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► To cite this version:

Van-Tuan Nguyen, The Nhan Le, An Thanh Ngo. RCChE2019-020 Synthesis of hollow nanospheres Zinc Phosphate via soft template method. the 12th Regional Conference on Chemical Engineering (RCChE 2019), Oct 2019, HO CHI MINH CITY, Vietnam. ⟨hal-04611753⟩

HAL Id: hal-04611753

<https://hal.science/hal-04611753v1>

Submitted on 17 Jun 2024

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RCChE2019-020

Synthesis of hollow nanospheres Zinc Phosphate via soft template method

Van-Tuan Nguyen *, Nhan Le The, An Thanh Ngo

Physio-chemistry Department, Faculty of Chemical engineering, Ho Chi Minh University of Technology, 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh city

*Corresponding author: nguyenvantuanflv@gmail.com

ARTICLE INFO

Received (2/Aug. RCChE 2019)
Received in revised form
(10/Sept. RCChE 2019)
Accepted (12/Sept. RCChE 2019)

Keywords

nano hollow, hollow Zinc phosphate, surfactant.

ABSTRACT

This study focuses on the synthesis of nano hollow zinc phosphate via soft- template method through precipitation process of $Zn(NO_3)_2$ and $(NH_4)_2HPO_4$. The surfactant investigated in process was sodium dodecyl sulfate (SDS). Moreover, long-chain alcohol (as co-surfactant) was also added to the solution in order to study the interaction between the two surfactants. Besides, the addition of electrolytes and the surfactant concentration were also researched to find out the optimal condition. The TEM results showed that hollow zinc phosphate nanoparticles with size of 20 - 50nm and wall thickness of about 5 nm was formed with the presence of n-octanol and SDS. It could be figured that the mixture of SDS and n-octanol form spherical micelles which are considered as templates for synthesizing particles.

I. INTRODUCTION

Recently, biomaterial has been paid special attention owing to their enormously potential application. According to IUPAC definition, biomaterials are materials which are exploited in contact with living tissues, organisms, or microorganisms [1]. They are often used for a medical application, such as carrying, enhancing, or replacing a natural function. Such functions may be relatively passive, like being used for a heart valve, or may be bioactive with a more interactive functionality such as hydroxy-apatite coated hip implants [2]. Biomaterials are also employed routinely in dental applications [3], surgery [4], and drug delivery [5]. For instance, a construct containing drug products could be put into the body, which tolerates the release of a drug for an extended period. A biomaterial may also be an autograft, allograft or xenograft used as a transplant material [6].

The most outstanding biomaterial is hollow nanospheres particles which is a special nanomaterial being named on the basis of their morphologies (displayed by **Figure 1**). The word “hollow” means “having a hole or empty space inside”.

With empty space inside, any structures could be classified as “hollow structures”. That term usually refers to those containing considerably an extensively blank space inside the particles. On balance, the definition of “hollow nanostructure” is a solid structure with void space inside a distinct shell, and its dimensions are in the nanometer or micrometer range.

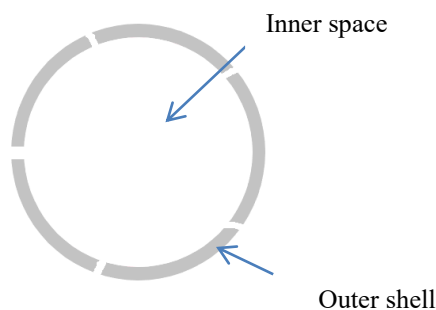


Figure 1: Hollow nanospheres particles

About application aspect, the hollow structures have been used to load and control releasing systems for specific materials, such as drugs [7], genes [8], peptides [9], and biological molecules [10] because of their blank space. Moreover, they can also be used to modulate refractive index, increase the active area for catalysis and adsorption, improve particles ability to changes in volume, and expand the array of imaging markers suitable for early detection of cancer [11].

Thus, my research team has formed the idea of synthesizing hollow particle materials nano zinc phosphate with high biological compatibility, nano size, hollow cavity, large surface area to apply in drug delivery, catalysis, and energy storage. The synthesis of hollow spherical zinc phosphate nanoparticles has also been implemented by a number of research groups, however, authors are usually a single surfactant of 1,1,1-Tris (hydroxymethyl) ethane (TME) [12] or sodium dodecyl sulfate [13]. Using these single surfactant bring drawback for controlling not only the size but also the morphology of particles. Accordingly, my team has employed mixed micelles including SDS and medium, long-chain alcohol to investigate particle formation. Besides, both electrolytes and SDS concentration are also researched to access their impacts on synthesis of material. The results from this study will provide detailed information of surfactant role in the synthesis of materials such as the ability to adjust the particle diameter, the ability to create hollow, etc.

