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Synthesis of hydroxyapatite nanoparticles through polyelectrolyte-modified microemulsions

ABSTRACT

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The paper is focused on the formation of hydroxyapatite nanoparticles (HAp) in polyelectrolyte-modified microemulsions, in a microemulsion template phase consisting of cyclohexane, water, cationic surfactant and cosurfactant, in the presence of Na-polyacrylate (PAA) as an anionic polyelectrolyte. It is shown that PAA, can be incorporated into the individual inverse microemulsion droplets. The microemulsion droplets and PAA-filled microemulsion droplets can be successfully used as a template phase for the nanoparticles formation. Prepared HAp in presence of polyelectrolyte has a different morphology from samples which are synthesized in absence of polyelectrolyte. PAA leads to formation of needle-like HAp (20-30nm in diameter and 100-200nm in length). Formation of HAp at room temperature was confirmed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Size and morphology of the HAp samples were characterized using transmission electron microscopy (TEM).

Keywords: *Microemulsion; Polyelectrolyte-modified microemulsion; Hydroxyapatite; Na-polyacrylate.*

INTRODUCTION

Hydroxyapatite with the structural formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is the major constituent of human bone and teeth. Synthetic HAp has excellent biocompatibility and bioactivity, so it is useful in reconstruction of damaged bone or tooth zones. HAp can also be applied in other fields of industrial or technological interests such as water purification, fertilizers production, drug delivery carrier in tissue engineering and non-viral gene delivery carrier [1-4]. The function of HAp in all of these applications is largely influenced by its morphology, crystallinity, and crystal size distribution. Various synthesis methods, including co-precipitation, hydrothermal reactions, sol-gel synthesis, pyrolysis of aerosols, and recently microemulsion, have been used for the preparation of HAp.

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Among these methods, the microemulsion method is one of the most flexible and convenient methods, being able to deliver a particle size and morphology in nanometer scale with minimum agglomeration [5-8].

Microemulsion, i.e. thermodynamically stable, optically clear isotropic dispersions of two immiscible liquids consisting of nano-sized droplets of one liquid in another, In such way the system is stabilized by added surfactant. Different types of microemulsion were known, such as water-in-oil (w/o), oil-in-water (o/w). In case of a water-in-oil microemulsion, reverse micelles are formed when the aqueous phase is dispersed as microdroplets surrounded by a monolayer of surfactant in the continuous organic phase.

However, one problem is that the bending elasticity and stability of the surfactant film is often not strong enough to confine the growth of the particles to the interior of the microemulsion droplet. To overcome this problem, a component should be added which improves the surfactant film stability; controls the particle growth processes and stabilizes the particles against flocculation during the re-dispersion process. Recently different authors have shown that water-soluble polymers (polyelectrolytes) can be incorporated into inverse microemulsion droplets [9-12]. On the other hand, the polyelectrolytes can control the size and shape of the nanoparticles during the formation process, polyelectrolyte-modified microemulsion can be successfully used as a new type of template for synthesis of nanoparticles with controlled size, shape, and morphology.

The aim of the present study is to use the cetyltrimethylammonium Bromide-based microemulsion in the presence of anionic polyelectrolyte, i.e. Na-Polyacrylate as a template phase for the formation of HAp.

EXPERIMENTAL

The starting materials used in this work included $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, NH_4OH , cyclohexane, n-pentanol, cetyltrimethylammonium bromide, CTAB with 99% purity, Na-Polyacrylate (PAA), and deionized water. All chemicals were prepared with analytical grade and were used without further purification. Aqueous solutions

were made by dissolving sufficient amounts of reagents in deionized water. All prepared sample solutions had a Ca/P ratio equal to 1.67 (stoichiometric ratio of HAp). The Na-polyacrylate was used as commercial product with low molar mass ($M_w = 8000 \text{ g/mol}$).

