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Formation of Needle Like Hydroxyl Apatite by Polyelectrolyte-modified Inverse Microemulsion Technique

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ABSTRACT

In this work needle like hydroxy apatite were synthesized in a reverse microemulsion droplets of water in cyclohexane, separated by a cationic surfactant and co-surfactant, in the presence of Na-polyacrylate (PAA) as an anionic polyelectrolyte. Characterization of the as formed HAp nanoparticles at the room temperature were carried out by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Size and morphology of the samples were investigated using scaning and transmission electron microscopy (SEM and TEM). The results obtained confirm incorperation of PAA as a template in controlling of the size and morphology of HAp nanoparticles into the individual microemulsion droplets.

Keyword: Cationic surfactant; Reverse microemulsion droplet; Hydroxy apatite; Anionic polyelectrolyte; Na-polyacrylate.

1. INTRODUCTION

Investigation of the new inorganic and inorganic/ organic composite nanomaterials and nano-structures is a rapidly developing and expanding area of research with tremendous potential for industrial applications. The main advantages of these nanomaterials are their specific physical (optical, mechanic, magnetic), chemical (reaction-activity, catalytic), and biomedical (curing, delivery, release) properties [1]. Among the different approaches exploited (for example wet synthesis [2], evaporation [3], lithography [4]) for fabrication of the nanoscale materials based on physical or chemical principles, mimic biomineralization process is one of the most interesting and sophisticated methods, especially for the synthesis of complex inorganic nanomaterials with dimensional, structural, and morphological, specificity inside the confined spherical water-in-oil (w/o) inverse microemulsions [5-8]. In this case, microemulsion droplets have been used as "nano-reactors" for

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making ultrafine particles. Since the first use of microemulsions in 1982 [9] to produce ultrafine catalyst particles, an appreciable amount of research has been performed on this subject [10-27]. However, one problem is that the bending elasticity and stability of the surfactant film that is not often strong enough to confine the growth of the particles in the interior of microemulsion droplets [28]. To overcome this problem, a component should be added to improve the surfactant film stability, control of the particle growth processes and stabilize 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 [29-32]. In this condition, the polyelectrolytes can control the size and shape of the nanoparticles during the formation process and polyelectroly-te-modified microemulsion can be successfully used as a new type of template for synthesis of nanoparticles with controlled size, shape, and morphology. Using this approach, we synthesized needle like hydroxyl apatite in a microemulsion template phase consisting of cyclohexane, water, cationic surfactant and co-surfactant, in the presence of Na-polyacrylate (PAA) as an anionic polyelectrolyte.

2. EXPERIMENTAL

Materials and methods

2.1. Materials

All of chemicals, $Ca(NO_3)_2.4H_2O$, $(NH_4)_2HPO_4$, NH_4OH, cyclohexane, n-pentanol and cetyltrimethylammonium bromide (CTAB with 99% purity) were supplied from Merck and Na-Polyacrylate (PAA) with low molar mass (M_W = 8000 g/mol) from commerce. All the chemicals were of analytical grade and used without any further purification.

2.2. Method

1 mL of $Ca(NO_3)_2.4H_2O$ (0.1 M) was added to a microemulsion template phase consisting of 1.82 g CTAB (cationic surfactant) in 60 ml cyclohexane, 1.6 ml n-pentanol (co-surfactant) and 0.1 M Na-polyacrylate (PAA) as an anionic polyelectrolyte and was stirred for about 15 minutes to obtain a transparent solution. For formation of HAp, 1 ml of aqueous solution of $(NH_4)_2HPO_4$ (0.6 M) was directly injected to the above prepared reverse microemulsion system under vigorous stirring and the pH of prepared system was then adjusted to a range of 9-10, by adding a small amount of ammonia to the system and the transparent solution obtained upon vigorous stirring for about 30 minutes was aged with continuous stirring at room temperature for one day. Addition of small amount of ethanol into the transparent solution obtained gives a white slurry. This slurry was centrifuged and the formed colloidal HAp has been collected. The precipitates were finally washed with ethanol for three times and dried at 50°C for 24 h.

