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Synthesis, liquid – Liquid extraction and deposition of hydroxyapatite nanorod composites

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A B S T R A C T

Hydroxyapatite (HA) nanorods were prepared by a wet chemical precipitation method. Lauryl gallate (LG) and hexadecylphosphonic acid (HDPA) showed strong adsorption on HA and allowed for the transfer of the synthesized HA nanorods from the aqueous to n-butanol phase at the interface of the two immiscible liquids. The extracted non-agglomerated HA particles were used for the fabrication of composite HA-polymer films. In this approach, the problems related to particle agglomeration during the drying stage were avoided. The analysis of the adsorption mechanisms indicated that LG and HDPA are promising extractors for agglomerate free processing of nanomaterials in the liquid-liquid extraction method.

1. Introduction

Hydroxyapatite (HA)-polymer nanocomposites are important materials for biomedical and water purification applications [1,2]. One of the problems related to the synthesis of HA nanoparticles and their application for the fabrication of nanocomposites is related to the strong tendency of HA to agglomerate. The reduction of the surface area and self-condensation of the surface OH groups promote the agglomeration of as-precipitated HA nanoparticles during the drying stage.

In this investigation, a liquid-liquid extraction method has been developed in an effort to avoid HA agglomeration, resulting from the drying process. Synthesized HA nanoparticles were transferred from the unstable suspension in water to an organic solvent through the interface of the two immiscible liquids. This process resulted in the formation of stable suspensions of well dispersed HA particles in an organic solvent. We demonstrated the processing advantages of this strategy for the fabrication of HA-biopolymer nanocomposite films, containing a water insoluble polymer. The success in the liquid-liquid extraction of HA was largely the result of the use of novel extractors, such as lauryl gallate (LG) and hexadecylphosphonic acid (HDPA), which showed strong adsorption on HA particles. It was found in the literature that LG is important antibacterial [3] and antitumor [4] agent. HDPA belongs to the family of organophosphonates, which are widely used for the surface modification of biomaterials [5,6]. Phosphonate additives promote biomineralization and improve biocompatibility and chemical stability of implant materials [7,8]. We report new applications of LG and HDPA as advanced extractors for HA, which allowed for high extraction efficiency. The approach offers a simple and efficient strategy for the synthesis other nanomaterials and composites.

2. Experimental procedures

Lauryl gallate (LG), hexadecylphosphonic acid (HDPA), Ca $(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$, NH_4OH, poly(methyl methacrylate) (PMMA) and n-butanol (Aldrich) were used. HA precipitation was performed at a temperature of 70 °C by the slow addition of a 0.6 M $(NH_4)_2HPO_4$ solution to a 1.0 M $Ca(NO_3)_2$ solution. The pH of the solutions was adjusted to 11 by the addition of NH_4OH. Then LG or HDPA solutions in n-butanol were added. After ultrasonication and stirring for 10 min, the HA particles were extracted to the n-butanol phase. The mass ratio of HA to the extractants was 3:1.

The suspensions of the extracted HA were added to PMMA solution in acetone and obtained stable suspensions were used for spray coating of stainless steel substrates. The mass ratio of HA and PMMA in the suspensions was 4:1.

Electron microscopy investigations were performed using a JEOL JSM-7000F scanning electron microscope (SEM) and FEI Tecnai Osiris transmission electron microscope (TEM). FTIR studieswere performed on Bruker Vertex 70 spectrometer. X-ray diffraction

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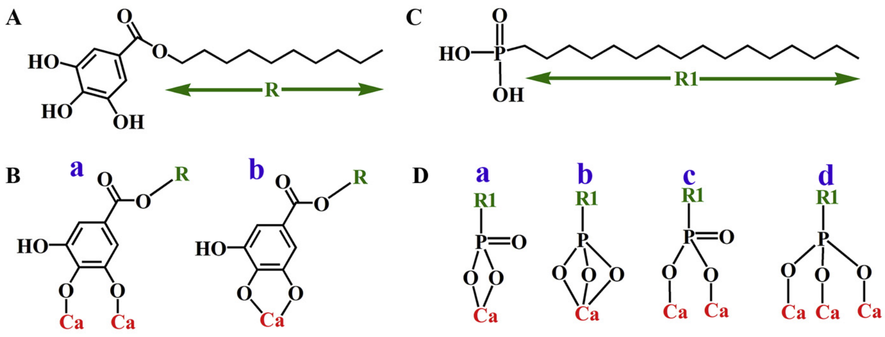

Fig. 1. (A) Chemical structure of LG, (B) adsorption of LG, involving (a) bridging, (b) chelation, (C) chemical structure of HDPA, (D) adsorption of HDPA, involving (a, b) chelation, (c, d) bridging.