Synthesis route

After dissolving 1.82g CTAB in 60ml cyclohexane and 1.6ml n-pentanol, reverse micelle solution with 0.1M concentration was obtained and then 1 ml of 1M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 4% (w/v) of polymeric aqueous solution was injected slowly into the reverse micelle solution. Transparent solution was obtained upon vigorous stirring the system for about 15 min. for formation of HAp precursors, under vigorous stirring, 1ml of 0.6M $(\text{NH}_4)_2\text{HPO}_4$ aqueous solution was directly added to the above reverse microemulsion system, then a small amount of ammonia was added to the system to adjust pH in the range of 9-10. Transparent solution was obtained upon vigorous stirring the system for about 30 min, then aged with continuous stirring at room temperature for one day. Finally a small amount of ethanol was added into the transparent solution to afford the production of white slurry, which was centrifuged to collect the white colloidal HAp. The precipitates were washed with ethanol for three times and dried at 50°C for 24h. Dried products were characterized by XRD (Philips expert pro. with Cu K α radiation ($\lambda=0.154 \text{ nm}$)), scanning electron microscope (SEM; Philips XL30). Transmission electron microscope (TEM; Philips), and Fourier-transform infrared spectroscopy (FT-IR; Thermo Nicolet Nexus 870).

RESULTS AND DISCUSSION

Polyelectrolyte-modified microemulsions seem to be very interesting template phases for the nanoparticles formation due to the special features of the incorporated polyelectrolyte.

The “innovation effect” of polyelectrolytes in inverse microemulsions with regard to the nanoparticle formation process can lead to:

- The increase of the film stability of the microemulsion droplets due to polyelectrolyte-surfactant interactions,

- The control/inhibition of the nanoparticle growth process due to polyelectrolyte-nanoparticle interactions,
- The stabilization of the nanoparticles (electrosteric stabilization) due to polyelectrolyte-nanoparticle interactions.

However, these effects have to be optimized with regard to the polyelectrolyte, the type of microemulsion as well as the type of used nanoparticles.

In the following study, our interest was focused on preparing of HAp by microemulsion method in presence of PAA [13,14].

Figure 1a shows the FT-IR of synthesized HAp in the presence of polyelectrolyte. The IR characteristic peaks of phosphate groups appeared between 1090-1030 and 600-560 cm^{-1} . The absorption bands at 3420 and 1640 cm^{-1} were assigned to the bending mode of the adsorbed water, while the sharp peak at 3570 cm^{-1} is assigned to the stretching vibration of the lattice OH^- ions, and a medium sharp peak at 630 cm^{-1} is assigned to the OH^- group of HAp [15]. For comparing, the FT-IR of synthesized HAp in the absence of polyelectrolyte is displayed in Figure 1b, the weak bands of the CO_3^{2-} group (870, 1415, 1450, and 1540 cm^{-1}) in this fig, indicated that the CO_3^{2-} substituting came from a reaction between atmospheric carbon dioxide and high-solution pH (>9) [16]. There is an increase in the intensity of the absorption bands of OH^- and CO_3^{2-} in the presence of Na-Polyacrylate [17-19].

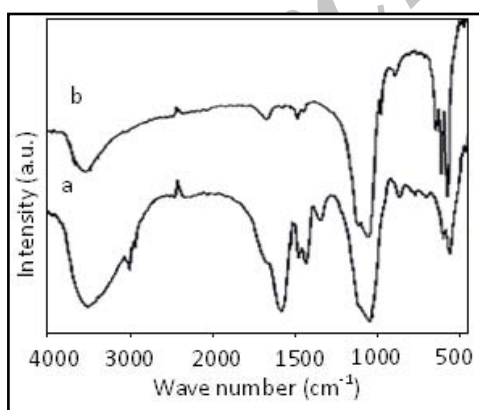


Fig. 1. FT-IR spectra of synthesized HAp (a) in the polyelectrolyte-modified microemulsion system, (b) in microemulsion system.

Figure 2a, 2b shows the XRD patterns of the obtained particles via Polyelectrolyte-modified microemulsion in the presence of PAA at room

temperature. Using low temperature may be the cause of poor crystalline nature of the prepared HAp. The crystallinity of the HAp powders synthesized via reverse microemulsion was much better than those synthesized via polyelectrolyte-modified microemulsion because the peaks of HA/PAA composite in comparison to the pure HAp are broader. Through the XRD and FT-IR, it proved that the synthesized crystals were all HAp.

