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Monodisperse selenium-substituted hydroxyapatite: Controllable synthesis and biocompatibility

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ABSTRACT

Hydroxyapatite (HA) is the major inorganic component of natural bone tissue. As an essential trace element, selenium involves in antioxidation and anticancer of human body. So far, ion-doped hydroxyapatites (HAs) are widely investigated owing to their great applications in field of biomaterial, biological labeling. In this paper, series of monodisperse HA doped with SeO_3^{2-} (SeHA) was successfully synthesized based on the liquid–solid–solution (LSS) strategy. The obtained samples were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and energy-dispersive spectrometer (EDS). The results indicated that the SeO_3^{2-} doping level of the Se/(P + Se) molar ratio of 0– 0.4 can be requisitely controlled, and the morphology of SeHA nanoparticles varied from nanorods to nanoneedles with increasing Se/(P + Se) molar ratio. Significantly, the as-synthesized SeHA nanocrystals exhibit a low cytotoxicity for osteoblastic cells, showing exciting potentials for application in artificial scaffold materials inhibiting of tumor growth in bone.

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), an important calcium phosphate, is well known as the major inorganic component of natural bone tissue. Synthetic HA has been a promising biomaterial for the tissue engineering and bone repair due to its excellent biocompatibility, osteoconduction, bioactivity as well as chemical similarity to the natural bone [1–5]. In addition, it has other important applications in cell imaging, drug delivery and water treatment [6–12]. Various methods have been developed to synthesize ions doped HA, such as wet chemical precipitation, sol–gel process, microemulsion process and hydrothermal reaction [13–17]. However, Synthetic HA has poor flexural strength and fracture toughness, which largely restricts its application in the hard tissue repair [18]. Therefore, more attempts are made to improve the properties of HA. Recently, many researchers draw attention to ions doped HA (e.g. F^-, Mg^{2+}, Zn^{2+}, Sr^{2+}, and CO_3^{2-} ions). After doping, the mechanical and biological properties of HA can be changed, which make it have potential application in field of biomaterial, biological labeling and nanodevices [19,20]. For example, it has been reported that Mg^{2+} and Sr^{2+} doped HA can promote osteoblast cells growth [21].

Selenium (Se) is one of the essential trace elements for human health. 3– 20 mg of selenium element has been found in human body, and most of selenium is scattered in the liver, pancreas and kidney. Selenium plays an important role in the antioxidation of the body. As an important component of antioxidase (glutathione peroxidase), selenium maintains homeostasis of free radical in the body with vitamin E [22]. Furthermore, it has been reported that selenium can be used as an efficient anticancer agent [23]. Chen et al. developed selenium-deposited and chitosan-coated Titania nanotubes with anticancer and antibacterial properties, which inhibit the growth of cancerous osteoblasts [24]. It has been reported that apatite coatings with selenite ions possessed antibacterial properties [25]. Therefore, selenium has attracted increasing attention in the field of preventing cancer.

Undoubtedly, selenium-substituted hydroxyapatites (SeHA) nanoparticles by partially replacing phosphate groups with selenite groups have great potential in the fabrication of novel biomedical materials. As it was reported, SeHA nanoparticles were usually synthesized in aqueous solution by hydrothermal methods, precipitation methods and so on, they were easy to form clusters (agglomerate), and even had flaws in the uniformity of sizes [26–29]. Although the thermochemical radius of the divalent selenite ions (0.239 nm) is very similar

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Table 1
Quantities of reactant for the synthetized samples.

Sample	$Ca(NO_3)_2$ (mmol)	Na_2SeO_3 (mmol)	Na_3PO_4 (mmol)	Se/(P + Se)
HA-0	1.875	0	1.125	0
SeHA-0.05	1.875	0.056	1.069	0.05
SeHA-0.1	1.875	0.113	1.013	0.10
SeHA-0.15	1.875	0.168	0.956	0.15
SeHA-0.2	1.875	0.225	0.900	0.20
SeHA-0.3	1.875	0.338	0.788	0.30
SeHA-0.4	1.875	0.450	0.675	0.40
SeHA-0.5	1.875	0.563	0.563	0.50
SeHA-0.55	1.875	0.619	0.506	0.55

to the radius of the trivalent phosphate ions (0.238 nm), but selenites are a flat trigonal pyramidal shape whereas phosphates are tetrahedral, which will significantly affect the morphology and size of the prepared SeHA nanoparticles, and their potential application [30]. It is still a noteworthy challenge of how to obtain the uniformity of monodisperse SeHA nanoparticles.

