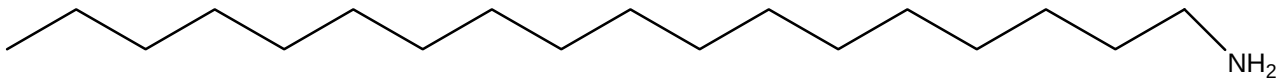
James Puthussery
August 3, 2010

Synthesis of iron pyrite nanocrystals

Current synthesis of pyrite (FeS_2) nanocrystals

Pot

$FeCl_2.4H_2O$ (100 mg, 0.5 mmol)
Octadecylamine (10 g, 0.14 mol)



Octadecylamine

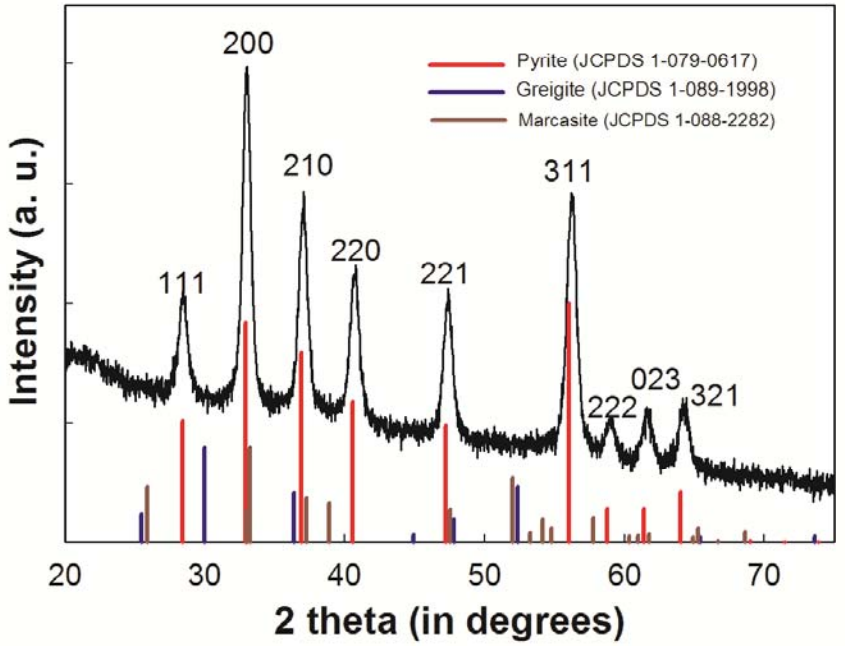
Inject

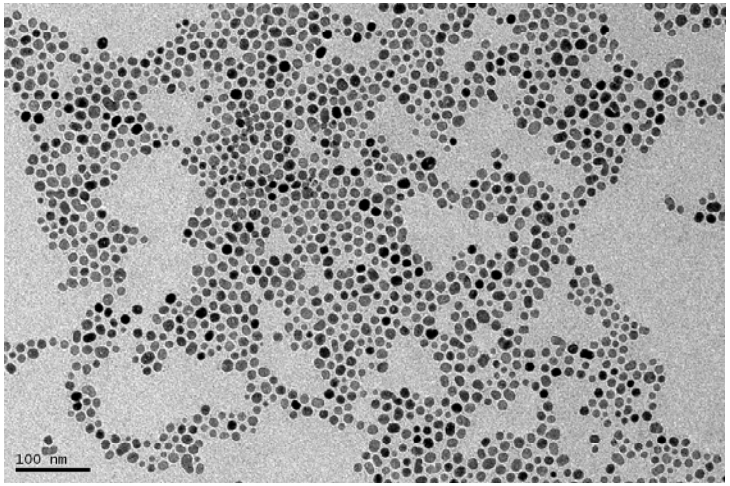
Phenyl ether (5mL)
Sulfur (96 mg, 3 mmol)

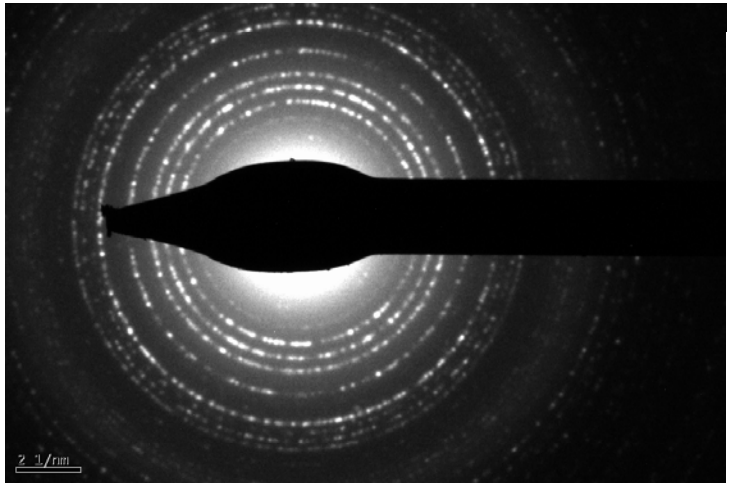
Injection at 220 C
Cooking for 3 h

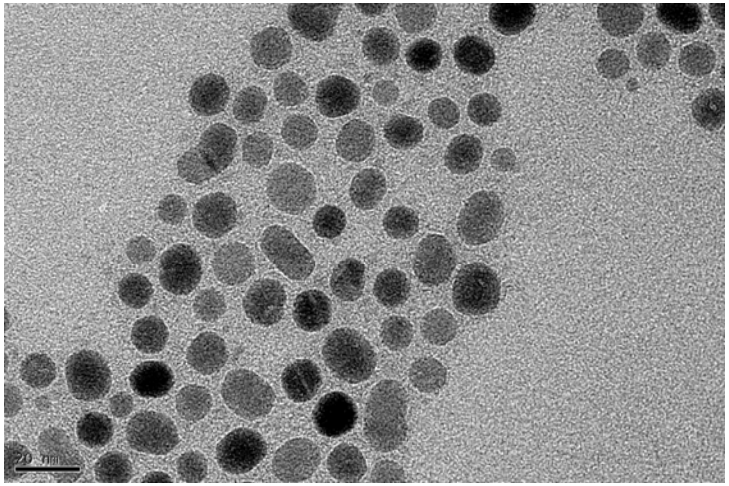
Degas at 120 C for 1h

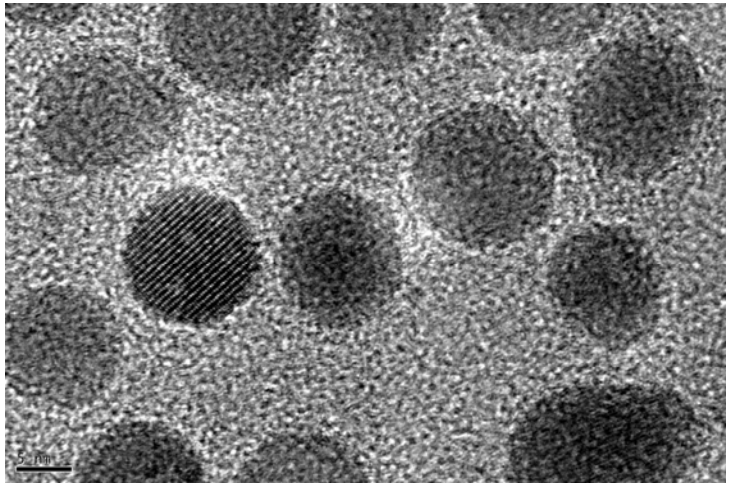
The reaction yield varies from 5 mg (8%) to 15 mg (25%).



