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Novel ultraviolet emitting low energy nitrogen ion implanted magnesium ion incorporated nanocrystalline calcium phosphate

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The effect of low energy nitrogen ion (N^+) implantation on microwave synthesized magnesium ion incorporated hydroxyapatite (HAp-$Ca_{10}(PO_4)_6(OH)_2$) was analyzed with fluences of 1×10^{14}, 1×10^{15} and 1×10^{16} ions/cm^2. The implant enhanced surface roughness, pore size (35%) and bioactivity along with a considerable decrease in the crystallite size (21%) and resistivity. Enhanced photoluminescence (PL) at 352 nm was observed at 1×10^{14} ions/cm^2. The surface turned to hydrophilic and hydrophobic at lower fluence ($<1\times10^{14}$ ions/cm^2) and higher fluence ($>1\times10^{16}$ ions/cm^2) respectively. Ion implantation is a cost-effective and rapid technique to modify the surface of magnesium ion incorporated HAp. The ion implanted sample has multifunctional properties and could be used for biomedical, biosensing applications and also utilized as a novel environmental friendly, rare-earth free ultraviolet phosphor material.

1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is often used as a bone graft material due to its biocompatibility [1]. The solubility of HAp was varied by incorporating different metal ions (Na^+, Mg^{2+}, Ba^{2+}, and Sr^{2+}). Among them, magnesium ions play a crucial role in the mineralization metabolism [2]. There are various techniques to synthesize nanosized HAp viz., microwave irradiation [3].

There are many methods to modify the surface of the implants to increase biocompatibility viz, laser irradiation [4], electron [5], plasma and ion beam implantation [6,7]. Implantation provides selective surface modification without affecting the bulk properties and improves the bioactivity of the biomedical implants [8]. The nitrogen and argon ion implantations were found to enhance the elastic modulus and the hardness of the HAp films [9]. Many reports are available on toxic europium doped HAp [10,11]. Here we report for the first time the effect of low energy nitrogen ion implantation on nontoxic magnesium ion incorporated nanocrystalline hydroxyapatite and the ultraviolet emission from the implanted sample.

2. Materials and methods

The microwave technique was used to synthesize magnesium ion incorporated nanocrystalline HAp. To a solution diammonium hydrogen phosphate (0.6 M), calcium nitrate tetrahydrate (1.0 M) and magnesium chloride hexahydrate (0.1 M) in deionized water were added under stirring (pH 10) and subsequently subjected to microwave irradiation (900 W and 2.45 GHz) for 30 min and dried in hot air oven at 80 °C. The synthesized powder ascribed MgHAp (pristine) made to pellets and annealed at 200 °C for 2 h and subjected to ion implantation. The samples were implanted by 30 keV nitrogen ions (N^+) with a charge state of +1 using 150 kV accelerator with various ion fluences viz., 1×10^{14} ions/cm^2, 1×10^{15} ions/cm^2 and 1×10^{16} ions/cm^2 was attributed as 14MgHAp, 15MgHAp and 16MgHAp respectively. The crystal structure of the samples were examined by STOE diffractometer using CuK_α radiation ($\lambda = 0.1540$ nm). Resistivity was measured using four probe setup. The contact angle measurement and *in vitro* bioactivity of the samples were also done [12]. The surface characterization was carried out using atomic force microscopy (AFM, NT-MDT-SOLVER PRO EC, Russia), scanning electron microscopy (FEI Quanta FEG 200) and PL (Spectra Physics, argon ion laser).

3. Results and discussion

The depth of penetration of N^+ ions was 144 nm. The respective electronic and nuclear energy losses were 0.840 keV/nm and 0.687 keV/nm (using SRIM-2008 program).

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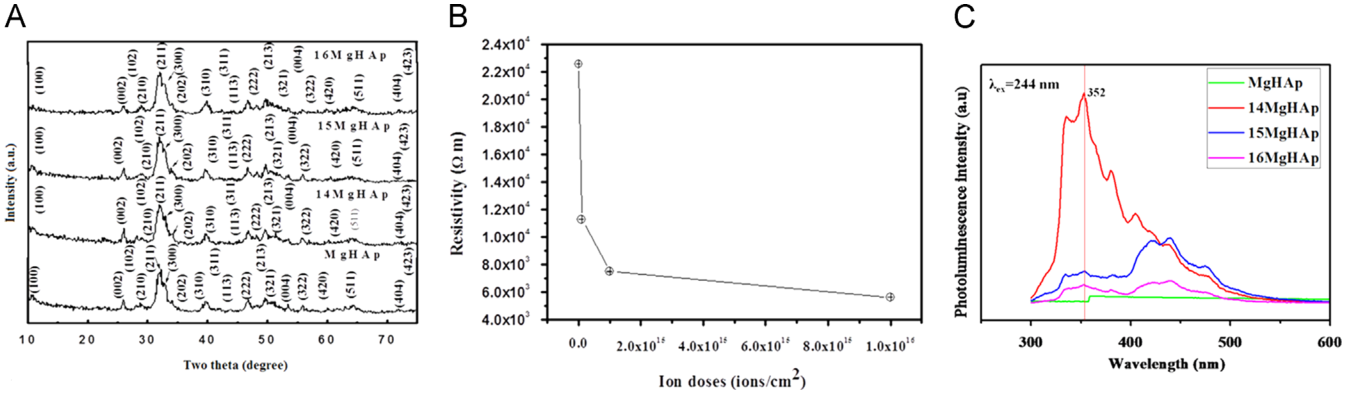

Fig. 1. (A) GIXRD patterns of the samples. (B) Measurement of resistivity versus ion doses. (C) Photoluminescence spectra of (a) pristine, (b) 14MgHAp, (c) 15MgHAp and (d) 16MgHAp.

