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Bioactive nano-titania ceramics with biomechanical compatibility prepared by doping with piezoelectric $BaTiO_3$

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Abstract

Piezoelectric $BaTiO_3$ was employed as a crystal growth inhibitor additive for the preparation of bioactive nano-titania ceramics in this study. It is found that the additive could significantly inhibit nano-titania ceramic crystal growth during the pressureless sintering process. This inhibitory ability has great effects on the mechanical properties and bioactivities of the nano-titania ceramics, making it possible to obtain bioactive nano-titania ceramics with mechanical properties analogous to human bone. In this study, the crystal grain sizes of the nano-titania ceramics ranged from 18 to 68 nm and the particle sizes ranged from 187 to 580 nm by changing the additive content from 1% to 20%. The elastic modulus of the nano-titania ceramics ranged from 6.2 to 10.6 GPa, which is analogous to that of human bone, by adjusting the additive content. The piezoelectric properties of the additive also showed the enhancing effects on the bioactivity of the nano-titania ceramics, which made the osteoblasts proliferate faster on the nano-titania ceramics in cell culture experiments. It might be a potential way to prepare bioactive nano-titania ceramics with biomechanical compatibility by using $BaTiO_3$ as a crystal growth inhibitor.

Keywords: Nano-titania ceramics; $BaTiO_3$; Bioactivity; Grain growth inhibitor; Biomechanical compatibility

1. Introduction

Nano-titania ceramics has been proved to be a potential bioactive material for bony tissue applications. It induced apatite formation in simulated body fluid and enhanced osteoblast differentiation [1–3], which implies that it could form bioactive bonding with bony tissue in the biological environment. It could even inhibit the activity of germs in the biological environment, which would make clinical applications less infectious [4–6].

However, it is very difficult to produce nanophase titania ceramics, because of the aggregation of crystals during the sintering process for ceramics preparation. A number of additives have been employed to inhibit crystal growth during this process, such as MgO [7]. In our previous studies [8,9], hydroxyapatite (HA) was successfully used as an additive to inhibit the crystal growth of titania for biomedical applications. The HA additive not only inhibits the crystal growth of titania, thereby making the ceramics bioactive and biomechanically compatible, but also improves the bioactivity of the ceramic by the bioactivity of the additive itself.

Barium titanate ($BaTiO_3$) has also been reported to be a potential bioactive material. It could induce apatite formation in simulated body fluid [10,11], and it could enhance bone formation in the biological environment because of its piezoelectric properties [12,13]. In order to obtain bioactive nono-titania ceramics with higher bioactivity and better piezoelectric properties, barium titania was employed in this study to act as a grain growth inhibitor in the preparation of a new type of nano-titania ceramic. The effects of

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the $BaTiO_3$ additive content on the particle size, the bioactivity and the biomechanical compatibility of bioactive nano-titania ceramics are reported in this paper.

2. Materials and methods

2.1. Materials preparation

The nano-titania powder used in this study was synthesized by the sulfate process in Zhejiang Mingri Nano-powder Co, and had an average grain size of 10 nm. For details of the method, see Ref. [14]. Its X-ray diffraction (XRD) pattern showed the powder to be in anatase phase. Nano-$BaTiO_3$ powder supplied by Hebei Kingway Chemical Industry, with an average grain size less than 100 nm, was used as a grain growth inhibitor.

The nano-titania powders were doped with different amounts of $BaTiO_3$ (Table 1). The mixed powders were then milled in ethanol by an ultrasonic generator for 10–20 min. After the powders were dried at room temperature, the mixtures were subjected to cold isostatic pressing at 180 MPa for 30 min for casting and then sintered at 1000 °C for 2 h to obtain nanocomposite ceramics in a normal muffle furnace. The nanocomposite ceramics were cut into ϕ 10 × 2 mm for scanning electron microscopy (SEM; JSW-5900LV-JEOL) and thin-film XRD (TF-XRD; X'pert Pro MPD, Philips) analysis. Moreover, pure TiO_2 ceramic was prepared as control.