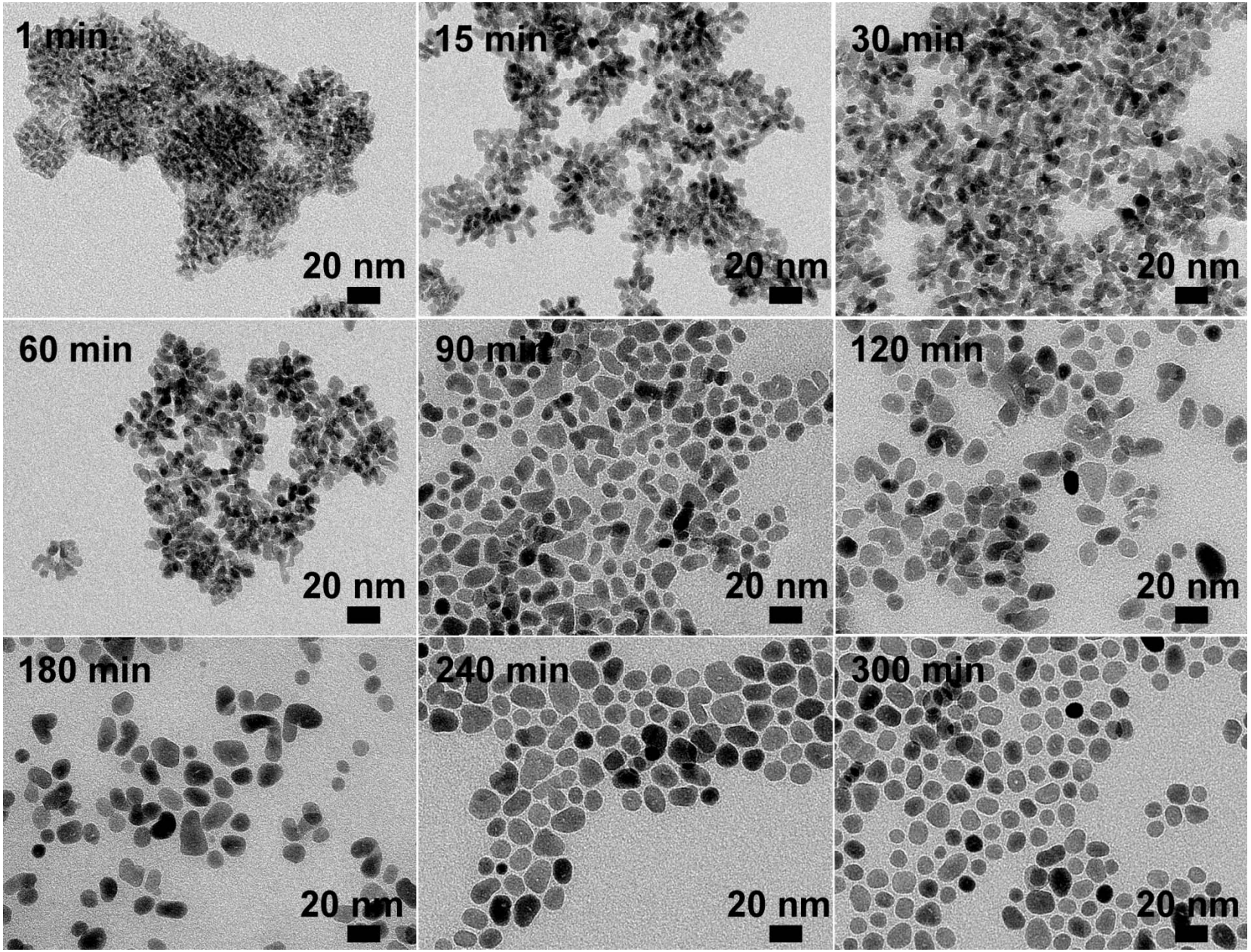

100 nm

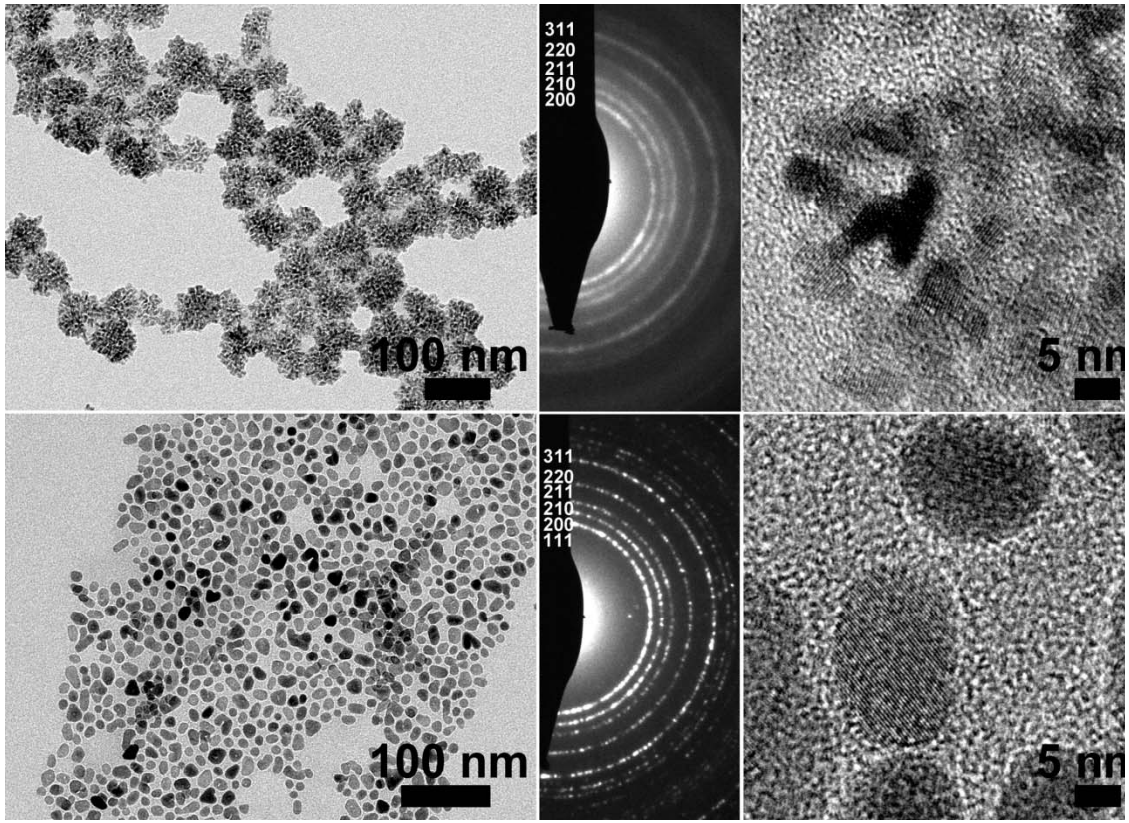

2 1/nm

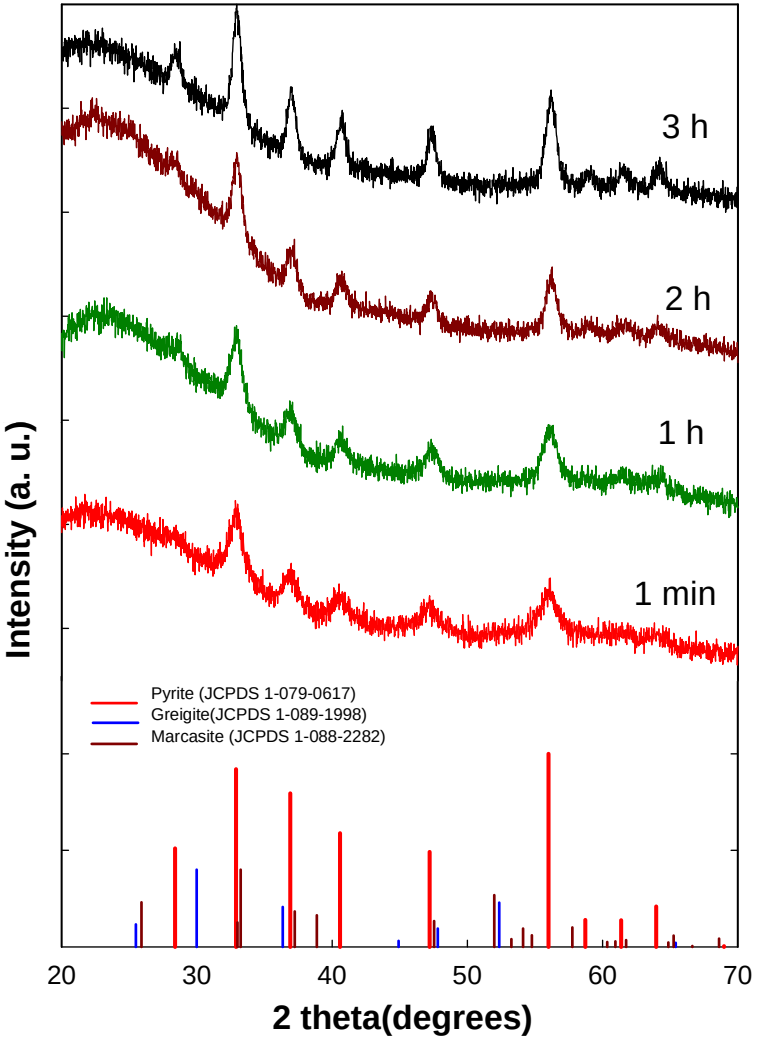

20 nm


5 nm

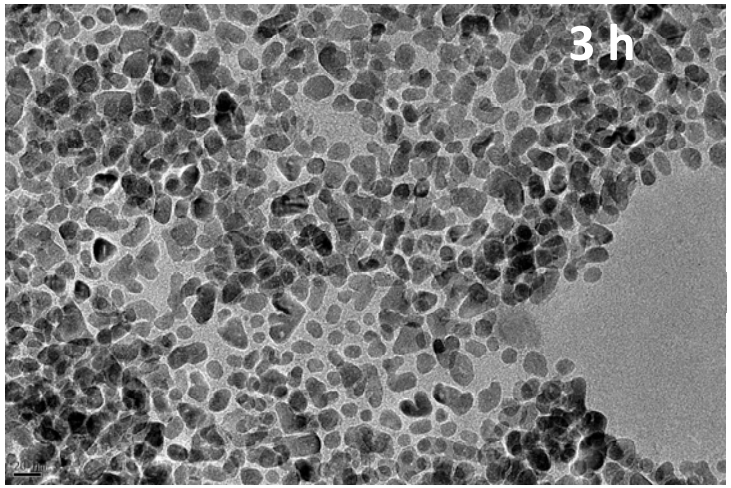
Progress of the reaction

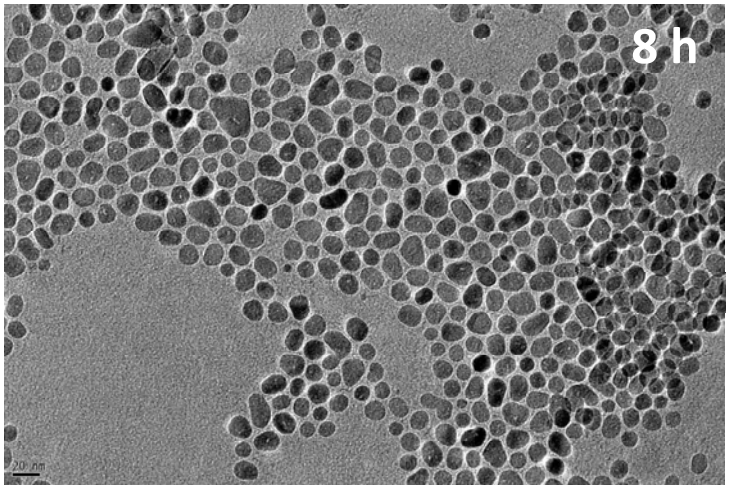



100 nm
311
220
211
210
200
5 nm
100 nm
311
220
211
210
200
111
5 nm

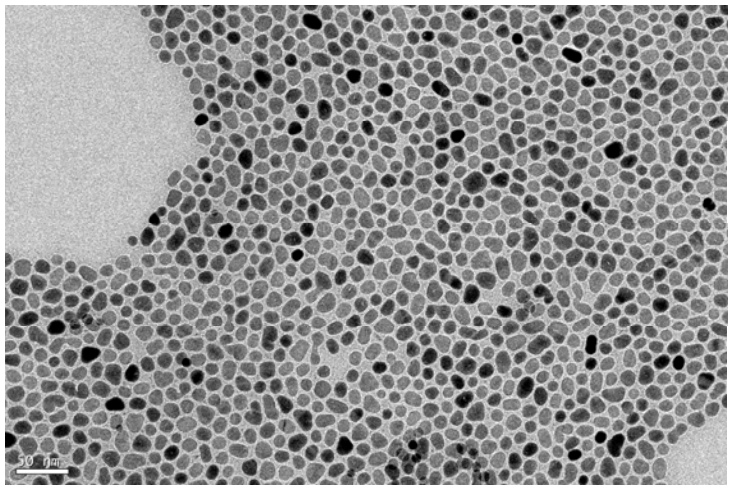

3 h
2 h
1 h
1 min
Intensity (a. u.)
Pyrite (JCPDS 1-079-0617)
Greigite(JCPDS 1-089-1998)
Marcasite (JCPDS 1-088-2282)
20
30
