

Pulsed laser ablation of hydroxyapatite in ethanol

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Abstract Pulsed laser ablation in liquid medium was successfully employed to synthesize hydroxyapatite colloidal nanoparticles. The crystalline phase, particle morphology, size distribution and microstructure of the hydroxyapatite nanoparticles were investigated in detail. The obtained hydroxyapatite nanoparticles had spherical shape with sizes ranging from 5 to 20 nm. The laser ablation and the nanoparticle forming process were discussed with explosive ejection mechanism by investigating change of surface morphology on target. The analytical results of XPS, FT-IR and Raman spectroscopy confirms that the stoichiometry and bonding properties of the hydroxyapatite nanoparticles are in good agreement with reported bulk hydroxyapatite materials.

Key words Pulsed laser ablation, Hydroxyapatite, Nanoparticle

1. Introduction

Calcium phosphates, notably hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has attracted a lot of interest due to its similarity with mineral bone. Hydroxyapatite, which is very similar to hard tissue of human body, shows excellent biocompatibility and bioactivities with respect to human hard tissues. In addition, it has been widely used not only as biomedical implant material, but also drug delivery system and DNA isolation [1, 2]. Previous studies reported that 20–50 nm hydroxyapatite nanoparticles play an important role in biomineral formation. It is suggested that the basic inorganic building blocks of tooth and bone may be these nanosized apatite particles [3]. Tens to hundreds of these nanoblocks combines into self-assembled biomaterials with collagen matrix or cells reacted with non-apatitic highly reactive labile ions such as CO_3^{2-} , PO_4^{3-} , HPO_4^{2-} on cell-material interface, and shows unique physicochemical features such as mechanical strength, insensitivity to growth/dissolution and flexible structure [4]. These unique properties depend on the morphology and size of the hydroxyapatite. For aiming at better and more effective biomedical applications, development of novel synthetic routes for nanosized hydroxyapatite is very important.

A various approaches have been introduced for the preparation of hydroxyapatite nanoparticles and their functionalization [5]. Conventionally, solid state reaction,

acid-base, precipitation, hydrothermal and sol-gel methods were used for synthesis of hydroxyapatite powders or other nanoparticles [6, 7]. However, those methods need long reaction time and several process steps for fabrication. Also, chemical additives in procedure may be incorporated to hydroxyapatite particles as impurities, which results in bad influence to human body clinically [8]. One novel technique for fabrication of hydroxyapatite nanoparticles is pulsed laser ablation (PLA) in liquid medium. PLA of solid target in liquid has been a promising technique for producing nanoparticles for analytical and bioanalytical applications as well as the rapid synthesis of complex materials because the experimental procedure is simple and above all, chemical additive is unnecessary [9]. However, to date, there is little report on the preparation of hydroxyapatite nanoparticles by laser ablation in liquid medium. In this study, we report a novel synthetic approach to produce pure hydroxyapatite nanoparticles using PLA in liquid medium without any surfactant. The fabricated hydroxyapatite nanoparticles were characterized in terms of their crystallinity, microstructure and bonding property. Moreover, the laser ablation process was discussed by a thermally induced explosive ejection mechanism.

2. Experimental

The laser ablation process in liquid medium is illustrated well in previous literature [9]. Hydroxyapatite target (CELLYARDTM pellet, PENTAX) was fixed in the bottom of the glass vessel containing 5 ml high purity

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ethanol and the target was irradiated by a Nd:YAG pulse laser (repetition rate of 30 Hz, pulse width of 5~7 ns, maximum output of 60 mW) with third harmonic wavelength (355 nm). The laser was focused to spot with 1 mm in diameter on the hydroxyapatite target with a focal length about 250 mm. The target was rotated during laser ablation to avoid deep ablation traces by continuous irradiation of laser beam. The laser ablation to hydroxyapatite target was carried out for 1 hour at room temperature. The morphology of target before and after laser ablation in ethanol was analyzed by a field emission scanning electron microscope (Hitachi S-4800). The prepared colloidal suspension was dropped on a copper mesh coated with amorphous carbon film for observation of microstructure and particle morphology using transmission electron microscopy (JEOL JEM-2010). The size of nanoparticles was statistically analyzed using 150 nanoparticles in image of transmission electron microscopy (JEOL JEM-2010). The precipitates of colloidal suspension were prepared for the X-ray diffraction (XRD; Rigaku RAD-C, Cu K α radiation) measurement, X-ray photoelectron spectroscopy (XPS; Perkin-Elmer PHI-5600ci) and Raman spectroscopy (LabRam HR) analysis.

