.00	1.48	1.09	3.30
Pb	L series	2.96436	1.00	95.68	2.01	81.17
Total:				100.00		100.00

Figure S4. Energy-dispersive X-ray spectroscopy scanning transmission electron microscopy (EDX-STEM) elemental analysis of PbS-Na_2Se_2 molar ratio 4 : 1.

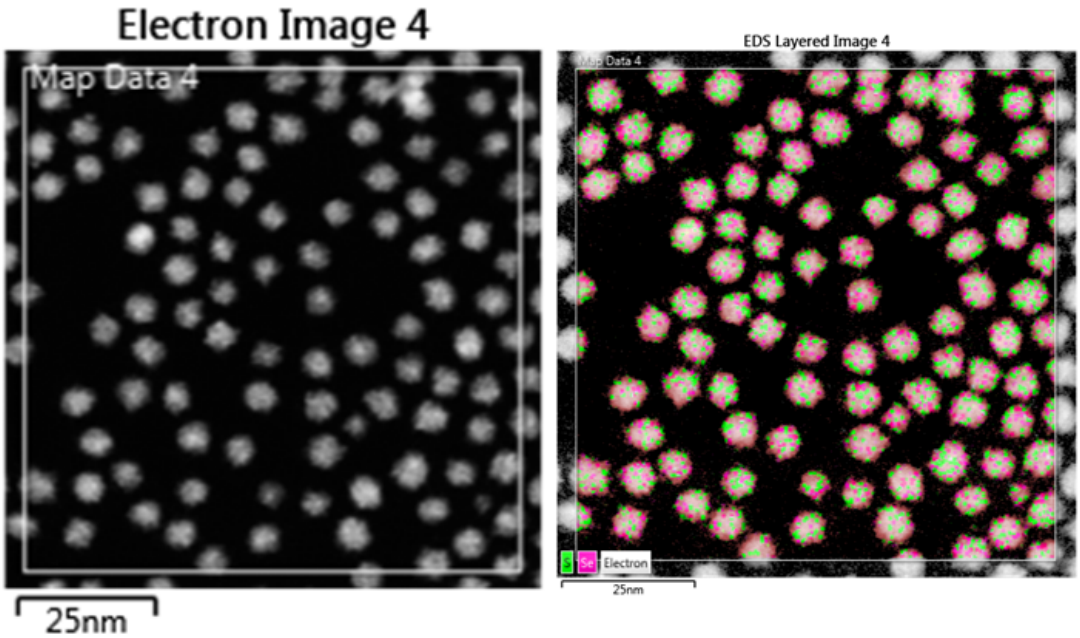


Figure S5. Elemental mapping analysis of PbS-Na_2Se_2 molar ratio 4 : 1. Selenium color is Pink. Sulfur color is green.

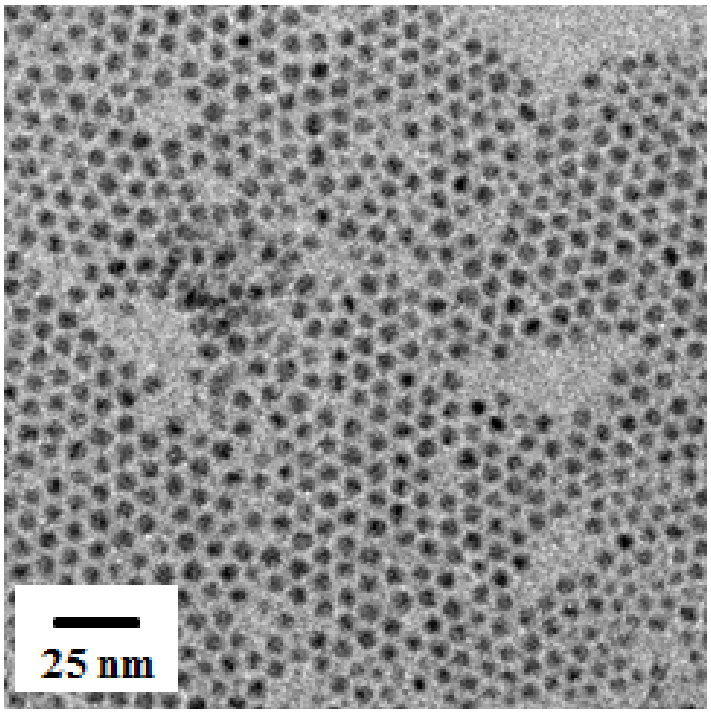


Figure S6. TEM image of Ag-Na_2Se_2 molar ratio 8 : 1. Nanoparticles size is 6.1 nm and standard deviation is 0.36

