

Synthesis of Cu^{II}-Nanocrystal Coordination Polymer by Microemulsion Method. Straightforward Experiment of Nanomaterial Synthesis for Science High School Students

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Abstract This work aims to demonstrate the experiment which was applied in the academic recreation club at science high school for learning about coordination chemistry and nanomaterial synthesis. Accordingly, the synthesis of the nanocrystal coordination polymer (NCP) by microemulsion method was employed as an example for this purpose. In this work, the general microemulsion (μ Em) method was modified in order to provide the straightforward procedure for the synthesis of Cu^{II}-NCP for high school students. The results from transmission electron microscopy (TEM) and infrared spectroscopy (IR) were also discussed with the students.

Keywords: nanocrystal coordination polymer, microemulsion method, nanomaterial synthesis, science high school students

Cite This Article: Kiattipoom Rodpun, "Synthesis of Cu^{II}-Nanocrystal Coordination Polymer by Microemulsion Method. Straightforward Experiment of Nanomaterial Synthesis for Science High School Students." *World Journal of Chemical Education*, vol. 5, no. 3 (2017): 107-111. doi: 10.12691/wjce-5-3-5.

1. Introduction

Mahidol Wittayanusorn School (MWITS) is the top high school in Thailand to specialize in science for gifted and talented students. To provide these students with guidance of scientific research method, the academic recreation club named "Nano must go on" was designed for 18 students who are interested in learning about the interdisciplinary nature of nanoscience and nanotechnology.

Most of the students in the "Nano must go on" club are interested in nanomaterial synthesis. Additionally, my knowledge and experience are related to the field of nanocrystal coordination polymers (NCPs) and microemulsion (μ Em) method as evidence in my scientific work which was published [1]. Thus, the concept of NCP synthesis in my previous report was modified in easy way as the mini experimental session "the synthesis of Cu^{II}-NCP by μ Em method" for the students at high school level.



"Nano must go on" club at MWITS

Coordination polymers (CPs) are the compounds which are constructed from repeated units of metal ions and organic ligands linked by coordination bonds and infinitely extending into one-, two-, and three-dimensional architectures [2]. Self-assembly of metal ions and organic ligands in solution is a general process to form CPs which mostly exists in the solid state in a range of topologies [3].

Nowadays, nanocrystal coordination polymers (NCPs) have attracted great attention as one of the most novel classes of highly tailorable nanoscale materials with numerous potential applications [4]. For instance, macroscopic solid CPs mostly show limited solution-based behavior [5], but decreasing their size down to the nanoscale can afford novel properties which are different from the bulk crystal, such as colloidal dispersibility [6]. The versatile nanoscale properties of NCPs can expand the utility of the macroscale CPs above and beyond structural investigations in terms of crystal engineering, which have formed the bulk of the work in the general research area.

2. Coordination Polymer of C_nCOOH

Di(2-pyridylmethyl)alkylamine-appended carboxylate ligands (C_nCOOH, n = number of methylene group in the alkyl chain) is an appropriate ligand to react with metal ion to achieve coordination polymers (CPs) [7]. To date, the majority of CPs utilizing C_nCOOH have been reported to form one-dimensional (1D) structures [8]. Herein, 5-[Di(2-pyridinylmethyl)amino]pentanoic acid (C₄COOH) and Cu^{II} ion were selected as precursors to synthesize CP