3. Results and Discussion

Fig. 1(a) shows XRD pattern of the hydroxyapatite nanoparticles collected from a colloidal suspension prepared by PLA in de-ionized water. The Bragg reflection peaks of the nanoparticles were indexed well to the hexagonal structured $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ in $P6_3m$ space group (JSPDS No. 09-0432). The XRD analysis indicated that the prepared hydroxyapatite nanoparticles did not contain any discernible crystalline impurity such as β -tricalcium phosphate (β -TCP). The hydroxyapatite sample had relatively broad XRD peaks compared to the sintered target, which means the formation of very small nanoparticles.

The particle morphology, particle size and crystallinity were investigated more closely by TEM as shown in Fig. 1(b). The morphology of the nanoparticles was spherical and uniform with diameters between 5 and 25 nm. Selected area electron diffraction (SAED) patterns shown in inset of Fig. 1(b) revealed bright polycrystalline diffraction rings without preferred orientation, and lattice spacing derived from the diffraction rings was in agreement with the hexagonal structured hydroxyapatite nanoparticles. Particle size distribution was analyzed statistically

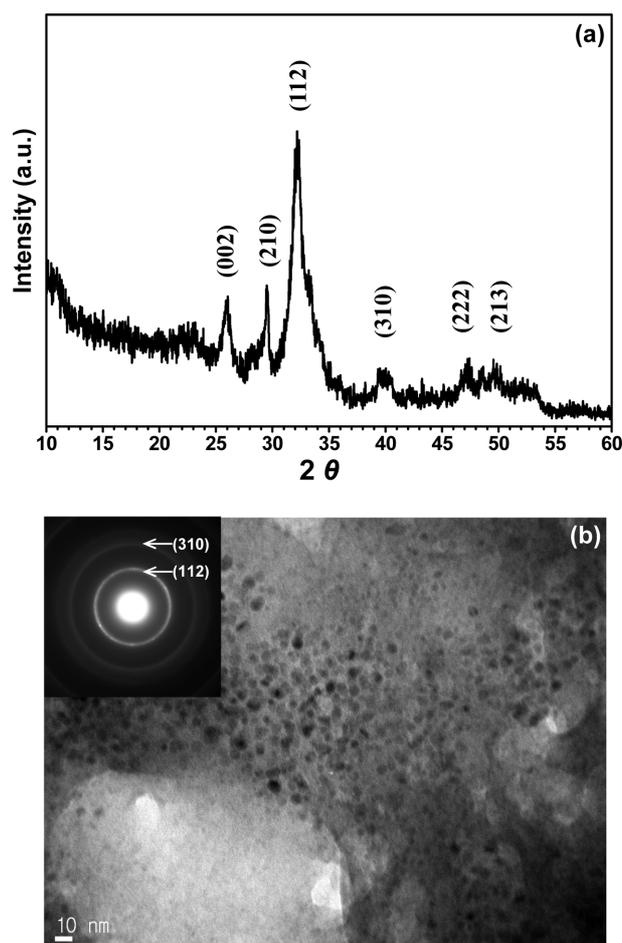


Fig. 1. (a) X-ray diffraction patterns of the hydroxyapatite nanoparticles collected from the colloidal suspension. (b) Typical TEM micrograph of prepared hydroxyapatite colloidal nanoparticle with corresponding electron diffraction patterns.

by random measuring crystal diameters of 150 nanoparticles in sight on obtained TEM image. During the measurement, no individual particle larger than 20 nm in size was found. Average nanoparticle size was 9.8 nm with the standard deviation of 2.5 nm.