40
50
60
70
2 theta(degrees)

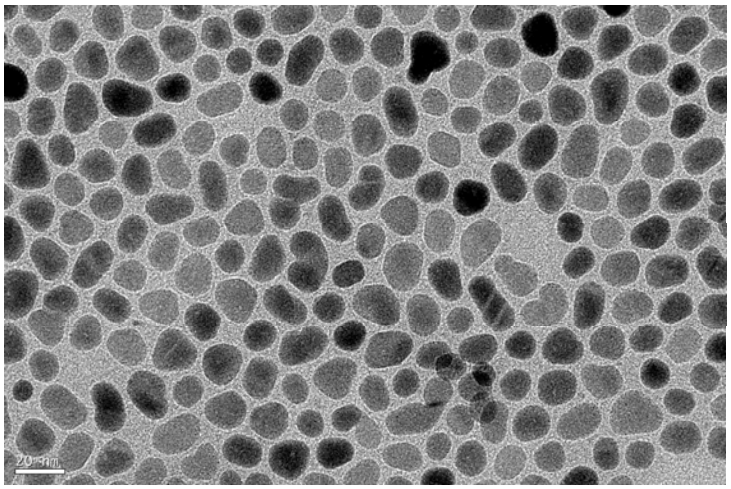
For larger reactions (5 times higher)





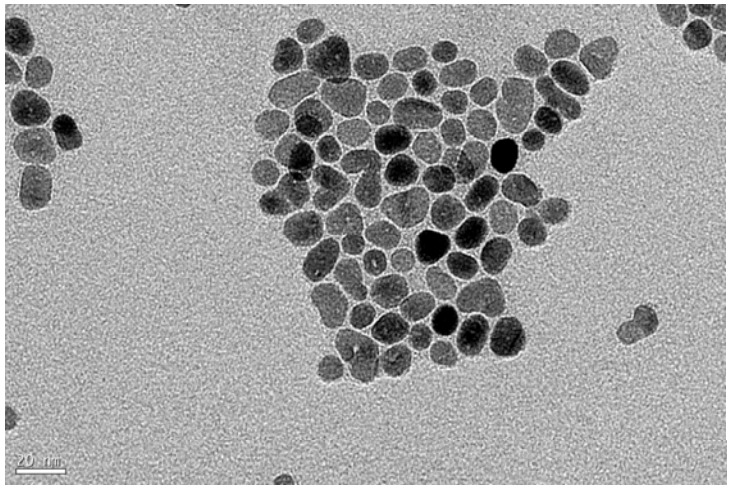
- ***Reaction proceeds at a slower rate compared to small scale reactions***
- ***Amount of the soluble product do not increase correspondingly and the yield of the reaction is as low as 4 to 8%***
- ***For the same concentration, the total time Fe precursor spends in the reaction pot determines the quality of the resulting nanocrystals***