2.3. Characterizations

Characterization of the samples were carried out by XRD (Philips expert pro. using Cu Kα radiation (λ = 0.154 nm)), Scanning Electron Microscope (Philips XL30), Transmission Electron Microscope (Philips) and Fourier-Transform Infrared spectroscopy (Thermo Nicolet Nexus 870).

3. RESULTS AND DISCUSSION

Figure 1 shows FT-IR spectra of the HAp prepared by inverse microemultion and through polyelectrolyte modified microemulsion process. In both of the cases characteristic peaks originated from bending and stretching vibration mode of phosphate groups appeared between 1090-1030 and 600-560 cm^{-1}. For Hap formed through polyelectrolyte modified microemulsion process, the bands at 1458 cm^{-1} and 1415 cm^{-1} have been assigned to scissoring of -CH- and bending of -CH-CO- of PAAc. The broad band at around 3300 cm^{-1} is due to stretching of OH of carboxylate groups and adsorbed water. The band at 1702 cm^{-1} is assigned to the stretching of carbonyl group in -COOH. Another band observed at 1641 cm^{-1} can

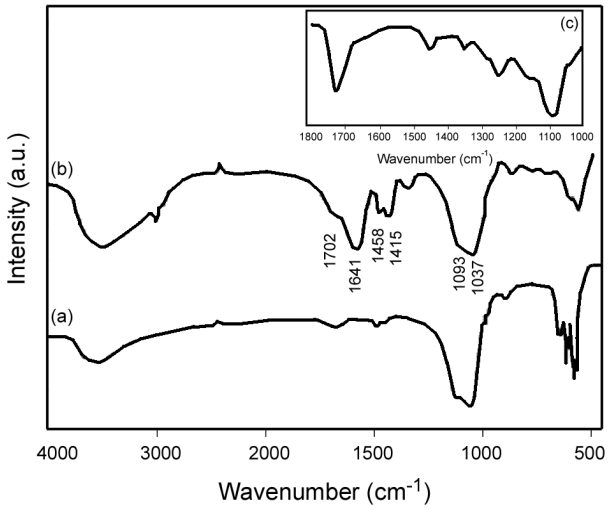


Figure 1: *FT-IR spectra of synthesized HAp (a) in microemulsion system, (b) in the polyelectrolyte-modified microemulsion system, (c) Polyacrylic acid.*

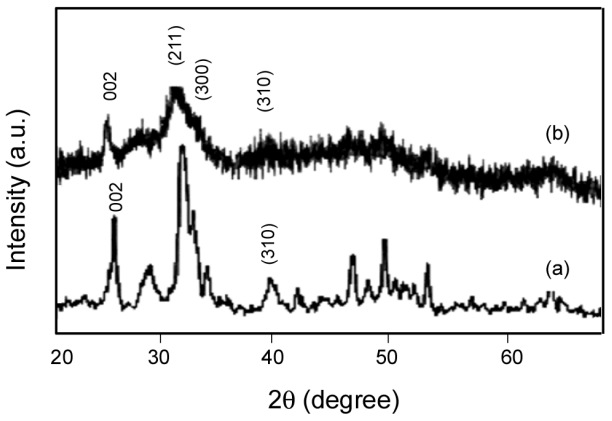


Figure 2: *XRD patterns of synthesized HAp (a) in microemulsion system, (b) in polyelectrolyte-modified microemulsion system.*

be related to HAP/PAAc composites and has been assigned to the asymmetric carbonyl stretching of dissociated carboxylate groups. This band is also present in PAAc but its intensity is low and appears when -COOH moieties dissociate to -COO-. It is clear that, dissociated carboxylate groups act as favorable sites for nucleation of hydroxyapatite. Carboxylate groups form complexes with Ca^{2+} in the solution and facilitate growth of hydroxyapatite crystals [33].