Investigation of surface morphology of PLA target is the best tool available to identify how particles are formed during laser ablation in liquid medium. The surface morphology change of the hydroxyapatite target during laser ablation in de-ionized water was shown in Fig. 2. After laser ablation, the surface roughness increased dramatically as seen in Fig. 2(b). When hydroxyapatite is ablated in vacuum or low pressure gas for film deposition, it was reported that mainly micron size particles were formed. This was explained by propagation of cracks that caused chipping of the micron scale particles [10]. However, in this case, the particles formed in liquid medium by laser ablation are sphere-like uniform nanoparticles with an average diameter of 9.8 nm. The

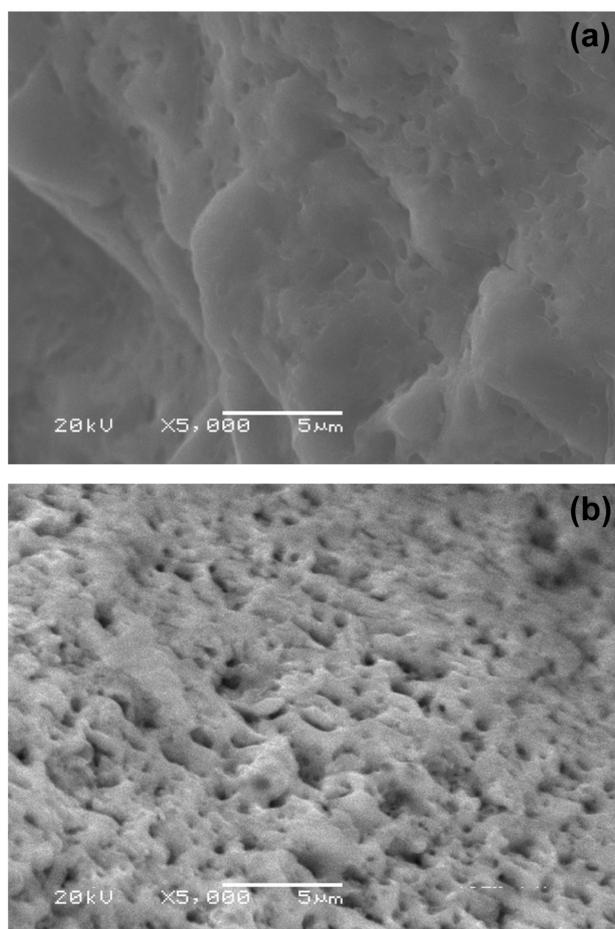


Fig. 2. Typical SEM micrographs of the hydroxyapatite target (a) before and (b) after laser ablation showing the remarkable change of the surface morphology induced by PLA.

size and shape of the particles indicate that crack propagation theory can not be applied to case of PLA in liquid medium. Therefore, we propose explosive ejection theory, which is one of the standard two models for ablation in interface between solid and liquid.

According to previous research of laser ablation in interface between solid and liquid, the two primary mechanisms for particle formation by pulsed laser ablation have been identified: thermal vaporization and explosive ejection [11]. In thermal vaporization, laser-induced plasma generated on a target in liquid confines species of atoms, ions and clusters with high energy. In the plasma induced by laser in liquid medium, the temperature and pressure can climb up instantly to 10^5 K and a few GPa range, respectively [12]. Those species with high energy can react and are quenched, when they contact with molecules of liquid medium, which induces nuclei of oxide or hydroxide via instantaneous hydrothermal oxidation [13]. However, in the case of laser ablation due to the thermal vaporization, the surface of