Herein, we have successfully synthesized monodisperse SeHA nanorods or/and nanoneedles via a hydrothermal synthetic route based on the liquid–solid–solution (LSS) strategy [20], and discussed the effect of selenite ions with different contents on the physicochemical properties of SeHA nanoparticles. Significantly, the prepared SeHA nanoparticles exhibit a low cytotoxicity, suggesting the promising materials for tissue engineering applications.

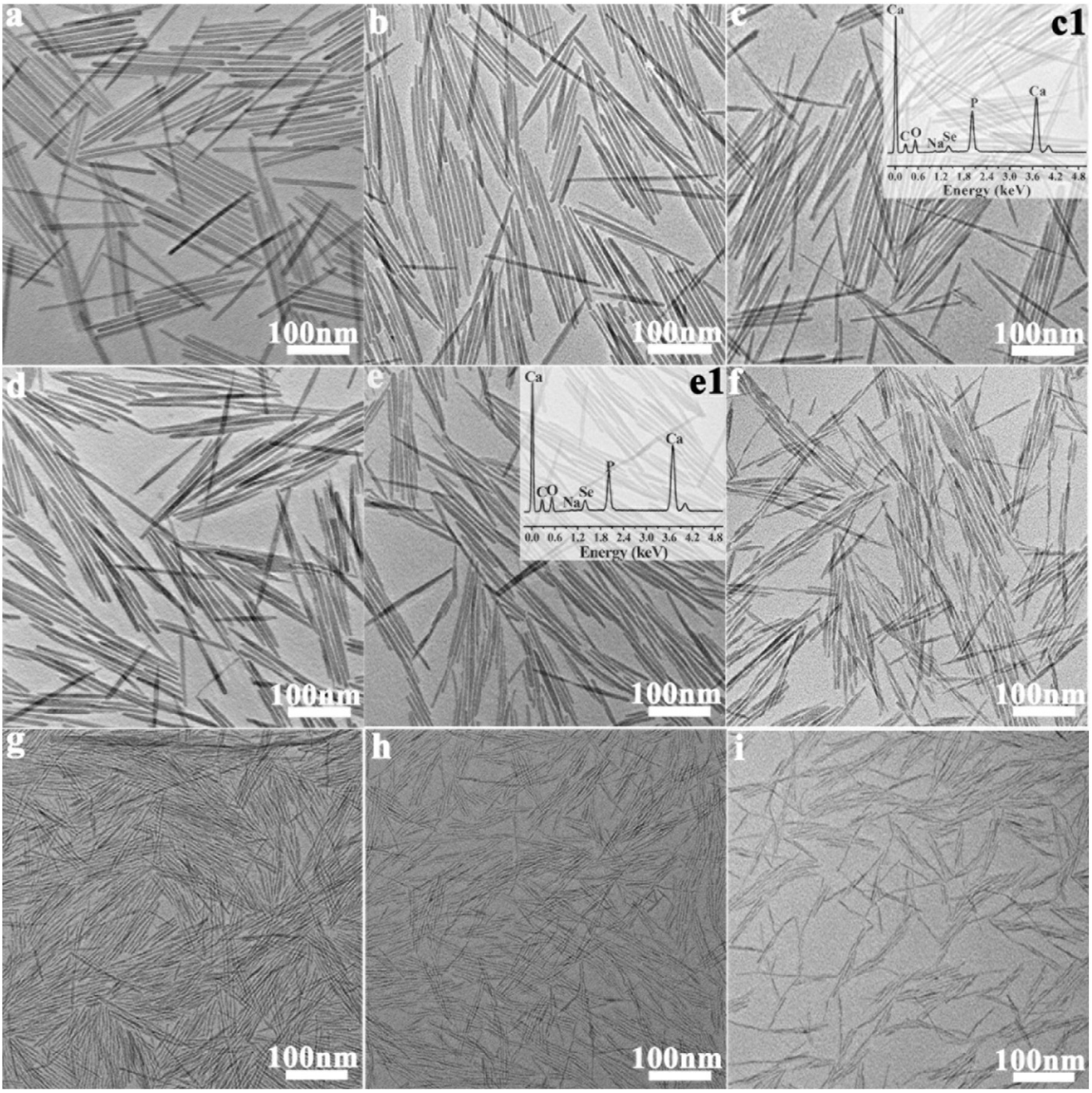

Fig. 1. TEM images of as-prepared samples with the molar ratio of Se/(P + Se) at 120 °C. a) 0, b) 0.05, c) 0.10, d) 0.15, e) 0.20, f) 0.30, g) 0.40, h) 0.50, i) 0.55, c1) and e1) EDS analysis of SeHA-0.1 and SeHA-0.2, respectively.