Figure 2 shows XRD diffraction patterns of HA nanoparticles prepared through the microemulsion and polyelectrolyte-modified microemulsion systems at room temperature. As it can be seen from this figure, the HAp synthesized via reverse microemulsion and polyelectrolyte-modified microemulsion systems have the similar XRD patterns consisting of those of standard XRD pattern (Reference JCPDS No. 09-0432) and confirm crystallinity of the HAp nanoparticles with diffraction peaks that can be assigned to the monophase low crystalline hydroxyapatite. Broadening peaks in XRD pattern of hydroxyapatite imply to the small size and low crystallinity of the formed Hap in similarity with the natural bone mineral. This peak broadening in polyelectrolyte-modified microemulsion system in comparison with the hydroxyapatite formed in microemulsion system can be considered as a sign of decreasing HAp size and crystallinity in the presence of PAA. The average crystalline size using the more intense peak was calculated to be 18 nm for HAp obtained by microemulsion and 6 nm for HAp prepared by polyelectrolyte modified microemulsion system using Debye- Scherrer formula [34]:

$$D = k\lambda / \beta \cos\theta \qquad (1)$$

where D is the mean grain size, k is a geometric factor, λ is the X-ray wavelength, β is the FWHM of diffraction peak and θ is the diffraction angle.

Figure 3 shows SEM micrograph of the synthesized HAp in inverse microemulsion (Figure 3a) and polyelectrolyte-modified microemulsion systems (Figures 3b, 3c, 3d). Well distributed needle like HAp nanopaticles on the outside surface of a void space in the figures 3b, 3c can be clearly attributed to the incorporation of PAA in the size and shape controlled formation of HAp nanoparticles due to the electrostatic interaction and bonding between functional groups of PAA outside of void space and Ca^{2+} ions inside of microemulsion droplets in polyelectrolyte-modified icroemulsion systems.

Figure 4 shows TEM micrograph of the HAp nanoparticles formed in inverse microemulsion (Figure 4a) and in the polyelectrolyte-modified microemulsion (Figure 4b) systems. Formation of

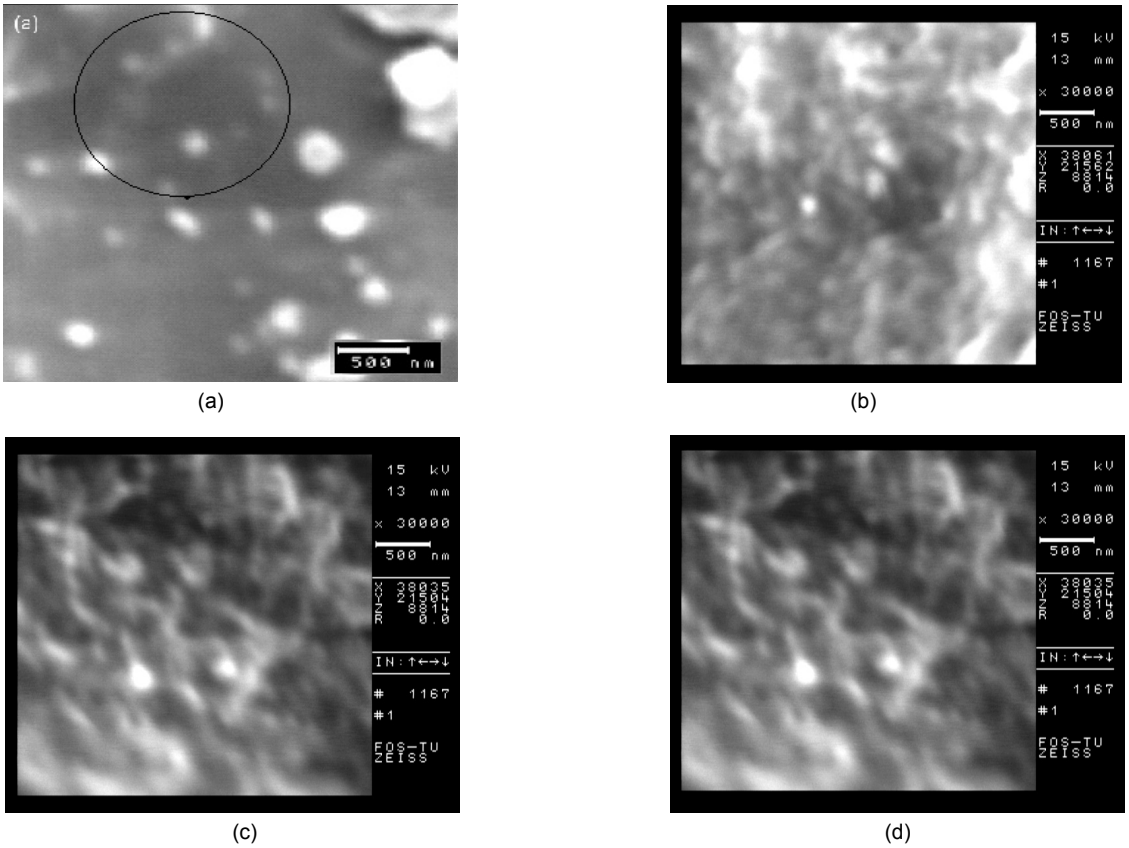
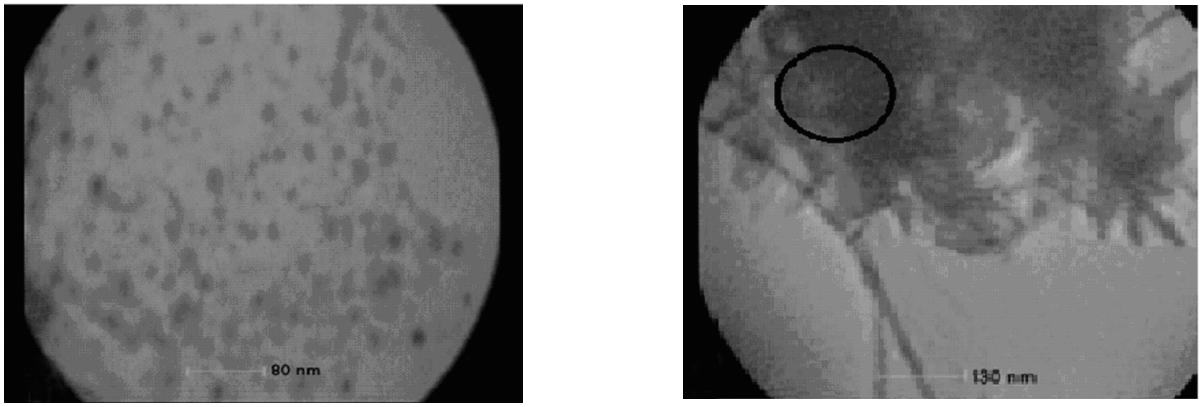


