The impact of surfactants on nanosphere zinc phosphate synthesis

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Abstract. Recently, biomaterials have attracted widespread concern because of their compatibilities with live bodies. Among advanced biomaterials, zinc phosphate nanospheres particles are potential candidates for delivering drug and dental restorations. However, their fabrication methods are complicated and non-eco-friendly. In this study, we report the impact of surfactant supplements on the wet chemical preparation of zinc phosphate. Experimentally, Di-propylene glycol (DPG) and Trimethylolpropane (TMP) were added to the solution in the preparation step to compare the morphology of synthesized particles with the non-surfactant process. The morphology was examined by transmission electron microscopy. The addition of surfactants changed particle shape to spherical with a diameter of less than 200 nm. Moreover, the synthesized particles with DPG had a solid form, while those with TMP had a hollow structure (a diameter of 50-70 nm and shell thickness of 5-7 nm). Furthermore, X-ray diffraction, Fourier transforms infrared, and Thermogravimetric analyses analyzed properties of hollow particles.

1. Introduction

Advanced materials with versatile properties have opened approaches for various applications. One of the examples is biomaterials, which have been modified to be in contact with live systems for medical purposes [1]. They are often used for a medical application, such as carrying, enhancing, or replacing a natural function. These functions may be inactive, likely being employed for collaborating functional bioactivity such as implants coated with hydroxy-apatite for hips [2]. Moreover, biomaterials are employed widely 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. The cancer nano-technological includes nano-carrier such as liposomes for innovative carrying systems for breast cancer healing and magnetic resonance imaging of nano-contrast agents for intervening neuro-oncological through extraordinary observation. The classification of carrier systems with structure varieties is shown below:

- Inorganic particles (Au [6], Fe3O4 [7], CdSe [8], and Zinc [9])
• Biomacromolecules (lactose [10], DNA [11], liposome [12], and collagen [13])

Besides, novel approaches to nanoparticle-based methods for high-specificity detection of DNA and proteins are available. Autografts, allografts, or xenografts are often used as transplant material [14]. However, there are still some obstacles in the synthesis of biomaterial, especially nanosphere particles. Typically, the smart biomaterial can be obtained by complicated and non-green methods such as thermal decomposition, hydrothermal/solvothermal, and reduction.

Recently, hydroxyl zinc phosphate has been mainly concerned for various applications such as drug delivery systems [15]. Jadhav et al. reported synthesizing hollow zinc phosphate nanospheres (HZnPNSs) using surfactants as soft templates [16]. Generally, surfactants have substantial impacts on synthesized particles because of their flexibility in solution. However, there were no reports on the role of surfactants in synthesizing nanosphere hydroxyl zinc phosphate. Dipropylene glycol (DPG) and Trimethylolpropane (TMP) were used in the fabrication process to compare gained particle structures with the non-surfactant process. The structures of obtained particles were observed through TEM images. Moreover, the properties of hollow zinc phosphate nanosphere particles (HZnPNSs) were also examined via X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and Thermogravimetric analyses (TGA) analysis.

2. Experimental

2.1. Material

Zinc phosphate hexahydrate [Zn (NO$_3$)$_2$.6H$_2$O] 99%, Dipropylene glycol (DPG) were bought from Xilong Scientific. Trimethylolpropane (TMP), Diammonium hydrogen phosphate [(NH$_4$)$_2$HPO$_4$] 99%, ammonia solution (28%), and ethanol were obtained from Sigma-Aldrich.