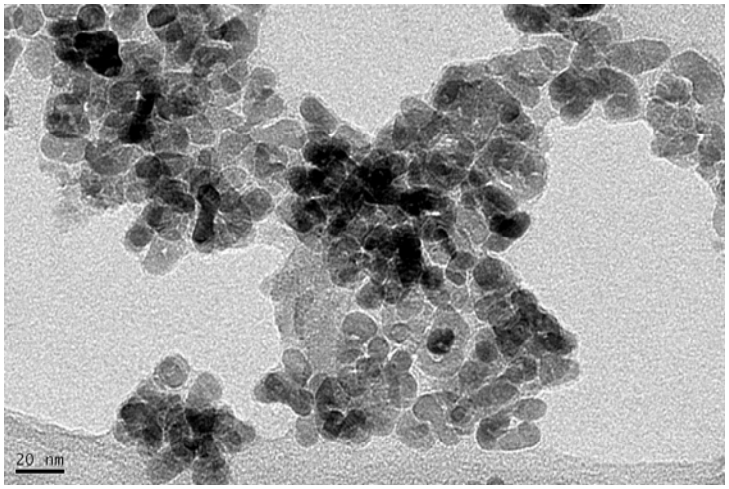


Effect of counter ion

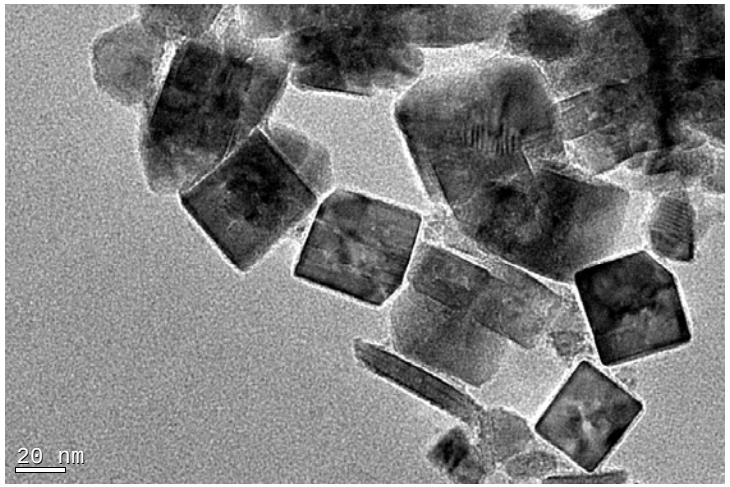
Iron chloride



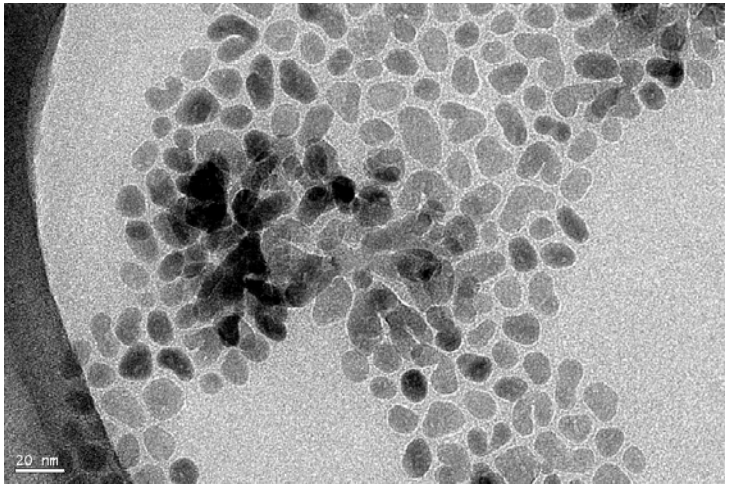
Iron bromide



Iron Iodide

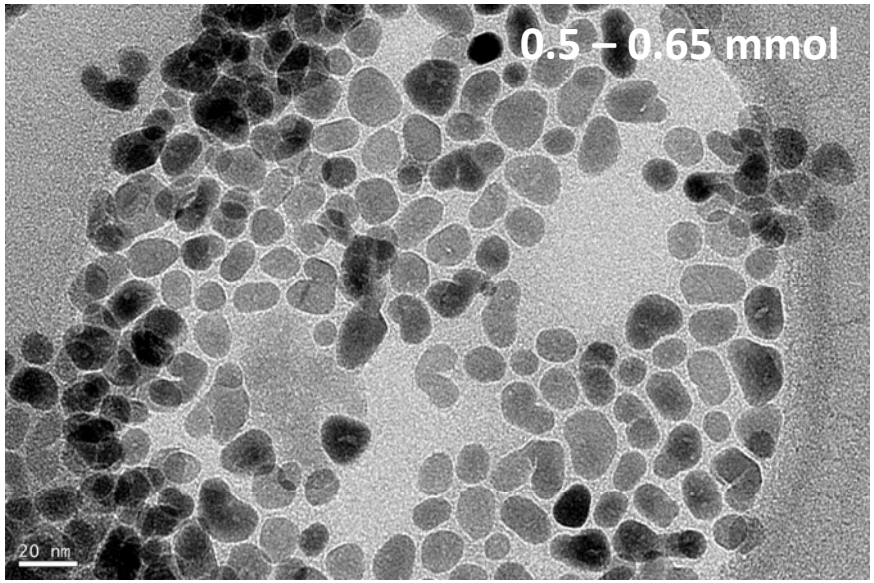


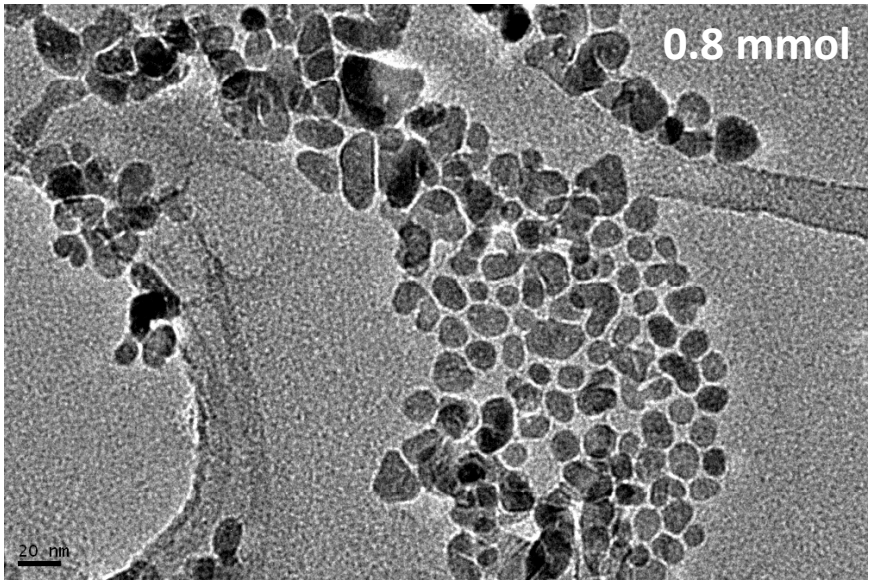
Iron bromide, 4h

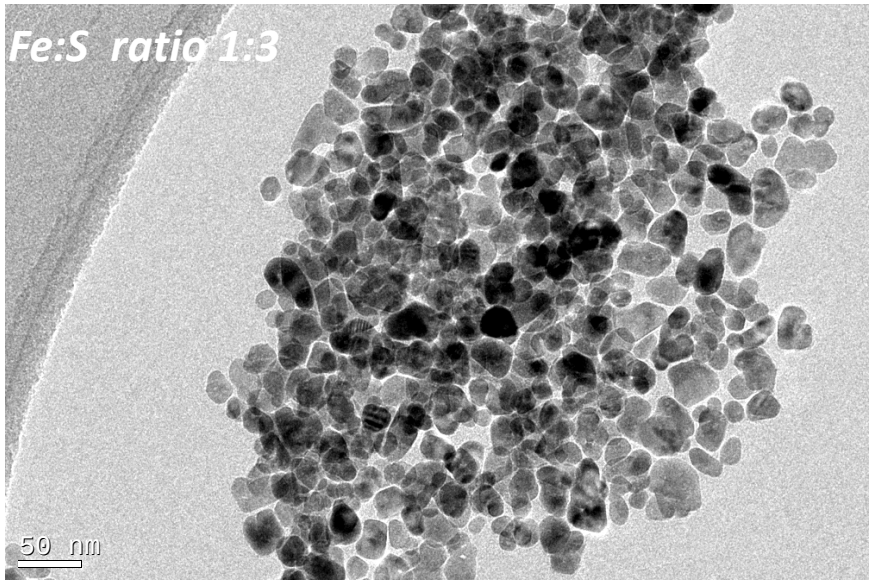


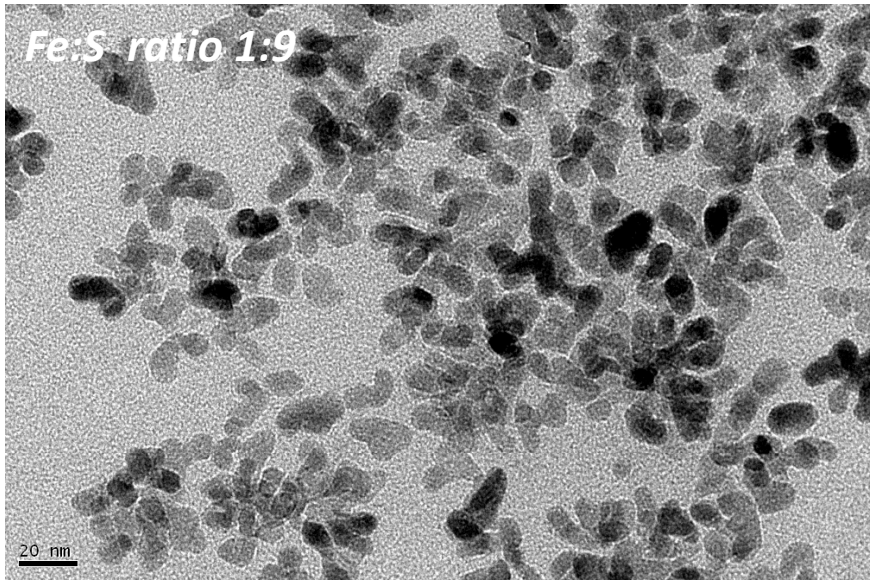
Other precursors such as iron oxalate and iron acetylacetonate gave insoluble products