Figure 3: *SEM image of formation HAp outside of water droplet: a) spheric shape of HAp in microemulsion system. b,c,d) needle like of HAp in polyelctrolyte modified microemulsion system.*

needle like HAp, in the polyelectrolyte-modified microemulsion systems confirm clearly intervention of PAA in controlling of the size and morphology of HA nanoparticles. While, in the absence of PAA, only the spherical nanoparticles without any aggregation were produced in the reverse micelles droplets. Interesting point in the electrolyte mediated systems is appearence of needle like aggregates of the spherical nHAp particles at the outer surface of the water droplets or vaccant space in the figure. So, by incorporating of PAA in the reverse micelles, the droplet size can be increased up to dimension much larger and even deformed their shapes to cylindrical micelles. In fact, the reverse micelles changed their shapes from linearly spherical nanoparticles growth to the *cylindrical crystal growth* along a single crystal direction under the restriction of the water conduit of the microemulsion. Needle formation was rather a generic feature of HAp. Schematic intervention of PAA and formation of nHAp on the outerside of the polyelectrolyte modifed microemultion droplets is shown in Figure 5.

A short survey on the results obtained in this work shows that the polyelectrolyte-modified microemulsion technique is a convenient method in the synthesis of inorganic nanocomposites in a controllable and preselected way. By using this method we were able to synthesize needle like HAp with the crystalline size of 22 nm. This result is in conformity with the finding of Koetz, J et al. [35]. They used 3-(N,N-dimethyldodecylammonio)propanesulfonate-based microemulsion in the presence and absence of cationic polyelectrolytes, i.e., poly(diallyldimethylammonium chloride) PDADMAC) and chitosan, as a template phase for the formation of ZnS and hydroxylapatite nanoparticles, respectively. They have reported formation of HAp in a larger particle size (greater than 300 nm) with different shape (spherical, triangular, or



(a) (b)