(Figure 1) and further employed as starting materials for the synthesis of nanocrystal coordination polymer (NCP). At macroscale, 1:1 ratio of C4COOH and Cu^{II} ion were used to synthesise CP; 0.100 mmol of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in water (2.0 mL) and carefully layered with a methanolic solution of C4COOH (0.100 mmol in 2.5 mL). Crystals suitable of C4COOH-CP for X-ray analysis were obtained within 2 days and were isolated, dried in air and weighed [9]. According to coordination topology of CP in Figure 1, three nitrogen atoms of C4COOH coordinate to one copper site, while the oxygen atoms of each carboxylate terminus coordinate unsymmetrically to an adjacent site, giving rise to the 1D coordination polymers. However, the potential applications of the CPs of C_nCOOH are restricted on account of their often poor solubility in many solvents as a result of their sturdy network structures of charged components. To overcome this disadvantage and to expand the scope of their utility, these CPs are necessary to be prepared on the nanoscale in the form of nanocrystals. At the nanoscale, these materials have the added advantages of high surface area, controllable size and morphology and solvent dispersibility, while maintaining benefits of bulk coordination polymers, namely a well-defined, highly

versatile and tailorable composition [10].

3. Synthesis of Nanocrystal Coordination Polymer by Microemulsion Method

A microemulsion (μEm) is a dispersion of two immiscible liquids together with an emulsifier or surfactant. The μEm s in which water, assisted by a surfactant, is dispersed homogeneously in a non-polar media are referred to as water-in-oil μEm s. For the water-in-oil μEm method, it is important to recognize that aqueous droplets (diameters ranging in nanometer scale), which are dispersed in the oil phase through surfactant stabilization, form reverse micelles which can act as nanoreactors [11].

Materials and methods for the synthesis of NCP were followed the reported procedure [1]. However, some details were modified in order to provide suitable experiment for high school students. Note that the ligand C4COOH was used in this work as no reported of the synthesis of NCP by C4COOH before.

The synthetic steps undertaken in the preparation of Cu^{II} -NCP by a microemulsion method are presented in Scheme 1, and described herein.

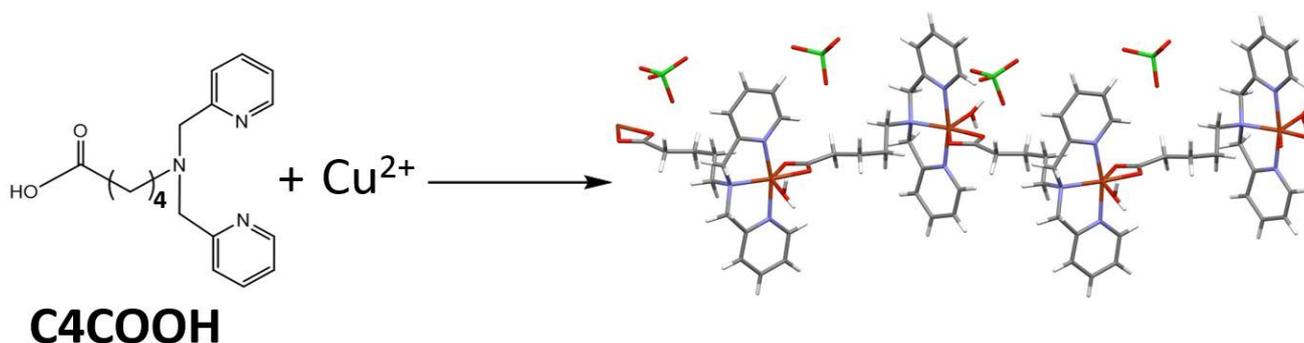
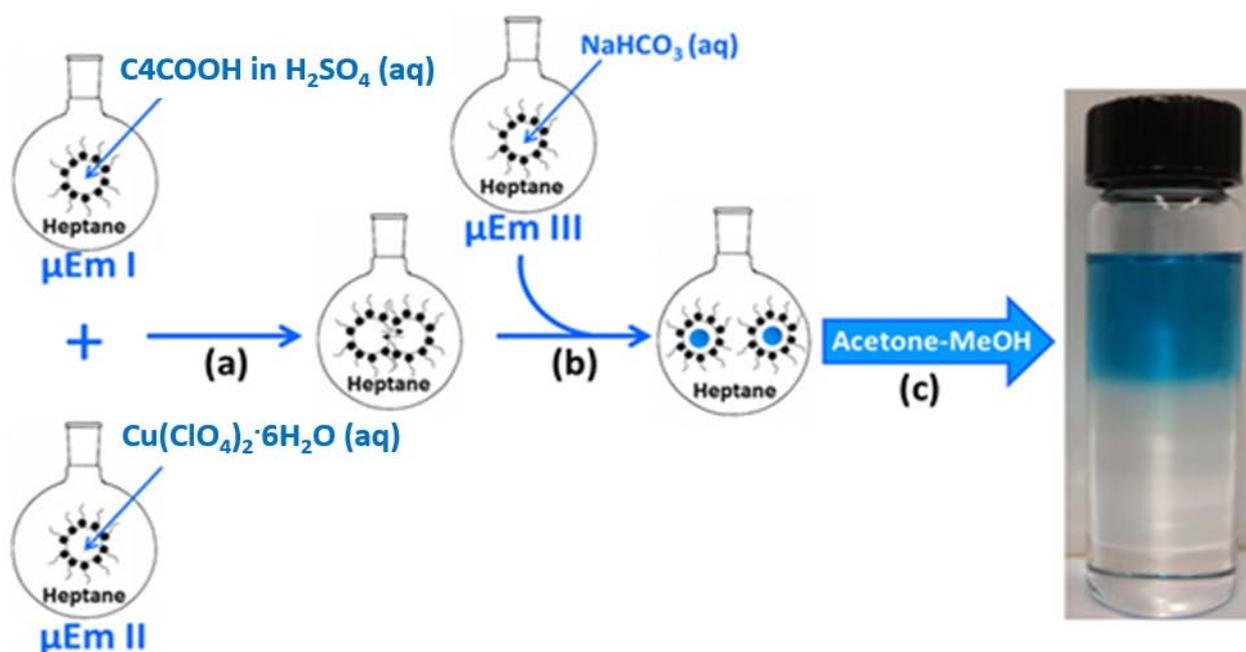


