



Improving the hardness of titanium via $\text{CaTiO}_3\text{:Er}^{3+}$ films for biomedical applications

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ABSTRACT

This study reports the synthesis of CaTiO_3 and $\text{CaTiO}_3\text{:Er}^{3+}$ films by hydrothermal treatment at 200 °C, producing homogeneous coatings for enhancing the surface hardness of Ti substrates. The crystal structure and morphologies of the CaTiO_3 films and $\text{CaTiO}_3\text{:Er}^{3+}$ films were investigated using XRD and SEM analyses. The deposition of the CaTiO_3 and $\text{CaTiO}_3\text{:Er}^{3+}$ films, led to a substantial enhancement in hardness. The hardness values of CaTiO_3 and $\text{CaTiO}_3\text{:