Table 1
Crystallite size, lattice parameters and volume of unit cell of the pristine, 14MgHAp, 15MgHAp and 16MgHAp.

Samples	**Crystallite size (±0.2 nm)**	**Lattice parameters (Å) (±0.01)**		**Volume of unit cell (Å)^3**
		a*=*b	***c***	
MgHAp	17.0	9.45	6.87	531
14MgHAp	14.2	9.44	6.88	531
15MgHAp	15.4	9.42	6.85	526
16MgHAp	13.4	9.44	6.87	530

The GIXRD patterns of the samples were (Fig. 1A) in good agreement with the JCPDS data of HAp (09-0432). There was no significant variation in the lattice parameters and volume of unit cell (calculated using MAUD) due to N^+ ion implantation (Table 1). The 21% decrease in the crystallite size, could be attributed to the increase in the structural defects due to implantation [13].

The resistivity of the MgHAp, 14MgHAp, 15MgHAp and 16MgHAp, was 2.2×10^4, 1.1×10^4, 7×10^3 and 6×10^3 Ω m respectively (Fig. 1 (B)). There was a drastic decrease (73%) in resistivity of 16MgHAp compared to MgHAp due to the N^+ ions bombardment, leading to the localized heating, generating O^{2-} and H^+ ions, and ionic polarization and also produced a dominant electronic energy loss, leading to an increased mobility of the free electrons [14].

Photoluminescence (PL) of the samples, excited at 244 nm, is shown in Fig. 1(C). The broad PL band of the pristine was due to the deep energy level. At lower fluence, a peak shift accompanied by a significant enhancement in intensity of PL emission (intense ultraviolet emission at 352 nm) was due to the surface defects, low diffusivity of N^+ ions, electron and hole pairs recombination [15]. The reduction in PL intensity at higher fluence could be attributed to the defects quenching. The intense PL emission of the samples could assist in the design of a biosensor for the *in-situ* monitoring of newly developed bone [16]. For the UV light emitting diode fabrication, AlGaN (Aluminum Gallium Nitride) based LED (244 nm) was employed to excite ion implanted samples for the emission of UV light [17].

The surface topography of the samples was as shown in Fig. 2 (A). The average surface roughness of MgHAp, 14MgHAp, 15MgHAp and 16MgHAp was 132 nm, 153 nm, 177 nm and 193 nm respectively. The surface roughness was enhanced (46%) owing to the generation of heat and subsequent melting and rapid quenching of surface due to implantation [18]. The respective average pore size of MgHAp, 14MgHAp, 15MgHAp and 16MgHAp was 2.6 (±0.1) (μm), 3.0 (±0.05) (μm), 2.9 (±0.1) (μm) and 3.5 (±0.1) (μm). The 35% increase in pore size in comparison with the pristine might be due to the localized heating and diffusion of N^+ ions.

The contact angle of the pristine and 14MgHAp was 12° and 14° respectively, revealing a hydrophilic surface (Fig. 2(B)) which might aid the DNA absorption. The contact angle of 15MgHAp and 16MgHAp was 66° and 77° respectively, exhibiting hydrophobic surface due to the change in surface chemistry and polar component of the surface energy [19] and in addition, could assist the absorption of protein, bovine serum albumin (BSA) [20].

The surface of the SBF (Simulated Body Fluid) soaked samples was as shown in Fig. 3(A). The small spherical apatites were deposited on the surface of the pristine. The deposited apatites on 14MgHAp were spherical and elongated whereas, on 15MgHAp and 16MgHAp, the deposited apatites were rod type and agglomerated respectively. The respective Ca/P ratios of pristine, 14MgHAp, 15MgHAp and 16MgHAp were 1.72, 1.75, 1.77 and 1.85 (Fig. 3(B)) which confirmed the increased apatite deposition and enhanced bioactivity on implantation due to the electronic energy loss and improved surface charge [9].

4. Conclusions

The magnesium ion incorporated hydroxyapatite was synthesized by microwave processing and was implanted by 30 keV N^+ ions. The implantation leads to a reduction in the crystallite size without any change of phase of HAp. The drastic decrease in the electrical resistivity exhibited by the implanted sample could assist healing of the bone fractures and improve the rate of bone mineralization. Moreover, by varying the fluence of the implantation ions, one can tailor the wettability (hydrophilicity and hydrophobicity) of the samples. The reduced wettability of the implanted samples could assist the protein absorption and decrease bacterial infection. The pore sizes could be engineered and aid the flow of body fluid into implants and enhance the cell attachments. The ion implantation enhanced the photoluminescence, surface roughness and *in vitro* bioactivity of the samples. Hence, this technique is a rapid and inexpensive tool to tailor the surface of the biocompatible MgHAp, the pore size, photoluminescence, electrical resistivity, wettability and bioactivity. These multifunctional properties could be employed for various biomedical and biosensor applications. In addition, material might also be regarded as an excellent candidate for ultraviolet emission and to fabricate UV-light-emitting diodes (LEDs), which are rare-earth free, environmental friendly and biocompatible.