Fe: S ratios

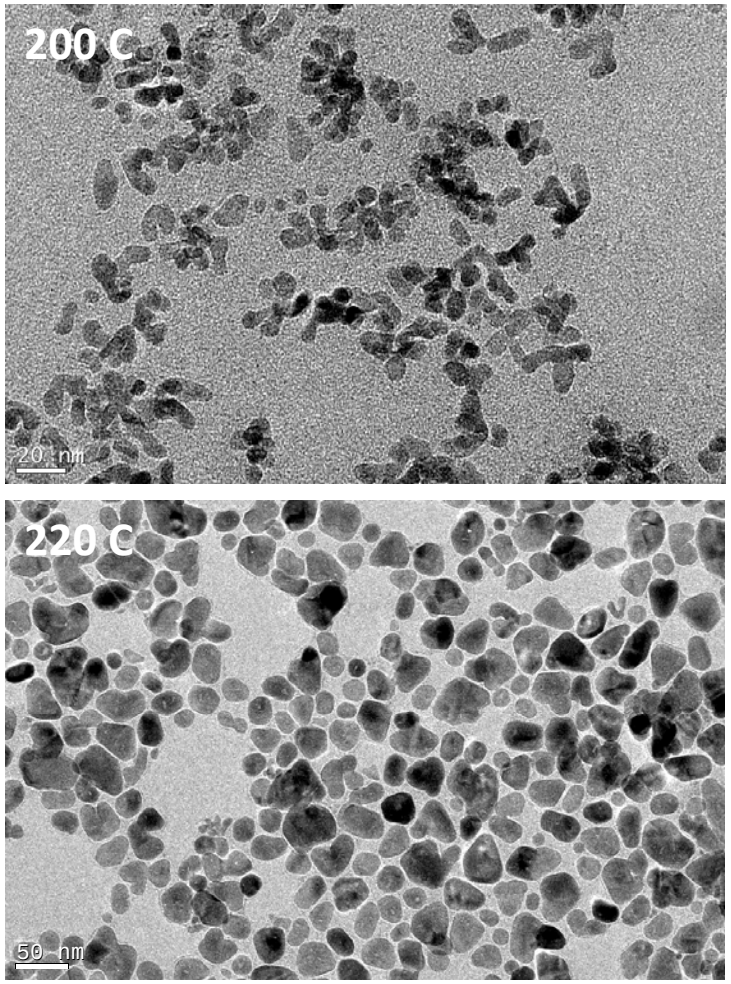

0.5 – 0.65 mmol
20 nm


0.8 mmol
20 nm


Fe:S ratio 1:3
50 nm


Fe:S ratio 1:9
20 nm

Temperature



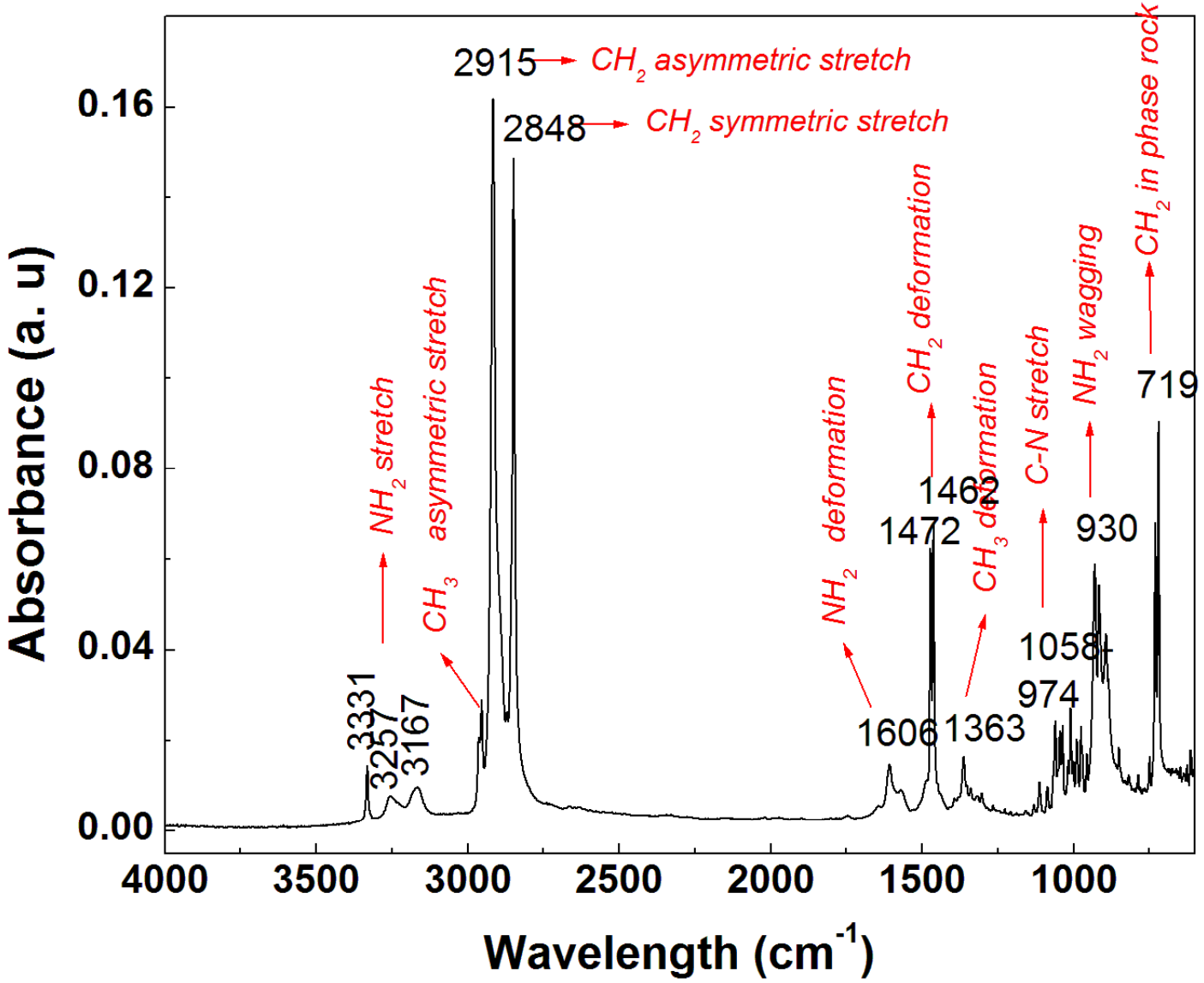
Lower temperatures gave amorphous iron sulfide products

Solvents

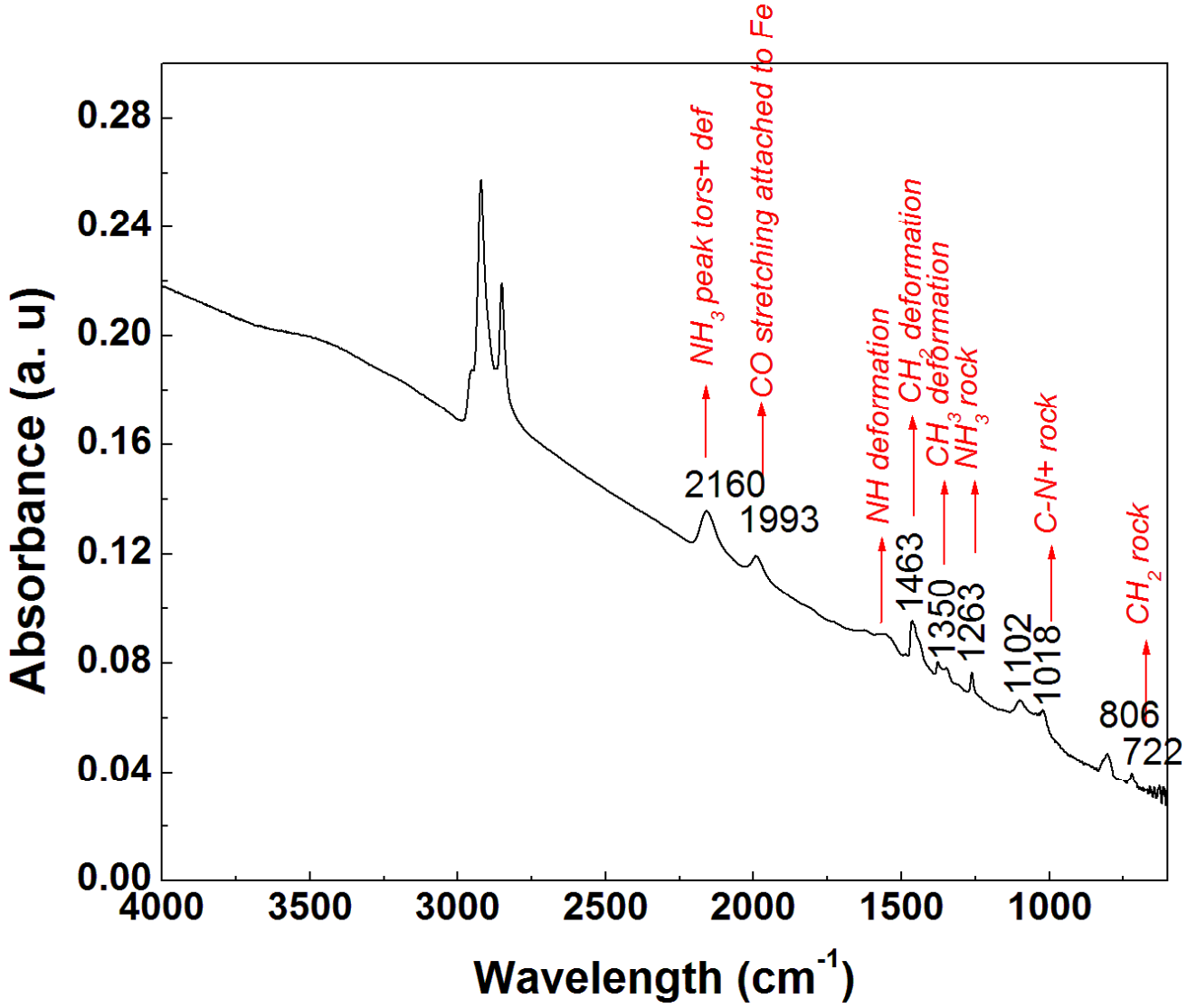
- *Other primary long chain amines gave the desired phase, but relatively lower yields*
- *Any noncoordinating solvents such as octadecene or squalane gave mixed phase materials*
- *Noncoordination injection solution don't have any influence on the reaction and the solubility of the product decreases if the injection solution exceeds 50% of total reaction*