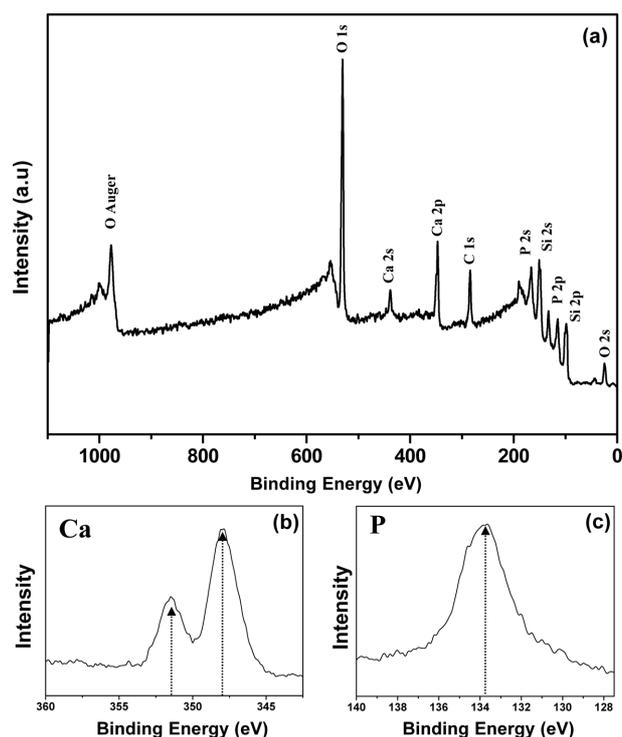


Fig. 3. (a) XPS survey scan spectrum of the hydroxyapatite nanoparticles and high resolution spectra of (b) Ca (2p) and (c) P (2p) regions.

target should be more flat and less rough than the case of explosive ejection [14]. It seems that this is not the case here. On the other hand, in explosive ejection, the molten droplets from nanometer to micrometer size are ejected directly from the target. The explosive ejection of molten droplet directly from the target is important for nanomaterial synthesis in PLA, because it avoids incongruent vaporization of multi-element targets and the stoichiometry of the target can be preserved in the nanomaterials [12].

In Fig. 2(b), the trace of explosive ejection phenomenon can be observed easily on the hydroxyapatite target used in PLA. When a target is heated more rapidly than dissipation of heat, the surface of target can pass its boiling point to the metastable superheated region, even in liquid phase. As the temperature reaches the thermodynamic critical temperature, the rate of homogeneous bubble nucleation is increased and the surface of target transits rapidly from superheated region to equilibrium liquid droplets [14]. This is called explosive boiling or ejection, which explains the formation of the sphere-like hydroxyapatite nanoparticles well during laser ablation in ethanol.

The surface composition of the hydroxyapatite nanoparticles collected from the colloidal suspension was

analyzed using XPS. A typical survey XPS spectrum from the hydroxyapatite nanoparticles is shown in Fig. 3(a). Besides the expected Ca, P and O peaks, a small C (1s) peak was observed. This carbon is so-called adventitious carbon induced by adsorption of impurity hydrocarbons and used for binding energy calibration by setting its binding energy to 284.6 eV to correct for sample charging. Other peaks in 99.6 and 150.7 eV are induced by the Si substrate. Fig. 3(b,c) show the high resolution XPS spectra of the Ca (2p) and P (2p) regions of the hydroxyapatite nanoparticles. The binding energy of Ca (2p) was 347.5 and 352.2 eV, and that of P was 133.7 eV. The binding energy values of Ca and P are well agreement with reported value [15]. A molar ratio of Ca/P calculated from the ratio of the integrated intensity of the Ca to P lines was 2.1, which is approximately 20 % higher than the stoichiometric molar ratio of 1.67. Previous study of ablation of hydroxyapatite in vacuum showed the Ca/P molar ratio rise up to about

3.0 [16]. Hence, it is considered that ablation in liquid medium better preserves the chemical composition of the hydroxyapatite nanoparticles.

Fig. 4(a) displays the FT-IR spectrum of collected hydroxyapatite nanoparticles prepared by PLA in ethanol. The set of absorption bands agrees fairly well with the reported FT-IR data for pure hydroxyapatite [17]. A set of characteristic bands representing apatitic PO_4^{3-} groups is observed at 1090, 1050 cm^{-1} (ν_3 triply degenerated asymmetric stretching mode of the P-O bond) and 960 cm^{-1} (ν_1 symmetric stretching mode of the P-O bond). Additional absorption bands representing a ν_4 triply degenerated bending mode of the O-P-O bond at 570 cm^{-1} are also observed in the low wavenumber region. The broad band at 3300–3600 cm^{-1} corresponds to adsorbed water and stretching vibration (ν_s) of the lattice structural hydroxyl anions. The weak peak at 610 and 1640 cm^{-1} is assigned to the vibrational mode (ν_L) and bending mode (ν_2) of the lattice OH^- ions. In particular, the peaks observed at 1490 and 1430 cm^{-1} is attributed to carbonate (CO_3^{2-}) traces partially occupying OH^- positions.

