Synthesis of HA nanoparticles in the presence of anionic and cationic polyelectrolyte

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Abstract

Hydroxyapatite (HA) nanopowders have been synthesized by an inverse microemulsion system using cyclohexane, ananionic surfactant and aqueous solutions of calcium nitrate tetrahydrate and biammonium hydrogen phosphate in the presence of anionic and cationic polyelectrolyte with the inducement of ultrasound irradiation. The Prepared HA in the presence of anionic polyelectrolyte has a different morphology from samples which are synthesized in the presence of cationic polyelectrolyte. Cationic polyelectrolyte (poly diallyl dimethyl ammonium chloride PDADMAC) leads to the formation of needle-like HA (10nm in diameter and 100nm in length). Formation of HA at room temperature was confirmed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and morphology of the samples which were characterized using transmission electron microscopy (TEM).

Keywords: Hydroxyapatite; inverse microemulsion; nanoparticles; polyelectrolyte; polyelectrolyte–modified microemulsion.

Introduction

HA [$Ca_{10}(PO_4)_6(OH)_2$] is a principal inorganic constituent of bones and teeth. Synthetic HA has excellent biocompatibility and bioactivity; therefore it is useful in reconstruction of damaged bone or tooth zones. HA can also be applied in industrial and technological fields such as water purification, fertilizers production, drug delivery and non-viral gene delivery. HA is also a good candidate for applications in catalysts and ion exchanges due to its unique surface structure and substitutions. The preparation of HA powders with given characteristics of morphology, stoichiometry, crystallinity, and crystal size distribution is important in biomedicine and material science [1-4]. HA nanoparticles can be fabricatedby employing a variety of chemicals based on processing routessuch as co-precipitation, hydrothermal reactions, sol-gel synthesis, pyrolysis of aerosols, microemulsion, and the recently sonoelectron chemical method, and so on. It is worth mentioning that using microemulsions and ultrasound irradiation are two synthetic methods for nanosized sulfides that have been studied intensively and aroused more and more attention [5-8].

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Different types of microemulsion were known, such as water-in-oil (w/o), and oil-in-water (o/w). In the case of a water-in-oil microemulsion, reverse micelles are formed when the aqueous phase is dispersed as micro droplets 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 in the interior of the microemulsion droplet. To overcome this problem, a component that should be added improves the surfactant film stability; control 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 [9-12]. The aim of the present study is to use the microemulsion in the presence of anionic and cationic polyelectrolyte as a template phase of the formation of HA.

Experimental

The materials used in this work included $Ca(NO_3)_2.4H_2O$،$(NH_4)_2HPO_4$, NH_4OH, cyclohexane, n-butanol, sodium dodecyl sulfate SDS with 98% purity, Na-Polyacrylate (PAA), polydiallyldimethyl ammonium chloride (PDADMAC), 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.

Synthesis route A

After preparing the 0.1M solution of SDS in 60 mL cyclohexane and 3 mL n-butanol, 1 mL of 0.5M aqueous solution of $Ca(NO_3)_2.4H_2O$ was injected slowly into the surfactant solution. A transparent solution was obtained upon vigorous stirring of system for about 15 min. For the formation of HA precursors, under vigorous stirring, 1 mL of 0.3M aqueous solution of $(NH_4)_2HPO_4$ was directly added to the above-mentioned reverse microemulsion. Then, a small amount of ammonia was added to the system to adjust pH in the range of 9-10. After that the mixture solution was exposed to high-intensity ultrasound irradiation under ambient air for one hour. 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 HA. Dried products were characterized by XRD (Philips expert pro. With Cu Ka radiation (λ=0.154 nm)), Transmission electron microscope (TEM; Philips), and Fourier-transform infrared spectroscopy (FT-IR; Thermo Nicolet Nexus 870).