Figure 1. Complexation of Cu^{2+} ion with C4COOH forming coordination polymer (CP)



Scheme 1. Schematic representation of synthesis of Cu^{II} -NCP by three microemulsions. Details are described in the text

Firstly, $\mu\text{Em I}$ containing the ligand C4COOH in H_2SO_4 and $\mu\text{Em II}$ containing $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water were mixed together (a). After that, $\mu\text{Em III}$ containing NaHCO_3 was added to the μEm mixture to allow the complexation and crystallization of NCP (b). To extract the NCP, a mixture of acetone-methanol was added to the resultant μEm (c), resulting in a two-phase separation of the upper heptane phase and the lower acetone-methanol phase.

The precursors contained in the core of reverse micelles are often solubilized in aqueous media. However, the ligand C4COOH which was intended for use as a starting material for the synthesis of NCP is not soluble in water. It can however be dissolved in acid. In this work, therefore, the ligand C4COOH dissolved in acidic solution was used in the preparation of $\mu\text{Em I}$. The acidic conditions do not allow the formation of crystal complexes upon ligand contact with the metal ions (contained in $\mu\text{Em II}$); thus a third μEm was used ($\mu\text{Em III}$) containing a base in order to neutralize the mixture and allow the coordination reaction to proceed.

3.1. Preparation of Cu^{II} -NCP

$\mu\text{Em I}$ was prepared by dissolving 0.250 mmol C4COOH ligand in 1.50 mL of 0.1 M H_2SO_4 ; this solution was added drop wise with stirring to the AOT/heptane solution. $\mu\text{Em II}$ was prepared by dissolving 0.250 mmol $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 0.625 mL of deionized water; this solution was added dropwise with stirring to an AOT/heptane solution. $\mu\text{Em III}$ was prepared by adding 1.50 mL of a saturated solution of NaHCO_3 in deionized water; this solution was added dropwise with stirring to an AOT/heptane solution.