Fig. 4(b) shows the Raman scattering spectrum of the prepared hydroxyapatite nanoparticles. The band positions are in good agreement with published data on bulk hydroxyapatite powder [18]. The spectrum represents a very intense characteristic peak at 960 cm^{-1} owing to the symmetric stretching mode ν_1 (PO_4^{3-}). Apart from this ν_1 mode, the other stretching modes of the PO_4^{3-} groups are also observed, namely, ν_2 at 440 cm^{-1} , ν_4 at 590 cm^{-1} , and ν_3 at 1050 cm^{-1} region. The broad band at 3570 cm^{-1} corresponds to the stretching vibration of the hydroxyl groups.

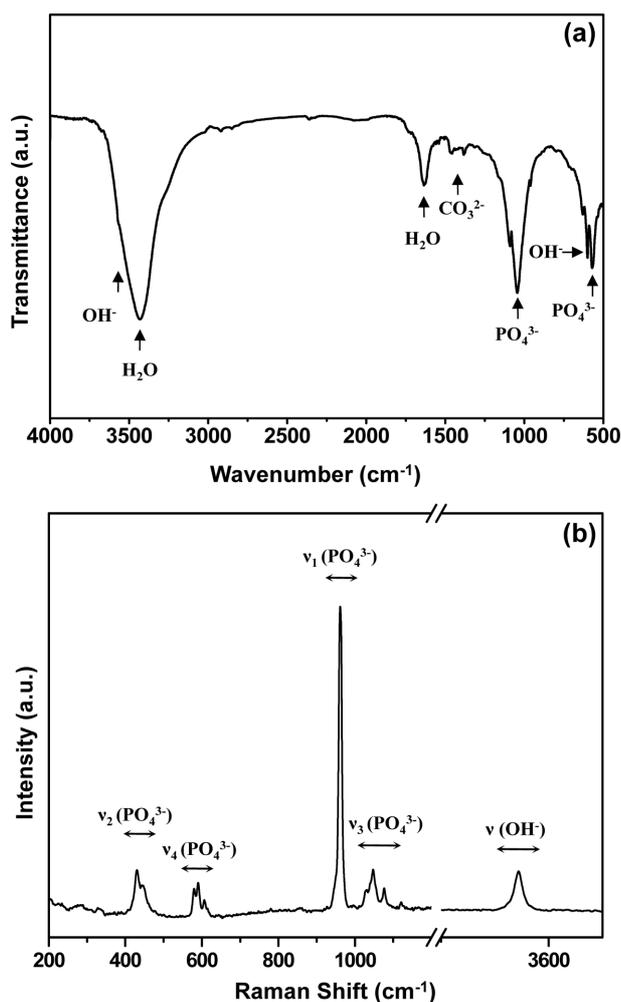


Fig. 4. (a) FT-IR and (b) Raman scattering spectrum of the hydroxyapatite nanoparticle.

4. Conclusion

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) colloidal nanoparticles was successfully synthesized via a simple synthetic route using pulsed laser ablation (PLA) in ethanol without any surfactant. The obtained hydroxyapatite nanoparticles were phase pure with uniform spherical shape, and its average size was 9.8 nm with standard deviation of 2.5 nm. The explosive ejection mechanism could explain the formation process of crystalline hydroxyapatite nanoparticles well, by which the molten droplets are ejected directly from the target during laser ablation. The analytical results showed that the prepared hydroxyapatite nanoparticles are highly crystalline and stoichiometric. These results confirm the PLA in liquid medium

can be an excellent candidate for the production of biomedical materials.

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