Synthesis route B

Route B was carried out similar to route A, but instead of using 1 mL of 0.5M $Ca(NO_3)_2.4H_2O$ aqueous solution, 1 mL of 0.5M Ca $(NO_3)_2.4H_2O$ in 4% (w/v) of polymeric aqueous solution (PDADMAC) was used to prepare HA nanoparticles.

Results and discussion

Polyelectrolyte-modified microemulsions seem to be very interesting template phases of the nanoparticles formation due to the special features of the incorporated polyelectrolyte, including polyelectrolyte-surfactant interactions, polyelectrolyte-nanoparticle interactions [19]. In this study, presence of polyelectrolyte changes the morphology and particle size of HA. In the presence of PAA and anionic

surfactant, particle size is larger, because polyelectrolyte-surfactant interactions decrease the film stability of the microemulsion droplets, but in the presence of polyelectrolyte with opposite charge, the particle size is smaller because polyelectrolyte-surfactant interactions increase the film stability of the microemulsion droplets [13, 14].

Figure 1 shows the FT-IR of HA nanoparticles. Figure 1 shows FT-IR spectra of the HA prepared by inverse microemulsion and through poly electrolyte modified microemulsion process. All three of the cases characteristic peaks originated from bending and stretching vibration mode of phosphate groups appeared between 1090-1030 and 600-560 cm^{-1}. The broad band at around 3300 cm^{-1} is due to stretching of OH of HA and adsorbed water. For HA formed through polyanionic modified microemulsion, the bands at 1450 cm^{-1} and 1415 cm^{-1} have been assigned to scissoring of –CH– and bending CH-CO– of PAA. The band at 1640 cm^{-1} is assigned to stretching from carbonyl of –COOH. For HA formed through polycationic modified microemulsion, the peak at 1700 cm^{-1} is assigned to the ester group of the PDADMC.

Figure2 shows the XRD patterns of the obtained particles in the microemulsion media at room temperature. As it can be seen from this figure, the HA synthesized with reverse microemulsion and polyelectrolyte modified microemulsion systems have the similar XRD pattern. The average crystalline size using the most intense peak was calculated to be 10 nm for HA obtained in the presence of cationic polyelectrolyte, 40nm for HA prepared in the absence of polyelectrolyte, and 100 nm for HA prepared in the presence of anionic polyelectrolyte using debye scherrer formula.

$$D = K\,\lambda/B\,COS\,\theta$$

Where D is the mean grain size, K is a geometric factor, λ is the X-ray wavelength, B is the FWHM of the diffraction peak and θ is the diffraction angle.

This means that the particle formation process in polyelectrolyte-modified microemulsions strongly depends on the type of polyelectrolyte and the PDADMAC solubilized into individual microemulsion droplets which can increase the templating effect of the microemulsion and stabilize the formed nanoparticles during the solvent evaporation and the redispersion process. Also a partial adsorption of the polycation onto the anionic surfactant film due to electrostatic attraction, leads to a change in the film properties consequently, it limits the growth of the nanoparticles.But, in the presence of the polyanion the repulsion of the same charged surfactant and polyanion prevents the attraction of the polyanion on the surfactant film; Therefore, emulsion droplets would not be stabled to restrain particles growth.
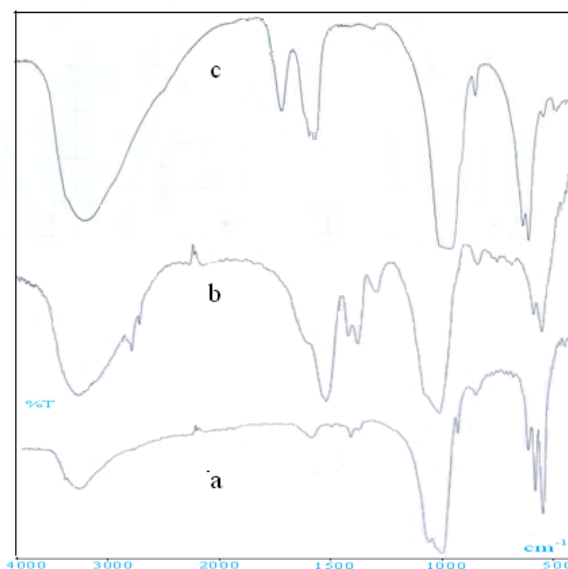
Figure 1. FT-IR spectra of synthesized HA (a) in the microemulsion system, (b) in the polyanionic-modified microemulsion system, (c) in the polycationic-modified microemulsion system
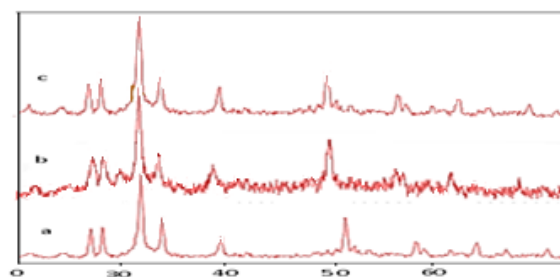