What is on the surface of the nanocrystals?

Octadecylamine

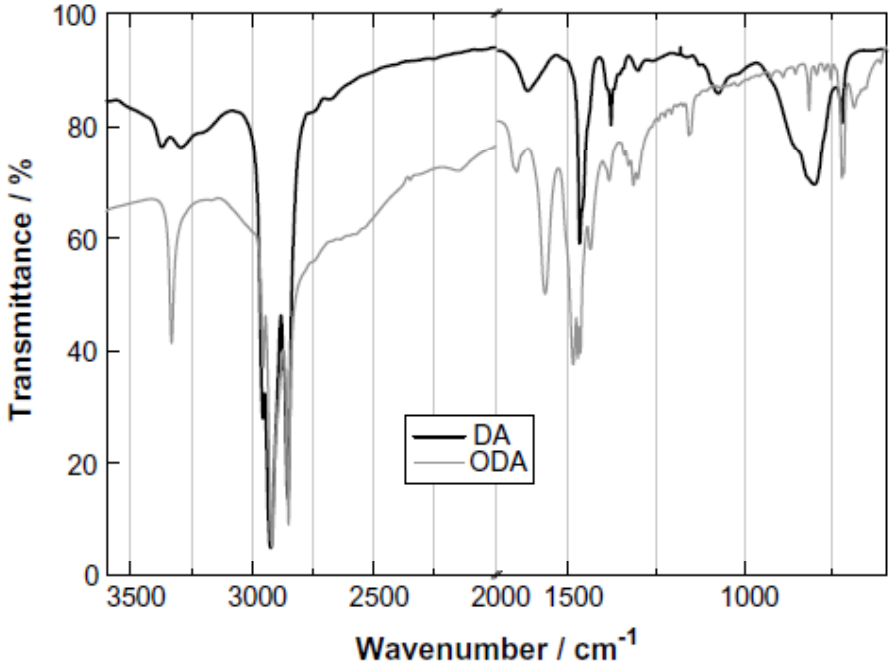


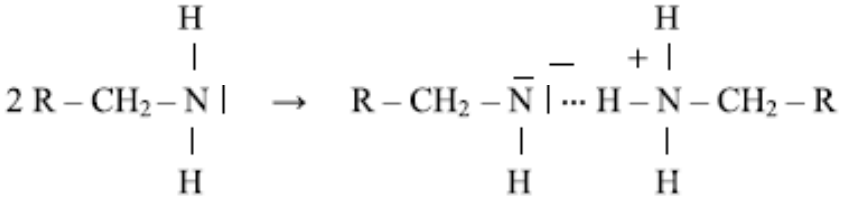
Pyrite nanocrystals



From the literature

Octadecylamine unlike othre amines exist as inner salts as proved by FT-IR studies





Ref: J Mol Str 924–926 (2009) 144–147

By FT-IR and NMR the existence of any inner salts are ruled out in the case of octadecylamine. The extra band is due to the presence of strong hydrogen bonds or amine hydrates.

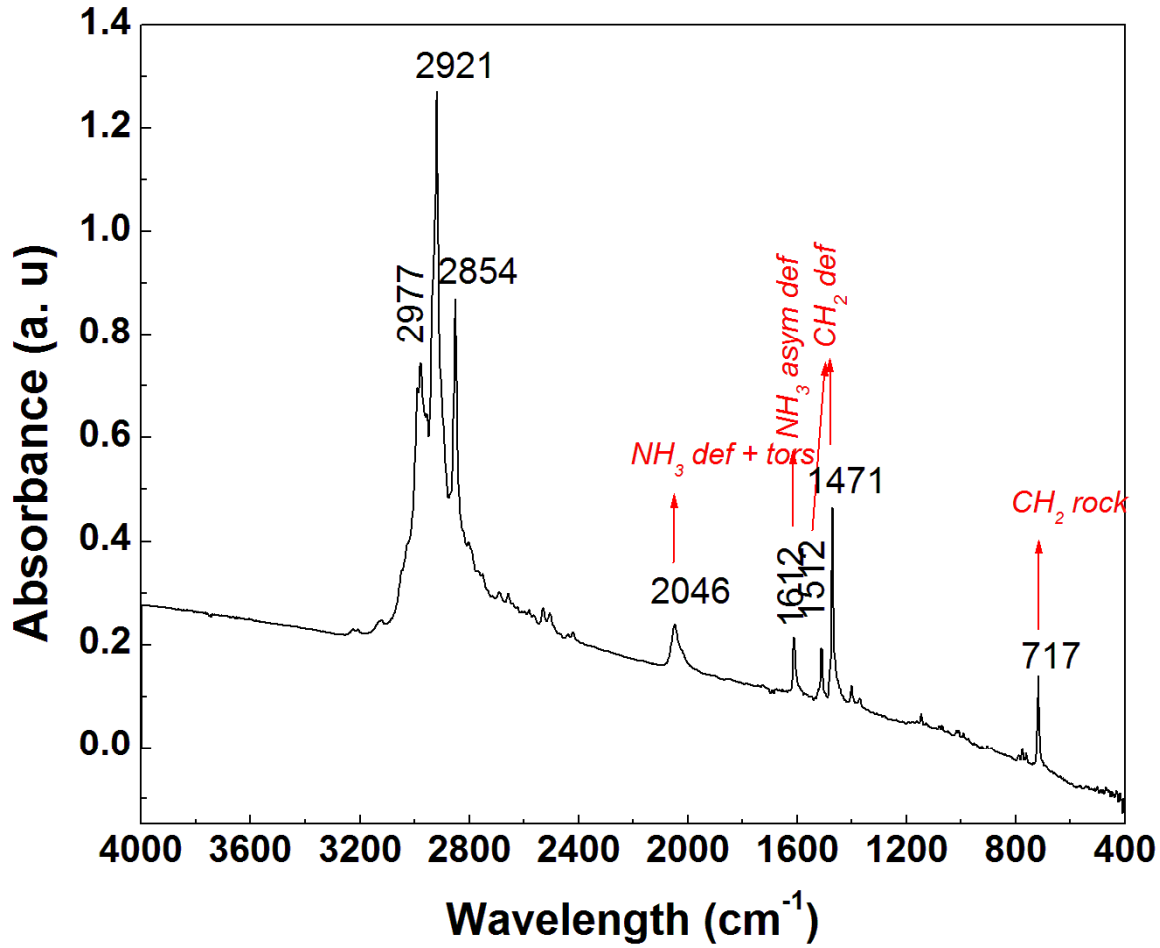
Ref: J Mol Str 924–926 (2010) 106-110

$$2CH_3(CH_2)_nNH_2 + CO_2 \underset{\Delta}{\rightleftharpoons} NH_3^+(CH_2)_nCH_3 + CH_3(CH_2)_nNHCO_2^-$$

Exposure of long chain fatty acids to CO_2 makes thiocarbamate and by controlled exposure with CO_2, they could produce ZnS nanorods.