II. MATERIAL AND METHODS

1. Materials and Reagents

Ethanol, 1-Hexanol, 1-Butanol, and Diammonium Hydrogen Phosphate $(\text{NH}_4)_2\text{HPO}_4$, AR) were purchased from Merck. Zinc Nitrate Hexahydrate, 1-Octanol, Sodium Chloride, were obtained from China. Sodium dodecyl sulfate was bought from Malaysia. Deionized water is obtained from Biological Laboratory (HCMUT).

2. Experimental Set-up

Firstly, the mixture encompassing surfactants and 50 ml deionized water is stirred in the beaker A within 10 minutes via magnetic stirrer. During that, 0.474 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is added into the beaker B containing 20 ml ethanol. Afterward, the solution in beaker B is pumped gradually to solution in beaker A and stir constantly together. 20 minutes later, the pH of the mixed solution is adjusted with ammonia 28 % solution. The following step is the addition of $(\text{NH}_4)_2\text{HPO}_4$ solution and mixes together within 40 minutes. Eventually, product is obtained by the filtration and sublimation process.

3. Physicochemical characterization

Synthetic materials were undergone FTIR analysis at the Institute of Applied Materials Science - Vietnam Institute of Misunderstanding and Science and Technology.

TEM analysis was conducted to the National Key Laboratory of Polymer and Composite Materials - Ho Chi Minh City Polytechnic University.

III. RESULTS AND DISCUSSION

1. Characterization of particles

FTIR spectra (shown in **Figure 2**) indicate the characteristic absorption of H_2O and ion PO_4^{3-} . The bonding water at 1638.48 cm^{-1} and O-H extends at 3437.48 cm^{-1} , indicating the presence of crystalline hydrates [14]. The presence of some absorption bands from 600 to 1400 cm^{-1} , divided into three peaks, characteristic for the long-term complex of PO_4^{3-} [15]. The absorption range at 1050.78 cm^{-1} is the symmetrical extension of PO_4^{3-} . A peak at the number of waves of 1384.91 and 664.91 cm^{-1} is observed due to the asymmetric extension of the corresponding curvature of PO_4^{3-} and P-O [16]. From FTIR result, it confirmed that zinc phosphate was successfully synthesized.

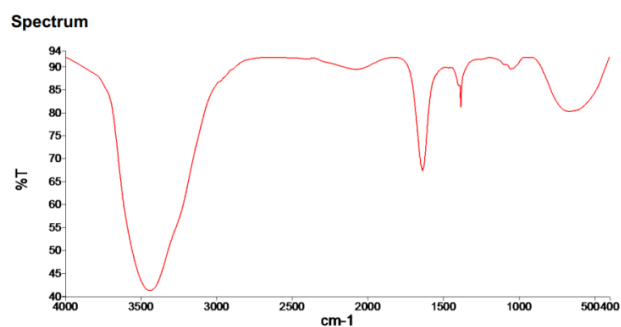


Figure 2: FTIR spectra of HZnPNSs

2. Effect of co-surfactants

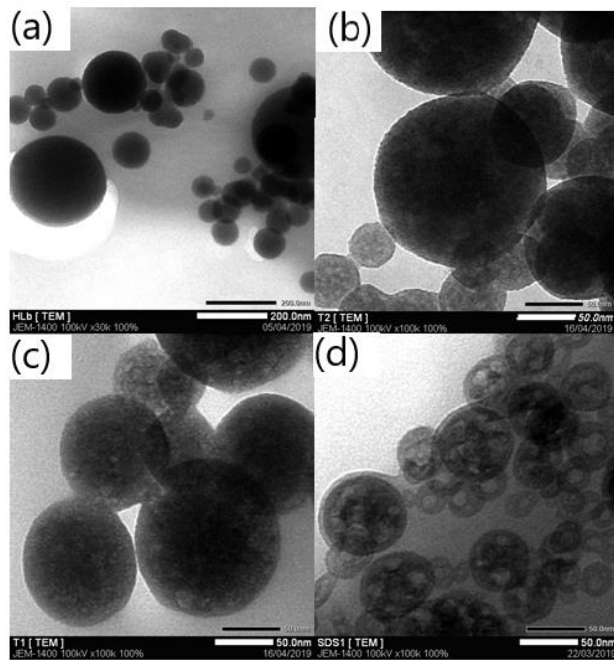


Figure 3: TEM image of particles synthesized with various co-surfactant (a) without co-surfactant; (b) 1-butanol; (c) 1-hexanol; (d) 1-octanol

The TEM results (**Figure 3**) indicate that addition of co-surfactants such as long-chain alcohol gives the priority for forming smaller particles.