Figure 2. XRD patterns of synthesized HA (a) in the microemulsion system, (b) in the polyanionic-modified microemulsion system, (c) in the polycationic-modified microemulsion system

Figure 3 shows the SEM images of HA obtained in the absence and presence of the polyelectrolyte. The overall morphology of the obtained powders in the absence and presence of polyelectrolyte is quite different. These images suggest that the presence of polyelectrolyte has a great influence on the regularly nanoparticls distribution and morphology of the product due to polyelectrolyte-surfactant and polyelectrolyte-nanoparticle interactions in the polyelectrolyte-modified microemulsion droplets.
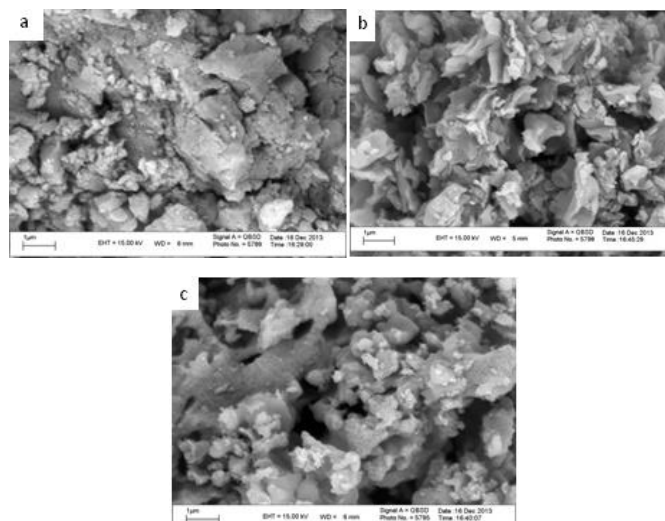
Figure 3. SEM micrographs of synthesized HA (a) in the microemulsion system, (b) in the polyanionic-modified microemulsion system, (c) in the polycationic-modified microemulsion system

Figure 4 shows the TEM image of HA synthesized by ultrasound-assisted microemulsion in the presence of cationic polyelectrolyte. The particle size was distributed uniformly at 10 nm, in the form of a needle-like shape. Crystal grew along a single crystal direction under the restriction of the water conduit of the microemulsion. This image clearly reveals that the size and morphology of HA found to be affected by the presence of cationic polyelectrolyte, in comparison with HA particles, prepared using microemulsion route [18,7,1,4].
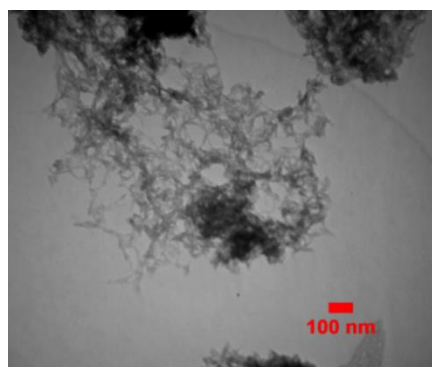