$\mu\text{Em II}$ was added dropwise with rapid stirring to $\mu\text{Em I}$. After the mixture was allowed to stir for 15 min, $\mu\text{Em III}$ was subsequently added dropwise with rapid stirring. The resultant μEm was allowed to stir for 1 h, after which stirring was discontinued. To recover the NCPs, a mixture of 1:1 acetone-methanol was added to the resultant μEm (μEm : acetone-methanol = 6:5). Two phases were formed after the acetone-methanol addition, and the Cu^{II} -NCP were found to partition into the upper heptane phase. The heptane phase was separated, to which another aliquot of acetone-methanol was subsequently added (heptane suspension: acetone-methanol = 1:1), resulting in the formation of two separate phases. The upper heptane phase containing the NCP was again separated and collected. This acetone-methanol washing procedure was repeated 2 more times to ensure complete removal of AOT. The resultant heptane suspension of NCP was centrifuged for 30 min at 10,000 rpm. After centrifugation, the supernatant was collected and retained for characterization.

4. Results

4.1. Solvent-dispersible Cu^{II} -NCP

Following the preparation of NCP within the AOT reverse micelles, a 1:1 mixture of acetone:methanol was added to the microemulsion system with the aim of

extracting the NCP by inducing a phase separation. The motivation behind this procedure has been previously described by Meledandri and co-workers in the context of metal nanoparticle extraction and recovery [12].

After the addition of acetone-methanol, the non-polar heptane phase (upper layer) of the Cu^{II} -NCP-containing sample was visibly blue in colour which was clear evidence that the Cu^{II} -NCP preferentially partition into the organic phase as opposed to the lower acetone-methanol phase or settling at the liquid-liquid interface. Upon separation and isolation of the heptane phase, Cu^{II} -NCP appeared well dispersed with no visible evidence of sedimentation.

4.2. Investigation of Cu^{II} -NCP Morphology by Transmission Electron Microscopy

Transmission electron microscopy (TEM) analysis not only confirmed the presence of Cu^{II} -NCP in the heptane phase, but allowed analysis of their size and morphology. Interestingly, TEM micrograph (Figure 2) shows the shape of the Cu^{II} -NCP as raspberry-like NCP clusters composed of what appears to be ultra-small seed crystals in the range of ~ 4-6 nm. In this study, the rate of $\mu\text{Em III}$ (NaHCO_3) addition is a key factor contributing to the mechanism of NCP formation, as basic NaHCO_3 causes deprotonation of the nitrogen donor atoms of the C4COOH ligand, thereby initiating complexation and crystallization.

4.3. Cu^{II} -NCP Characterization by Infrared Spectroscopy

ATR-IR spectroscopy was performed on an Cu^{II} -NCP sample in an attempt to ascertain the identity of any key functional groups that could potentially be responsible for rendering NCP surfaces hydrophobic. The IR spectrum of each NCP sample was also compared to that of the corresponding C4COOH ligand in solution, as well as its corresponding macroscopic counterpart CP (macroscopic coordination polymer which was prepared by diffusion crystallization technique) in order to investigate any changes that occur in the ligand spectrum i) upon coordination to the metal, and ii) upon preparation of the CP on the nanoscale. IR spectra of the C4COOH ligand, Cu^{II} - C4COOH CP (crystallised after NaHCO_3 addition and based on the optimal synthetic conditions for NCP preparation) and Cu^{II} - C4COOH NCP are shown in Figure 3.