2.2. Fabrication procedure

First, the 0.474 grams of Zinc phosphate hexahydrate were dissolved in 50 ml the mixture of DI water and ethanol (ratio 4:1) in beaker A via the magnetic stirrer. Afterwards, the ammonia solution adjusted the solution pH to obtain Zn(NH$_4$)$_2$$_2^+$ in aqueous. Next, 0.2 grams of [(NH$_4$)$_2$HPO$_4$] were dissolved in 50 ml of water (in beaker B). Then, the solution in beaker B was added into beaker A drop by drop by a burette. The magnetic stirring was kept until there was no solution in beaker B. Furthermore, the solution temperature was maintained at 15°C. The final solution was centrifuged at 8000 rpm within 20 minutes and filtered to obtain the precipitates. Lastly, the precipitates were dried in the oven at 80 °C for 2 hours to obtain the final zinc phosphate particles.
2.3. Material characterization

The transmission electron microscopy system (model JEM 1400) was employed to observe morphologies of all synthesized particles with the working condition of 100kV and the magnification of 10k. The lattice structure of HZnNPS was tested by XRD analysis (Kα₁: wavelength of 1.540598 Angstroms, Kα₂: wavelength of 1.544426 Angstroms). FT-IR was examined to detect vibration of major groups on HZnNPS. The TGA system (model TriStar II 3020 V1.03) was used to test the thermal stability of HZnNPS.

3. Result and discussion

3.1. Effect of surfactants on particle morphology

![TEM images of particles synthesized with a) non-surfactant, b) DPG, c) TMP](image)

Figure 2. TEM images of particles synthesized with a) non-surfactant, b) DPG, c) TMP
Figure 2 displayed the structure of particles synthesized with the conventional and surfactant route. There were three morphological trends of particles: unidentified shape with solid structure, solid nano-spheres, and hollow nano-spheres. Additionally, the particles from the non-surfactant route were bigger than those from the surfactant route.

Usually, the zinc phosphate particles synthesized in the wet chemical method undergo a nucleation process that is noticeably affected by $\Delta G$, proportional to surface tension value (Eq. 1) [17]. When applying surfactants in this process, their surface tension will decrease. Consequently, the energy barrier will decrease and facilitate nucleation.

$$\Delta G = \Delta G_S + \Delta G_V = 4\pi r^2 \gamma - \frac{4}{3} \pi r^3 \gamma \Delta G_V$$  \hspace{1cm} (1)

$$r_c = \frac{2\gamma}{\Delta G_V}$$ \hspace{1cm} (2)

Where $\Delta G$, $\Delta G_S$, and $\Delta G_V$ are overall excess free energy, the excess free energy of particle surface, and free energy change of the transformation per unit volume, respectively, $\gamma$ is solution surface energy, and $r_c$ is the critical radius of particles. Besides, Eq.(2) shows that the critical radius ($r_c$) is proportional to the surface tension of the solution. The presence of DPG and TMP in solution reduced the surface tension leading to the decrease of particle size according to Eq.(2). Thus, the particles synthesized with TMP and DPG were smaller than those synthesized without surfactant (Figure 2).

**Figure 3. Illustration of DPG, TMP molecule**

**Figure 4. Illustration of hollow hydroxyl zinc phosphate nanoparticles particles formation via TMP template**

Apart from controlling the particle size, surfactants also significantly impacted the particle structure through their micelle formation. Generally, when increasing surfactant concentration in water, surfactant molecules will spontaneously assemble to form micelles at an appropriate concentration. This concentration is called critical micelle concentration (CMC). In other words, to obtain micelle in surfactant solution, the used concentration must be greater than or equal to their CMC.
For DPG and TMP, their used concentrations (0.074 M) were greater than their CMC (estimated at nearly $10^{-3}$ M [18]); therefore, these experiments with DPG and TMP had the presence of their micelles. About the micelle structure, the factor deciding their shape is the packing parameter ($P$) [19] (described in Eq.(3)).

$$P = \frac{V_o}{a_e \cdot l_o}$$

where $V_o$: surfactant tail volume, $a_e$: equilibrium area per molecule at aggregation interface, $l_o$: tail length

Typically, $P$ is dependent on the hydrophilic head and hydrophobic tail. Moreover, the $\frac{V_o}{l_o}$ value of surfactants having hydrophobic tails with carbon and hydro molecules is nearly the same. To form spherical micelles, the surfactant structure requires a high value for $a_e$ for $P$ value less than $\frac{1}{3}$ [19].