Figure 4. TEM micrographs of synthesized HA in the polycationic-modified microemulsion system

Conclusion

This work shows that the particle formation process in this system depends on the type of polyelectrolyte. When polycation is used, HA with particle dimensions of 10nm are predominantly formed, and are well stabilized during the process of solvent evaporation and redispersion. This means that the polycation 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. Therefore, the polymer fulfills

the requirements of a size-regulating and stabilizing component in the process of nanoparticle formation and redispersion [14]. In general, PAA do not seem to be interesting in the form of significantly smaller, ultrafine nanoparticles. When PAA is used the particle diameter of the resulting dispersion increases drastically. This means the addition of a polyanion increases the tendency to form larger particle aggregates in the presence of anionic surfactants due to electrostatic repulsions.

Acknowledgements

References

[1] Y. Sun, G. Guo, D. Tao, Z. Wang, *J. Phys. Chem. Sol*., **2007**, *68*, 373-377.

[2] A.I. Iorgo, D. Berger, L. Alexandrescu, B.S. Vasile, *Chalco. Letters*., **2013**, *12*, 525- 531.

[3] W. Pon-on, S. Meejoo, I.M. Tang, *Mat. Chem. Phys*., **2008**, *112*, 453-460.

[4] G.C. Koumoulidis, A.T. Katsoulidis, A.K. Ladavos, *J. Col. Inter. scien*., **2003**, *259*, 254–260**.**

[5] P. Sharma, S. Singh, H.S. Virk, *J. Nanosci. Nanotechnol*., **2010**, *6*, 236- 243.

[6] J. Arensds, J. Chistoffersen, M.R. Chistoffersen, H. Eckert, *J. Cryst. Grow*., **1987**, *84*, 515-532.

[7] S. Singh, P. Bhardwaj, V. Singh, S. Aggar-wal, U.K. Mandal, *J. Colloid and Interface Sci*., **2008**, *319*, 322-329.

[8] M.A. Malik, M.Y. Wani, M.A. Hashim, *Arab. J. Chem*., **2012**, *5*, 397-417.

[9] M. Dios, F. Barroso, *J. Colloid Interface Sci*., **2009**, *333*, 741-748.

[10] D. Sarkar, S. Tikku, V. Thapar, R.S. Srinivasa, K. C. Khilar, *Coll. Sur. A: Physicochem. Eng.Aspects*., **2011**, *381*, 123-129.

[11] W. Meier, *Langmuir*., **1996**, *12*, 1188-1192.

[12] A.M. Bellocq, *Langmuir*., **1998**, *14*, 3730-3739.

[13] B. Jakobs, T. Sottmann, R. Strey, J. Allgaier, L. Willner, D. Richter., *Langmuir*, **1999**, *15*,6707-6711.

[14] J. Kotez, J. Bahnemann, G. Lucase, B. Tiersch, S. Kosmella, Coll. *Sur. A: Physicochem. Eng. Aspects*., **2004**, *250*, 423-430.

[15] J. Kotez, J. Baier, S. Kosmella, *Colloid. Polym. Sci.,* **2007***, 285,* 1719-1726.

[16] G.K. Lim, J. Wang, S.C. Ng, L.M. Gan, *Mater. Lett*., **1996**, *28*, 431-436.

[17] S. Mollazadeh, J. Javadpour, A. Khavandi, *Cera. Int*., **2007**, *33*, 1579-1583.

[18] Y. Wang, JingDi Chen., KunWei, ShuHua Zhang, XiDong Wang, *Mate. Lett*., **2006**, *60*, 3227-3231.

[19] A. Sinha, A. Guha, *Mater. Sci. Eng*., **2008**, *29*, 1330-1333.

How to cite this manuscript: Kobra Akhavan. "Synthesis of HA nanoparticles in the presence of anionic and cationic polyelectrolyte".
Iranian Chemical Communication, 2018, 1, 49-54.