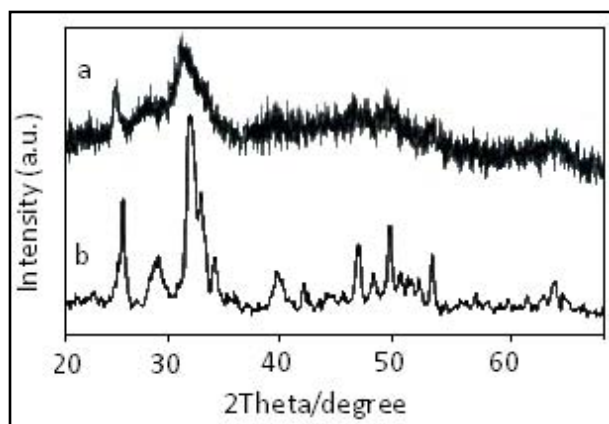


Fig. 2. XRD patterns of synthesized HAp (a) in the polyelectrolyte-modified microemulsion system, (b) in microemulsion system.

Figure 3a shows the morphology of HAp products in Polyelectrolyte-modified microemulsion, in the form of a needle-like shape. The particle size is about (20-30nm in diameter and 100-200nm in length). Figure 3b shows the morphology of HAp product in the microemulsion, in the form of a spherical. The particle size is about 5-15nm in diameter. Different morphologies and sizes are obtained in the absence and presence of PAA. In the absence of PAA, reverse micelles were mainly spherical, in this case, theoretically, the micelles were approximately equal to the maximum stretch out length of surfactant molecules, and therefore the aggregates were very small. As a result, only spherical particles of HAp were obtained. With incorporating of PAA in the reverse micelles, the droplet size increased up to dimension much larger and even deformed their shapes to cylindrical micelles. In fact, the reverse micelles changed their shapes from spherical to cylindrical. Crystal grew along a single crystal direction under the restriction of the water conduit of the microemulsion. Needle formation was rather a generic feature of HAp.

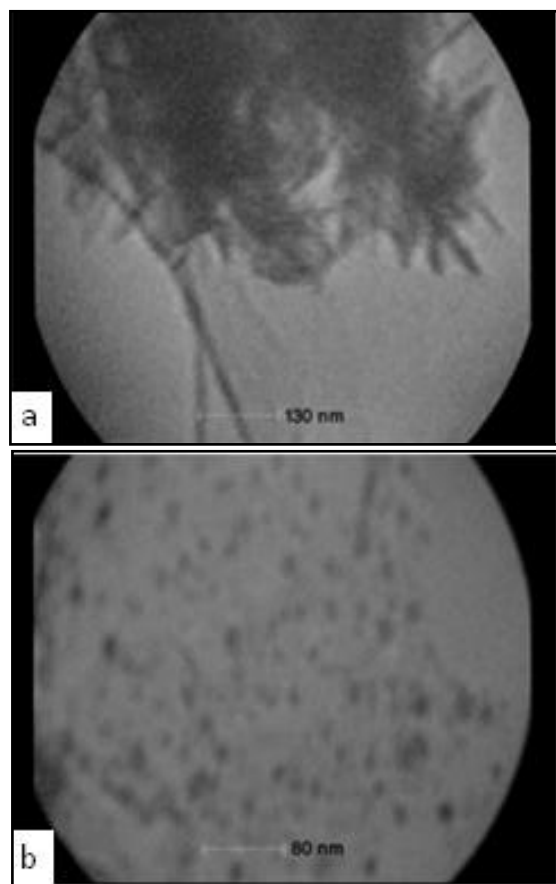


Fig. 3. TEM micrographs of synthesized HAP (a) in the polyelectrolyte-modified microemulsion system, (b) in microemulsion system.

CONCLUSION

Incorporation of PAA into individual microemulsion droplets can increase the templating effect of the microemulsions and stabilize the formed nanoparticles during the solvent evaporation. In the presence and absence of PAA, HAp nanoparticles were synthesized in different shapes such as sphere and needle like. Therefore, the polymer fulfills indeed the requirements of a size-regulating and stabilizing component in the process of nanoparticle formation. It could offer a novel approach to the fabrication of new colloid materials for the use in a wide range of technological applications.

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