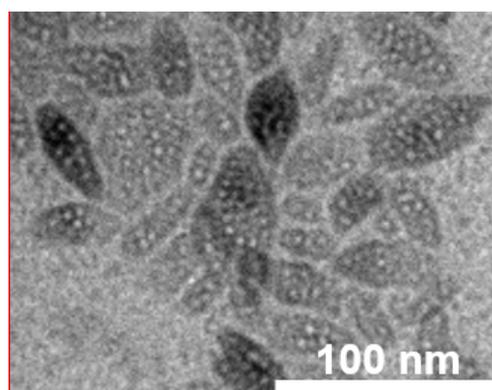


Figure 2. TEM image of Cu^{II} -NCP samples

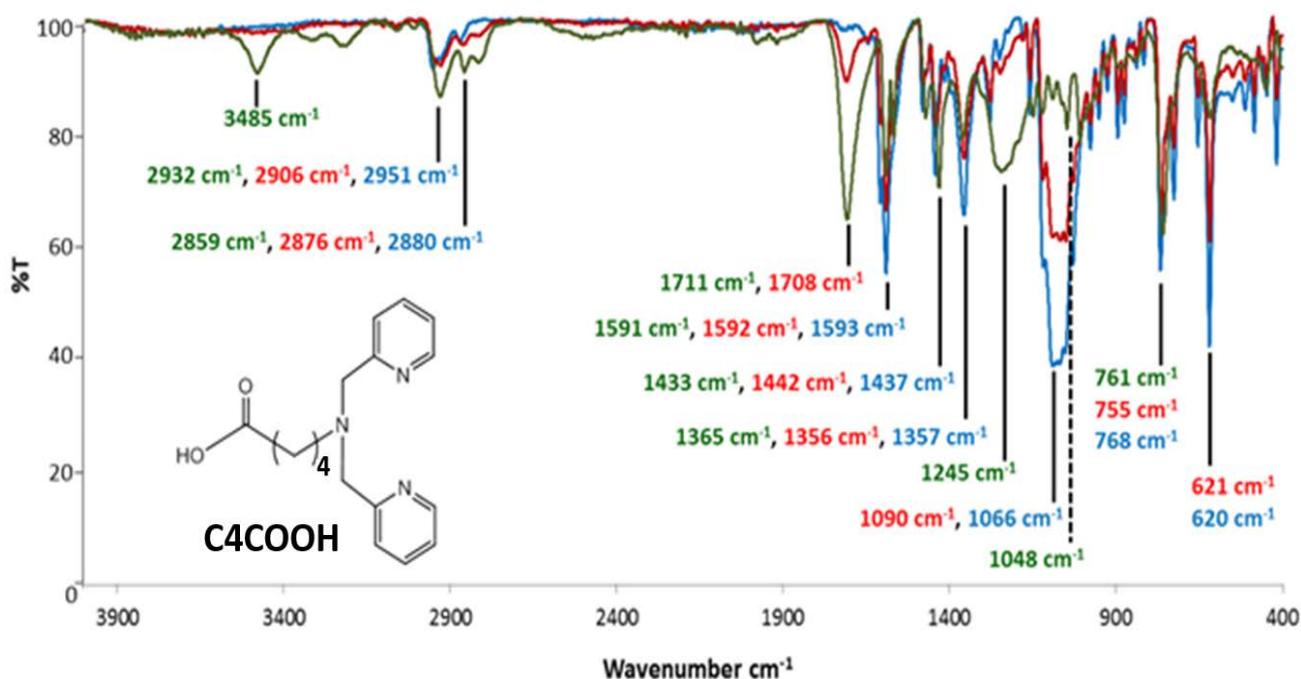


Figure 3. IR spectra of — C4COOH ligand, — Cu^{II}-CP and — Cu^{II}-NCP

Considering the IR spectrum of the ligand C4COOH, it contains noticeable bands at 3485 cm⁻¹ (N-H stretching mode), 2932 cm⁻¹ (asymmetric CH₂ stretching mode), 2859 cm⁻¹ (symmetric CH₂ stretching mode), 1711 cm⁻¹ (C=O stretching mode), 1591 cm⁻¹ (C=N stretching mode), 1433 cm⁻¹ (aromatic C=C stretching mode), 1365 cm⁻¹ (aromatic C-N stretching mode), 1245 cm⁻¹ (C-O stretching mode), 1048 cm⁻¹ (C-H scissoring mode) and 761 cm⁻¹ (C-H bending mode) [13]. The presence of the N-H stretching mode at 3485 cm⁻¹ of the ligand corresponds to the protonated nitrogen atoms of the free ligand in acidic solution of μ Em I. However, the N-H stretching band is absent from the spectrum of the corresponding Cu^{II}-CP and NCP). This result suggests that all donor nitrogen atoms of the free ligand were deprotonated and coordinated with the metal ions to form complex crystals. Also, the metal-carboxylate coordination of the ClO₄⁻ complex can be confirmed in both CP and NCP spectra by the absence of C-O stretching mode (1245 cm⁻¹), and the presence of the ClO₄⁻ vibrational modes at 1066 - 1090 cm⁻¹ and 620 - 621 cm⁻¹. Note that all of the vibrational modes in the spectrum of the NCP are similar to those of the corresponding CP, but with relative decreased transmittance (increased absorption), except in the case of the C=O stretching mode, which is interestingly absent from the spectrum of the NCP.

It is worth noting that very strong peaks of asymmetric and symmetric S=O stretching modes, typically observed at 1420 cm⁻¹ and 1000 cm⁻¹, respectively [14] are absent from the IR spectra of NCP. This rules out the possibility of residual AOT molecules in suspension conferring the heptane dispersibility of the NCP.

5. Discussion

This experiment can be used to discuss with students in terms of a preparation method to synthesize NCP inside

reverse micelles within a heptane-based microemulsion system. The μ Em method is a versatile strategy, which is potentially applicable to a plethora of other metal-ligand combinations. The Cu^{II}-NCP which was synthesized is new structures formed from a multidentate flexible bridging ligand and NaHCO₃ is a key factor in the mechanism of NCP formation; i.e. addition of NaHCO₃ leads to a unique raspberry-like morphology. The deprotonated ligand concentration is initially