(XRD) studies were performed using a powder diffractometer (Nicolet I2, CuK$_\alpha$ radiation).

3. Results and discussion

Liquid-liquid extraction of oxide and hydroxide nanomaterials offers many potential benefits, which have not been utilized for practical applications due to the lack of efficient extractors. Inspired by Nature's mechanisms of strong mussel adsorption on inorganic surfaces, which involves catechol groups of mussel's proteins [9], we used LG as an extractor for HA particles. The chemical structure of LG (Fig. 1A) includes a galloyl group, which similar to catechol, contains OH groups, bonded to adjacent carbon atoms of the aromatic ring. Previous investigations of catecholates and gallic acid adsorption showed that such molecules create bidentate chelating or bidentate bridging bonding with metal atoms on the

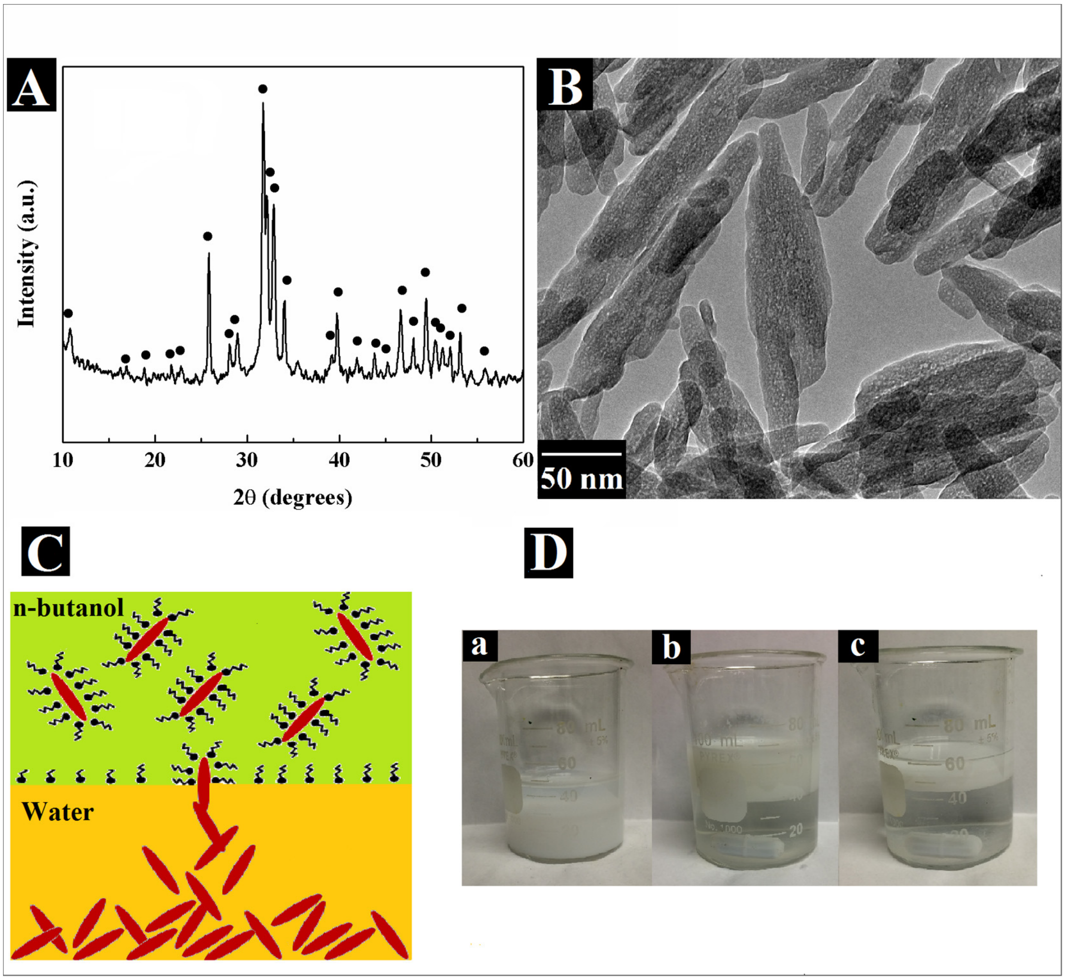

Fig. 2. (A) X-ray diffraction pattern of HA (●- JCPDS file 09-0432), (B) TEM image of HA, (C) schematic of liquid-liquid extraction, (D) (a) as precipitated HA, (b) HA extraction using LG, (c) HA extraction using HDPA.