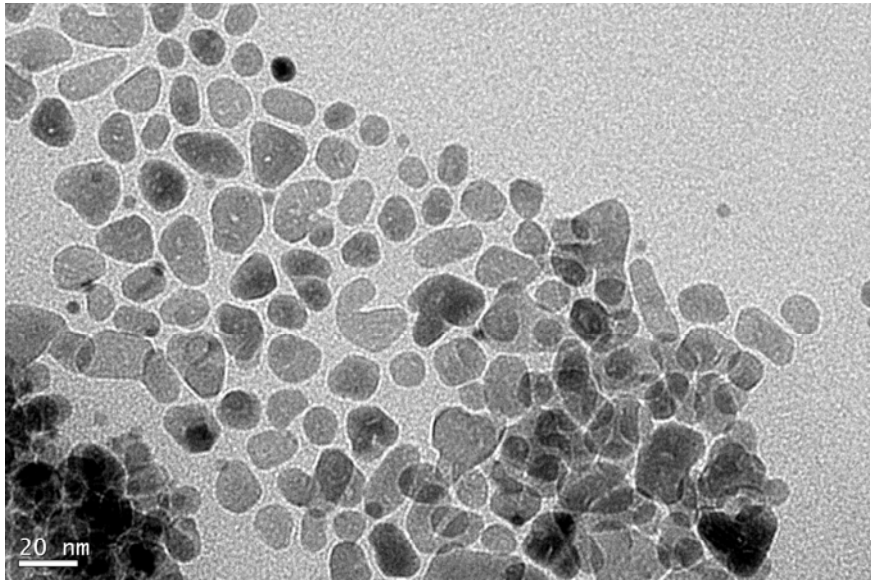
Ref: Nano Lett., 9, 2009, 2088

Octadecylammonium chloride

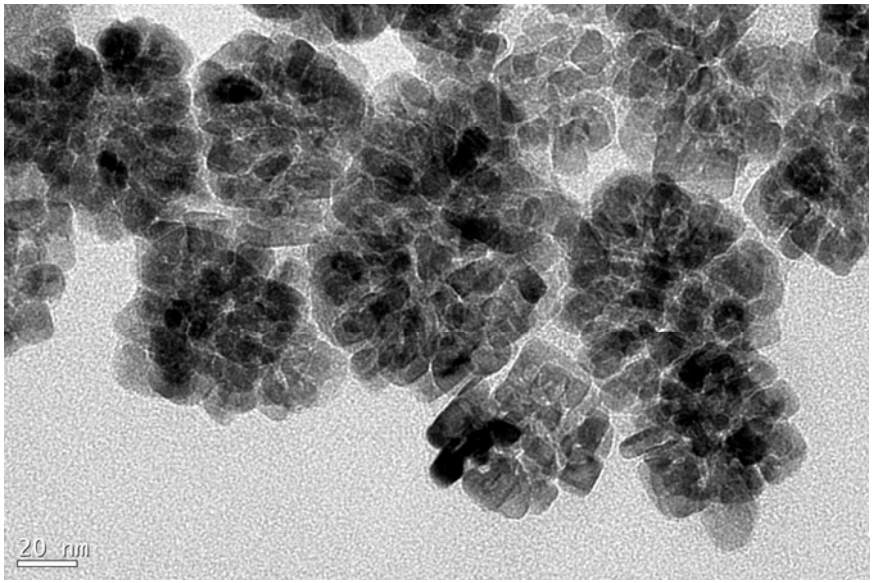


Presence of primary amine salt makes a difference in the nanocrystal morphology

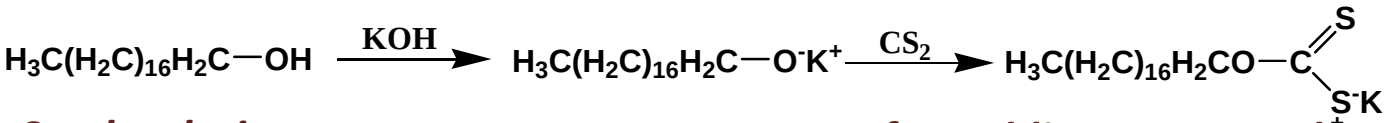
FeI_2, with OD-NH_3^+Cl (5%), 4h cooking



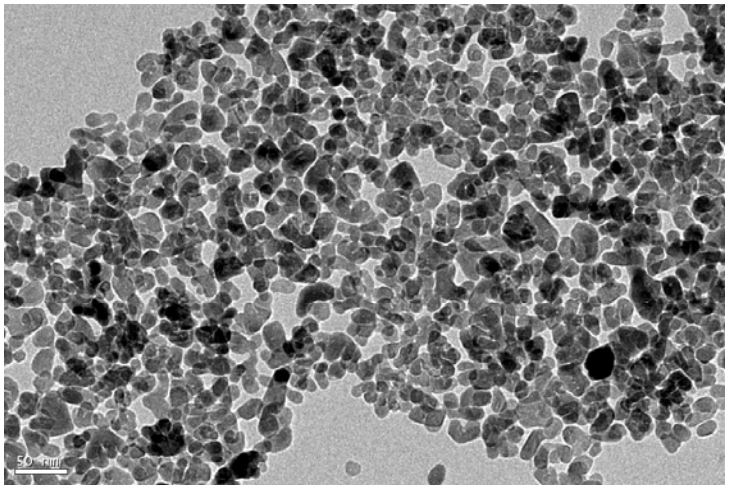
Blank, without OD-NH_3^+Cl, 4h cooking



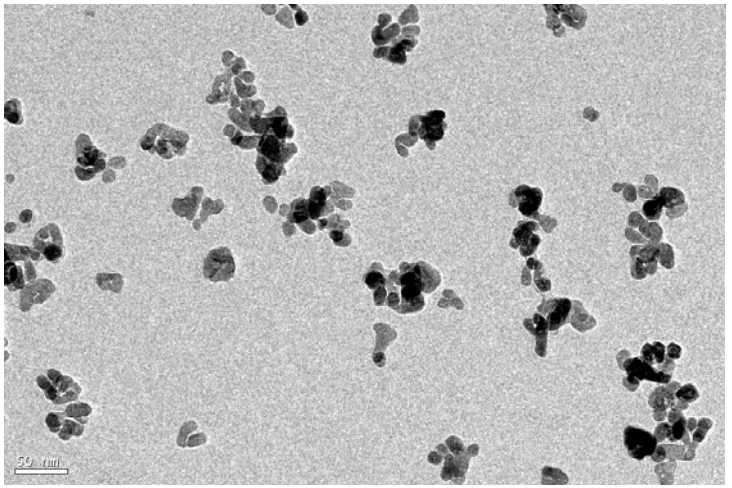
New ligands (xanthates and thiocarbamates) for stabilizing nanocrystals