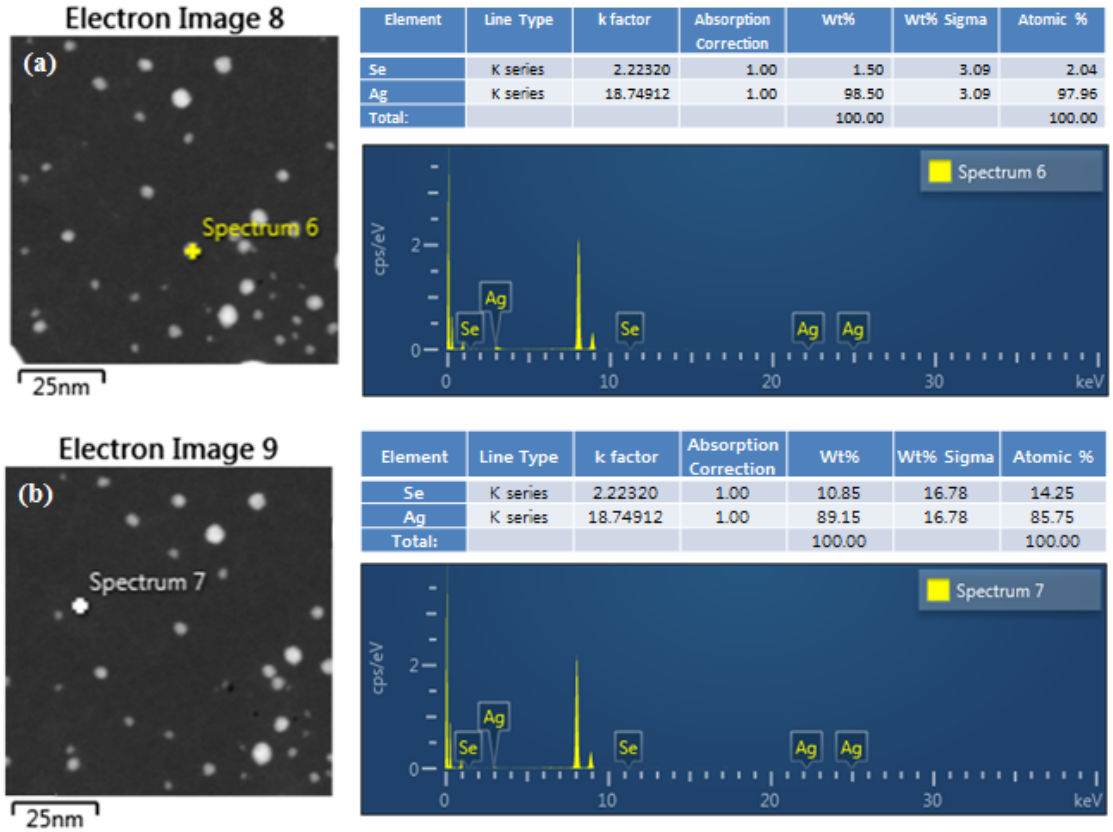


Figure S7. EDX-STEM elemental analysis of Ag-Na_2Se_2 molar ratio 4 : 1. (a) 5 nm nanoparticle (b) less than 2 nm nanoparticle.

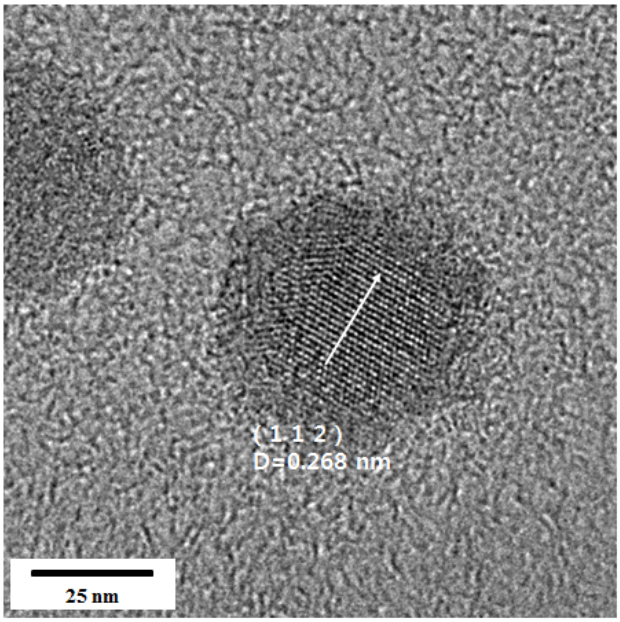


Figure S8. HR-TEM images of Ag-Na_2Se_2 molar ratio 1 : 4 with the distance between the lattice planes