Although having the same chemical formula ($\text{C}_{6}\text{H}_{14}\text{O}_{3}$), DPG and TMP show the radical difference in their structural formula. In DPG molecules, two OH groups do not contribute to the same side of the carbon chain (Figure 3) resulting in their low $a_e$ value. As a result, the DPG micelle shape cannot be spherical, and they might form other shapes such as bilayer. These micelles deterred particle agglomeration, which caused an unidentified shape for particles synthesized without surfactants. That is the reason why the formed particles with DPG were spherical with solid structures. Meanwhile, the hydrophilic heads (there OH groups) of TMP cluster together on one side. Thus, the total value of $a_e$ from these OH groups is higher and advantaged to form spherical micelle as soft-template for forming hollow nanospheres particle. The illustration of hollow particle formation via using TMP micelles as soft-template was described in Figure 4. After the spherical micelle preparation step, $\text{Zn(NH}_4\text{)}_2^{2+}$ ions were attached to the micelle surface by the electrostatic force between $\text{Zn(NH}_4\text{)}_2^{2+}$ and O’ group of micelles. Next, the $(\text{HPO}_4)_2^{-}$ ions of added solutions reacted with $\text{Zn(NH}_4\text{)}_2^{2+}$ to form the hydroxyl zinc phosphate shells covering micelles. Lastly, the hollow hydroxyl zinc phosphate nanospheres were gained after filtration and removal of micelles.

3.2. Properties of hollow zinc phosphate nanosphere

![Figure 5. a) XRD pattern and b) FTIR spectrum of HZnPNSs](image)

From the XRD pattern in Figure 5.a, it can be seen that the hollow nanosphere particles had a high crystallinity with ten firm peaks (19.3°, 21.16°, 22.45°, 24.65°, 28.28°, 28.96°, 31.35°, 34.13°, 36.73°, 39.31°). Besides, the maximum d spacing was highest at the peak of 19.3°. These peaks showed the
evidence of synthesizing $\text{Zn}_3(\text{PO}_4)_2$ and $\text{Zn}_3(\text{PO}_4)_2\cdot4\text{H}_2\text{O}$ (Hopeite) crystals successfully (confirmed by JCPDS 00-029-1390 and 00-026-1397 data).

The proof of $\text{Zn}_3(\text{PO}_4)_2$ and $\text{Zn}_3(\text{PO}_4)_2\cdot4\text{H}_2\text{O}$ formation were also supported through the FT-IR spectrum (Figure 5.b). The vibrations at 1469 and 817 cm$^{-1}$ showed the deformation band for OH groups. Furthermore, the $\nu_{\text{OH}}$ split into three bands at 2851, 2919, and 3203 cm$^{-1}$, confirming the presence of hydrate crystals in the sample [20]. Besides, there were three peaks for PO$_4^{3-}$ band at 584, 944, and 1066 cm$^{-1}$ [20].

**Figure 6.** a) TGA cure b) TGA derivative weight curve of HZnPNSs

Figure 6.a and 6.b described the mass change of HZnPNSs with various temperatures. Five dominant temperature peaks (92.91°C, 169.6°C, 335.51°C, 488.61°C, 752.26°C) showed the great weight change. The first two peaks indicated the physical weight loss of moisture in the sample (6.7%). From 200°C and 400°C, the mass loss was from the deformation of the remaining surfactants with 18.3%. Moreover, temperature from 400°C to 650°C with the peak at 488.61°C showed the steady dehydration of Hopeite crystal to form $\text{Zn}_3(\text{PO}_4)_2$ crystals (with the decrease of 16.2% total weight) [21]. The stability of sample weight in temperature over 820°C with 51.27% left before decreasing mass of 7.1% might be due to the break of large HZnPNSs.

4. **Conclusion**

Surfactants played an essential role in the control of morphologies of zinc phosphate particles. With the assistance of TMP and DPG surfactant, the particles became spherical due to the decrease of critical diameter in the Ostwald ripening process. Moreover, TMP with a proper structure formed spherical micelles as soft templates for fabricating HZnPNSs, a promising and innovative biomaterial for drug delivery systems.

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