low, hence NCP size saturation occurs rapidly as crystal growth is arrested before the next droplet addition. This leads to the ultra-small size of the seed crystals, which have been estimated to be in the range of 4 – 6 nm. The seed crystals can then act as nucleation templates, to provide sites for the formation of additional nuclei/seed crystals, upon further addition of NaHCO₃. This process continues until either the addition of NaHCO₃ is terminated, or the total amount of the ligand or metal ions present within the reverse micelles has been completely consumed, and the overall result is the formation of the raspberry-like NCP clusters composed of a number of ~4 – 6 nm seed crystals.

Seed crystal growth will proceed until the available monomer units in solution are consumed, and considering the 1:1 metal-ligand complex stoichiometry [9], and the excess of metal ions in solution, the CP, and therefore the NCP surfaces, likely terminate at a metal ion. This would lead to a high density of metal ions at the surface of the NCP. This would also explain the absence of the C=O stretching mode in the IR spectrum of the NCP, as all of the carboxylate oxygen atoms would be coordinated to metal ions. As the CP crystals prepared on the macroscale are not formed under conditions of large excess metal ions, prediction of the surface composition becomes more difficult. In this case, growth of the CP would not necessarily terminate at a metal ion, hence the presence of weak C=O stretching vibration observed in the IR spectrum of the CP.

6. Conclusion

In terms of the academic recreation club at high school level, the synthesis of Cu^{II}-nanocrystal coordination polymer by microemulsion method successfully provided the students with guidance of research method for nanomaterial synthesis. During the experimental session, the students can develop skills to handle with equipment and techniques in the laboratory. The teacher can give comments and recommendations on their experiment's plans, and determine appropriate solutions for different types of student's problems by applying their scientific knowledge to solve their problems. After this experiment, students were able to generate their own ideas in the concept of coordination chemistry and nanomaterial synthesis by applying or modifying the knowledge they learned from this work. At the last session, they were asked to present their experimental results through an entertaining science show.

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