All of the $TiO_2/BaTiO_3$ composite ceramics (TB01, TB05, TB10, TB15 and TB20) were polarized at a voltage of 2500 V for 30 min to produce polarized $TiO_2/BaTiO_3$ composite ceramics (PTB01, PTB05, PTB10, PTB15 and PTB20).

2.2. Mechanical tests

In accordance with the GB/T 4740-1999 standard compressive resistance test, each ceramic was cut into ϕ 10 × 20 mm samples. Before the mechanical tests, all the samples were ground with a No. 400 whetstone and cleaned in distilled water, then dried in an oven at 60 °C for 24 h. The compressive test was carried out at 1 mm min^{-1} on a multi-mechanical testing machine (SLP-5 Biomechanical Testing Machine, Chaoyang Instrument, Changchun, China). The elastic moduli of the ceramics were calculated from the compressive test curves.

2.3. Fast calcification solution soaking

The TiO_2, TB01, TB20 and PTB20 ceramics were cut into plates of ϕ 10 × 2 mm to study the formation of apatite. The four ceramics were soaked in 40 ml of fast calcification solution (FCS) for 5 or 10 days at 36.5 °C. FCS was prepared according to Ref. [15], with the following ionic concentrations: Na^+ (137 mM), K^+ (3.71 mM), Ca^{2+} (3.10 mM), Cl^- (145 mM) and $HPO_4{}^{2-}$ (1.86 mM). After the plates were taken out from the FCS, they were analyzed by SEM and TF-XRD.

2.4. Cell culture

TB and PTB series ceramic samples, of size ϕ 10 × 2 mm, were put into 24 multi-well plates for cell culture to test the biocompatibility of the materials according to ISO10993-5:1999. During the cell culture, pressure was exerted on the PTB series ceramic specimens to generate piezoelectric. Cells from the rat osteoblast-like cell line Ros17/28 were suspended, at a density of 5×10^3 cells ml^{-1}, in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% fetal bovine serum. Then 1 ml of the suspension was added to each well containing the substrates, and then placed under a standard cell culture conditions (i.e. 37 °C in a 5% CO_2 environment) for 2, 4 and 6 days. The cell medium was changed every 2 days. In this study, pure TiO_2 ceramic plates, ϕ 10 × 2 mm in size, were used as the control.

2.4.1. MTT assay

After 2, 4 and 6 days, 0.2 ml of 3-(4,5-dimethylthiazol-2-yl)-2,5-dipheyltetrazolium bromide (MTT) solution (5 mg ml^{-1} in DMEM) was added to each well. After the cells were cultured for a further 4 h, the plates were washed

Table 1
Nano-titania ceramics doped with different $BaTiO_3$ additive contents.

	Specimen							
	Pure TiO_2	TB01	TB05	TB10	TB15	TB20	Human bone[a]	Ti alloy[b]
TiO_2 content (vol.%)	100	99	95	90	85	80	–	–
$BaTiO_3$ content (vol.%)	0	1	5	10	15	20	–	–
Average grain size (nm)	103 ± 9.4	62.3 ± 6.5	68.2 ± 5.8	18.1 ± 2.6	41.9 ± 5.1	45.3 ± 4.4	–	–
Average particle size (nm)	319.2 ± 29.7	187.0 ± 22.4	222.1 ± 26.8	240.0 ± 22.9	399.4 ± 41.4	579.2 ± 55.7	–	–
Average compressive strength (MPa)	126.3 ± 11.1	178.1 ± 12.4	157.6 ± 10.2	132.2 ± 11.5	124.4 ± 9.8	89.0 ± 6.7	110–170	–
Average elastic modulus (GPa)	6.2 ± 0.5	10.6 ± 0.6	9.6 ± 0.4	9.1 ± 0.7	8.9 ± 0.5	7.1 ± 0.4	0.09–18.6	110

The grain size of TB10 is the smallest of all the ceramics, and with increasing $BaTiO_3$, the crystal particle size of titania composite ceramics also increased. However, the average compressive strength and average elastic modulus decreased with increasing $BaTiO_3$ additive contents.

[a] Data from Ref. [16].

[b] Data from Ref. [17].