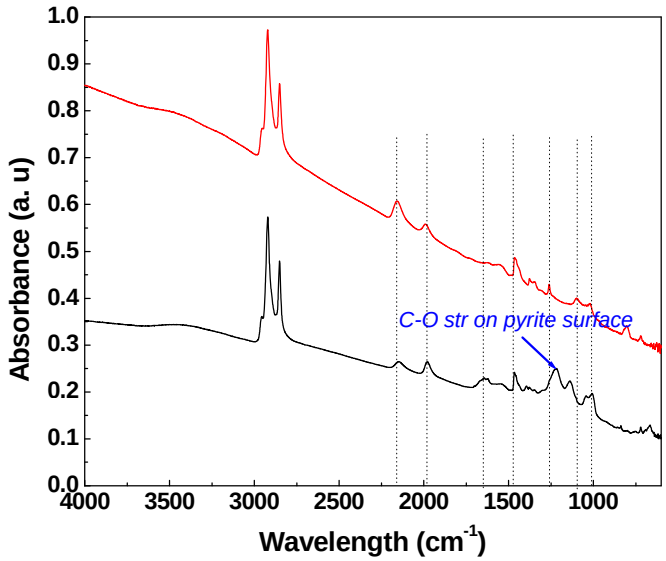


Stock solution



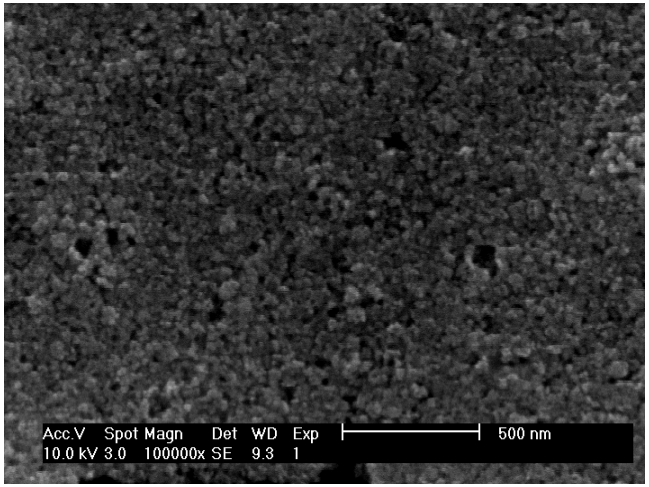
After adding pot. Octadecyl xanthate

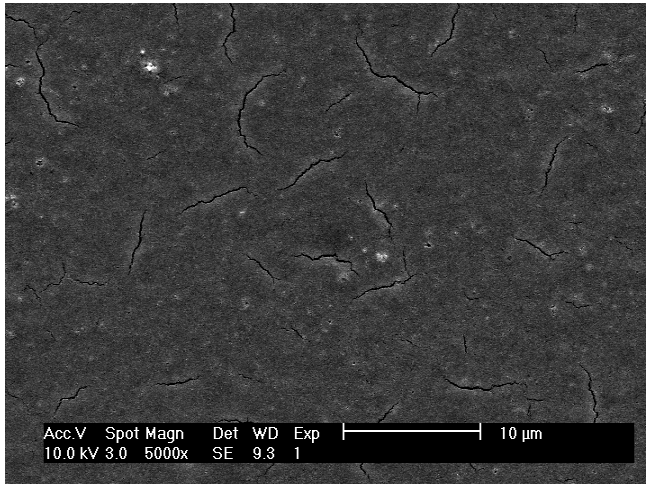


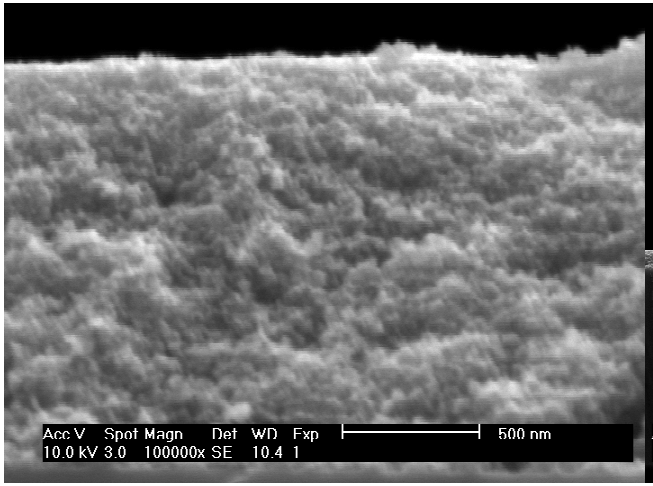


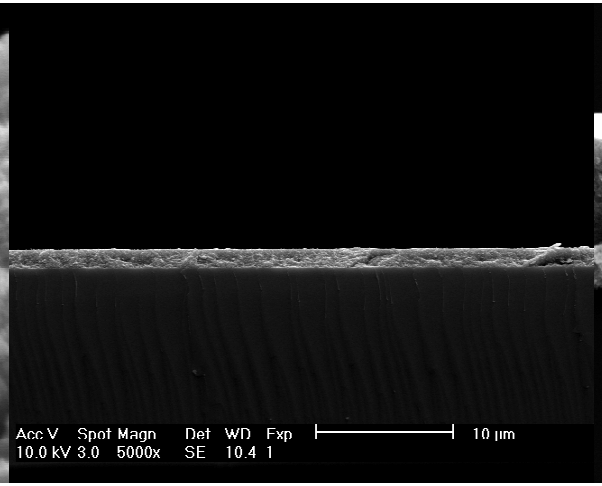
Shorter alkyl chain xanthate do not stabilize the nanocrystal solution.

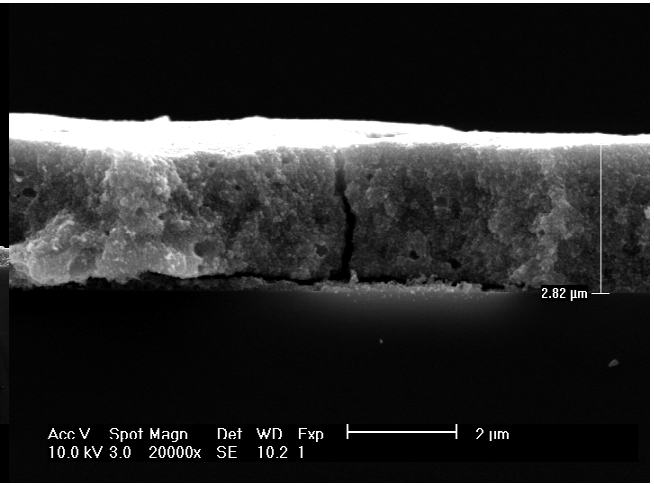
Making nanocrystal films





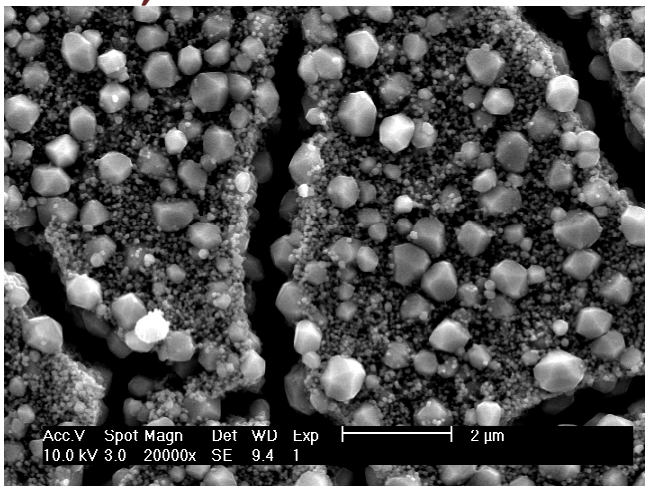


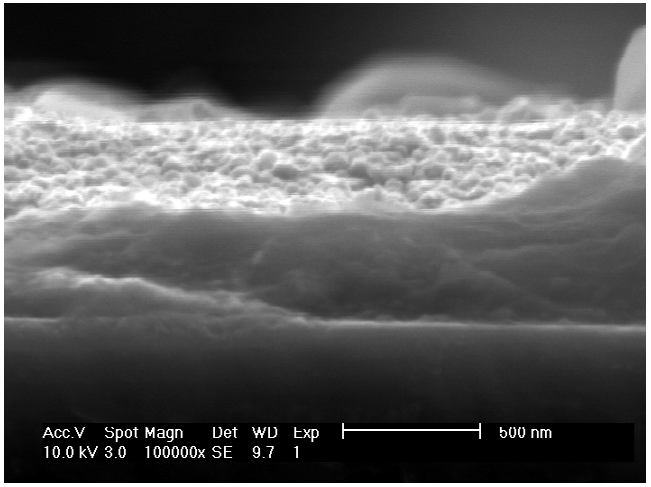




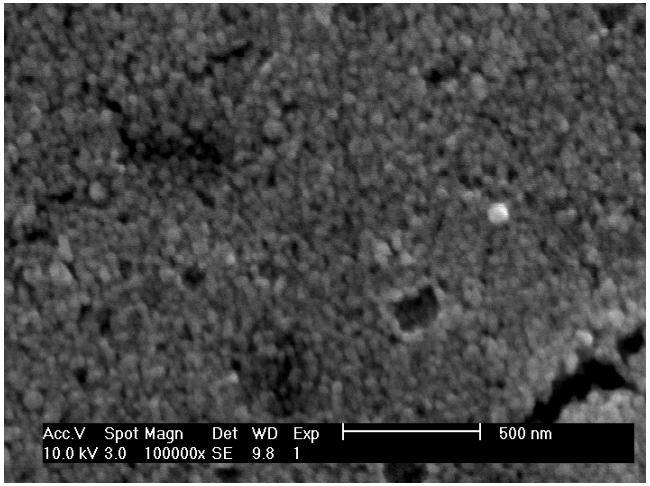
After annealing

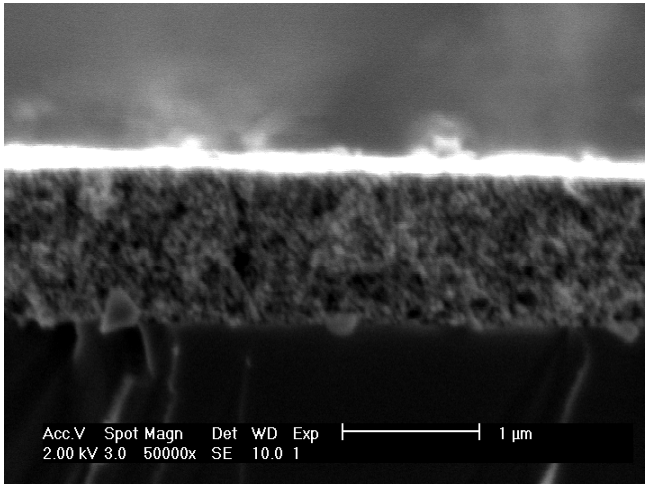
570 C, 7h





Heating to 550 C





Future work

- ***Optimize the annealing temperatures to get good films without cracking***
- ***Film treatment using various reagents to replace NCs with shorter chain ligands***