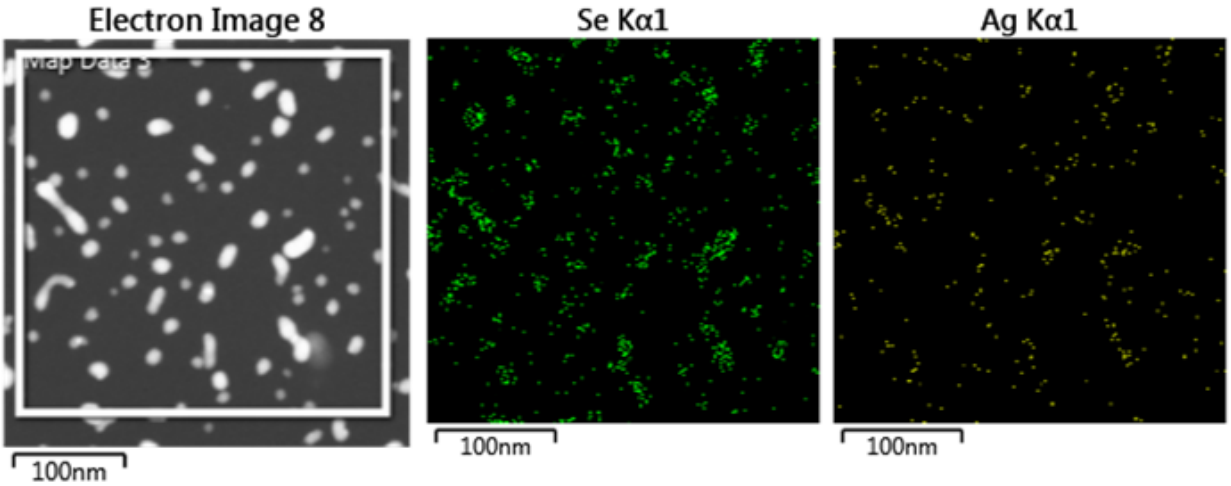


Figure S9. Elemental mapping analysis of Ag-Na_2Se_2 molar ratio 1 : 4.

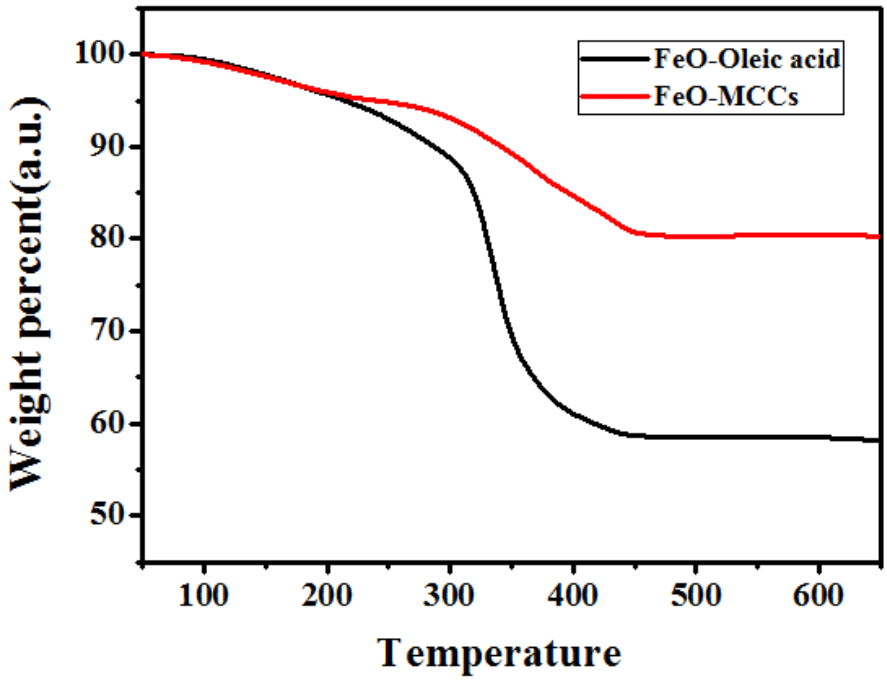


Figure S10. Thermogravimetric analysis of FeO-Oleic acid (black curve, FeO capping with oleic acid) and FeO-MCCs(red curve, FeO-Na_2Se_2 molar ratio 4 : 1)

REFERENCES

1. H. Choi, J.-H. Ko, Y.-H. Kim and S. Jeong, *J. Am. Chem. Soc.,* 2013, **135**, 5278.
2. H. Hiramatsu and F. E.Osterloh, *Chem. Mater.,* 2004, **16**, 2509-2511.
3. J. N. Park, K. J. An, Y. S. Hwang, J. G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang and T. H. Hyeon, *Nat. Mater.,* 2004, **4**, 891-895.