In mixed surfactant systems, not only the SDS molecule but also long-chain alcohol decreases the surface tension because long-chain alcohol is considered as nonionic surfactant. The measurements were conducted to define the surface tension of each experiment in this procedure and the result is illustrated in **Table 1**.

Table 1: Surface tension value

Experiment	Surfactants	γ (mN/m)
1	SDS	37
2	SDS/1-butanol	36
3	SDS/1-hexanol	31
4	SDS/1-octanol	27

It is obvious that the solution with a mixed surfactant of long-chain alcohol and SDS has smaller surface tension value than the one with SDS only (**Table 1**). Besides, the surface tension of different mixed surfactant systems is not the same due to the difference in the carbon chain. Traube's rule is the explanation for this phenomenon. According to

Traube's rule, each additional CH_2 group increases the surface tension reduction effect threefold. Thus, the surface tension of SDS/1-octanol is smaller than others (**Table 1**). The reduction of surface tension of the system will facilitate the process of stabilizing the micelles, reducing the flocculation phenomenon, thereby giving priority to the formation of hollow material particles. That is the reason why the particles synthesized by SDS/ 1-octanol solution (which have the smallest surface tension value) have larger hollow space and smaller size than other (**Figure 3**).

Besides, the addition of medium or long alcohol results in tightly packing of micelles. Consequently, **Figure 3** shows that the particles synthesized by mixed surfactants have a smaller size than the one without long-chain alcohol supplement. Besides, the particles synthesized by SDS/1-octanol have the smallest size.

The satisfactory explanation for this result is Patist's research [17]. Patist and his colleagues stated that only the complex micelles of dodecyl alcohol and SDS is the most stable and tightly packed. Other alcohols which have the mismatched carbons with SDS molecules lead to a decrease in the curvature of micelles (increase micelle size). The result of Patist also showed that the complex micelles of SDS/1-octanol and SDS/1-cetyl alcohol are the most unstable due to the fact that 1-octanol is less than SDS molecules 4 carbon atoms whereas 1-cetyl alcohol is more than SDS molecules 4 carbon atoms. Therefore, the mismatched carbons affect harmfully on micelle size (particle morphology). In this section, particles synthesized by SDS/1-octanol have the smallest size and largest hollow space due to the less mismatched carbons whereas 1-butanol has 4 carbon atoms in its structure and less than SDS 8 carbon atoms so the size of particle synthesized by SDS/1-butanol is bigger than the one synthesized by SDS/1-hexanol. In brief, the addition of medium and long-chain alcohol is beneficial for micelle formation; however, the tail length of alcohol plays an important role in forming micelles and their mismatched carbon with SDS molecule is as less as possible. Accordingly, the SDS/1-octanol mixture is the most suitable for synthesizing due to the less mismatched carbons.

3. Effect of SDS concentration

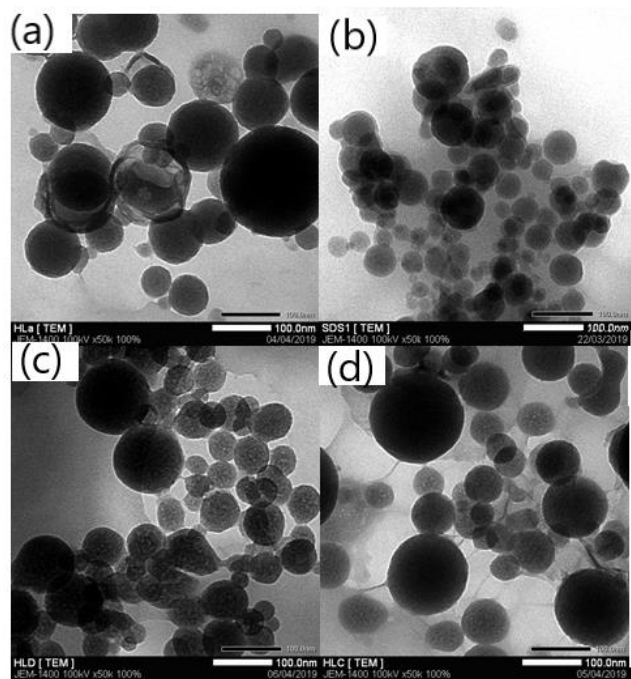


Figure 4: TEM image of particles synthesized with various SDS concentration (a) 50 mM; (b) 60 mM; (c) 70 mM; (d) 80 mM

The SDS concentrations are proportional to the N_{agg} and disproportionate to $[SDS]_{Free}$ value [18]. The increase in N_{agg} leads to make the micelles more stable because of the decrease of curvature. Therefore, to gain more stable micelles, the value of SDS concentration is as high as possible. That is the reason why the particle structure in the first experiment with the lowest SDS concentration (50mM) is not uniform like others (**Figure 5**).