Figure 4: *TEM micrographs of synthesized HAp (a) in microemulsion system, (b) in the polyelectrolyte-modified microemulsion system.*

rod-like particles) in an unmodified microemulsion system. But, in the presence of a stiff biopolymer, chitosan as a microemulsion modifier, a hybrid composite of hydroxylapatite, in fiber-like aggregate structure, consisting of individual small nanoparticles ordered along the polymer chain, in the presence of a biopolymer, chitosan. This finding shows that oligomeric chitosan was not able to be incorporated in the microemulsion droplets phase. While, by using a more flexible polyelectrolyte of low molar mass, e.g., the cationic polymer PDADMAC with M_n =7.000 g/mol, can form and produce hydroxylapatite nanoparticles with a small particle dimensions, which are well stabilized during the process of solvent evaporation and redispersion. This means that the PDADMAC of low molar mass *solubilized* into individual microemulsion droplets can increase the templating effect of the microemulsion and stabilize the formed nanoparticles during the solvent evaporation and the redispersion process. This results are completely in accordance with our finding that the particle formation process in polyelectrolyte-modified microemulsions strongly depends on the type of polyelectrolyte as well as the type of inorganic material used. Sodium polyacrylate which is a polymer with the chemical formula $[\text{-}CH_2\text{-}CH(COONa)\text{-}]_n$, and ability to absorb water as much as 200 to 300 times of its mass could be a good candidate to be used as a polyelectrolyte for incorporation in the reverse microemulsion droplets and preparation of the size and shape controlled nHAp. The main problem in this way is producing well distributed monodisperse nanoscalic emulsion droplets. Nowadays, this problem is solved by a high energy input, e.g., by means of an ultrasonic treatment, in combination with the addition of hydrophobes to overcome the problem in "Ostwald ripening" process [36]. In this

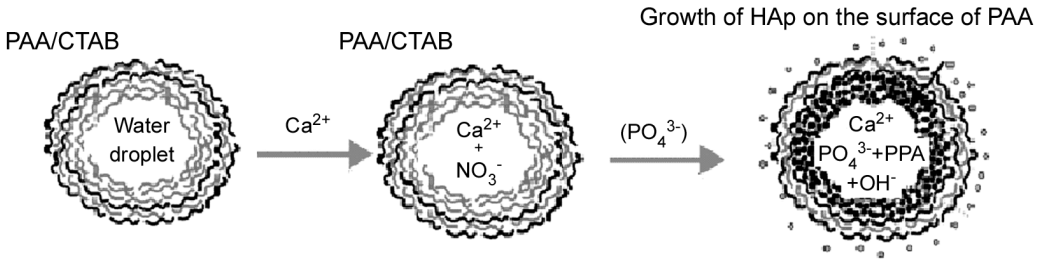


Figure 5: *Scematic illustration of the formation nHAp in outer side of the water droplets microrectors.*

way it becomes possible to produce oil-in-water or water-in-oil miniemulsions up to a droplet size of 100 nm. Especially polymer lattices can be successfully produced in such nanoscalic droplets.

4. CONCLUSIONS

- In general, our investigation shows that poly-electrolyte-modified microemulsion method is one of the most flexible and convenient methods, being able to perform synthesis of inorganic nanocomposites in a controllable and preselected way.
- Polyacrylic acid affects the degree of crystallinity, the coherent length of the perfect crystalline domains, as well as the dimensions and the morphology of the crystals.
- PAA can act as a template to control the size and morphology of nanomaterials into the individual microemulsion droplets.
- Increase of the templating effect of the poly-electrolyte into inverse microemulsion droplets stabilize the formed nanoparticles during the solvent evaporation.
- HAp nanoparticles can easily synthesize in different shapes such as spheres and needle like in the presence and absence of PAA.
- Therefore, the polymer indeed fulfills indeed the requirements of a size-regulating and stabilizing component in the process of nanoparticle for-mation [19].
- The particle dimensions in this process depend on the molar mass of the polymer, and the resulting supramolecular structures are mainly controled by the polyelectrolyte-nanoparticles and polyelectrolyte-surfactant interaction.
- Broadening of the X-ray diffraction reflections indicate a reduction of the coherent length along the long dimension (002) and the cross section (310) of the apatite crystals. The reduction is greater along the direction orthogonal to the c-axis, which can be rationalized by a preferential interaction of the carboxylate groups of the polyelectrolyte with the phosphate sites on the crystalline faces parallel to the c-axis.

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