Moreover, on the basis of the phase diagram, SDS micelles have diverse shapes that are depended on their concentration [19]. Besides, the second CMC of SDS investigated by conductivity method is nearly 65 mM [20]; therefore at this concentration, SDS molecules may form other shapes that are not spherical. That is the reason why the size of particles at the condition with 70 mM and 80 mM SDS is not as uniform as the one at 60 mM (**Figure 5**) due to the fact that their micelle shape may not be spherical and exist with other morphology such as rod-like.

As a whole, the concentration for synthesizing particles is as higher as possible; however, it should be lower than 65 mM to not form other shapes following by phase diagram. Thus, in this process, the most appropriate SDS concentration is 60 mM.

4. Effect of electrolytes

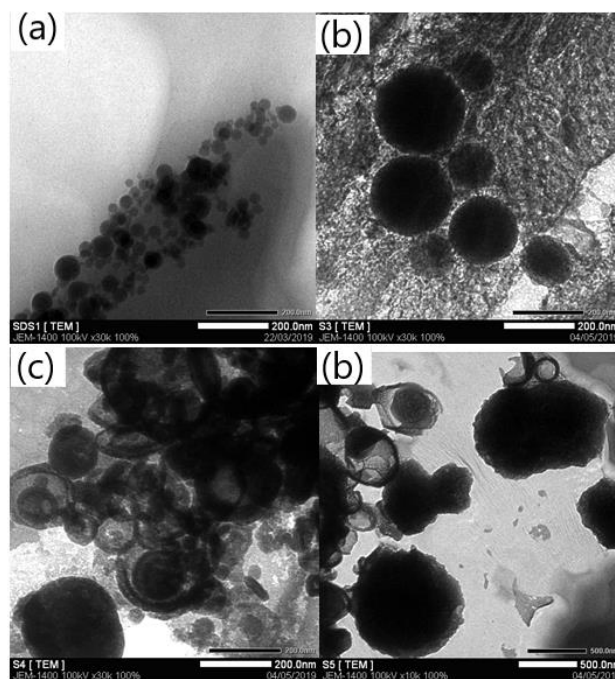


Figure 5: TEM image of particles synthesized with various sodium chloride concentration (a) 0 mM; (c) 50 mM; 100 mM; (d) 150 mM

As can be seen from **Figure 5**, it is clear that the size of particles synthesized with 150 mM NaCl has the largest size and particle size increases proportionally to the sodium chloride concentration. NaCl addition contributes to changes in the N_{agg} which decide the stability and size of the micelle. Besides, the sodium chloride concentrations are proportional to the N_{agg} [18]. The increase of N_{agg} leads to the bigger micelles; therefore the synthesized particle size is increased. Thus, the addition of sodium chloride increases the particle size.

Moreover, the SDS micelles can be seen as a colloid system and the addition of electrolyte (NaCl) cause a decrease of zeta potential. As a consequence, the micelles become unstable; thereby forming strange morphology on particles (See **Figure 5**). In other words, there is an increase in the extent of ion pairing and screening of Coulombic interactions between headgroup due to the increase of counter ion; thereby reducing the net effective headgroup size. Besides, the determination of the micelle shape is dependent on headgroup repulsion. Accordingly, the micelle surface fluctuation phenomenon happens and it created the instability of the micelle shapes [21]. Thus particles synthesized by sodium chloride do not have a particular shape in comparison with the one without sodium chloride (See **Figure 5**). To conclude, the combination of NaCl is

definitely disadvantageous for forming particles in this case due to forming a variety of shapes.

IV. CONCLUSION

Among these factors mentioned above, the most important element is the surfactant which is employed as a template for the synthesis process. The proper surfactant is sodium dodecyl sulfate which has a large head group for forming a spherical micelle. Besides, the SDS concentration should be as high as possible; however, its value must be in the spherical phase. Therefore, its suitable value is 60mM.

Moreover, the supplement of long-chain alcohols is highly recommended to aid the forming tighter micelle; however their mismatched carbon with SDS molecule must be smallest. Thus, the process using 60mM SDS/1-octanol showed the best result with synthesized particles which have approximate 20 nm of radius and 5nm of shell thickness and the largest hollow space inside.

Last but not least is the electrolyte addition which harmfully impacts micelle stability.

ACKNOWLEDGEMENT

This research was financially supported by Vietnam National University- Ho Chi Minh city (Subject Number: C2019-20-25).

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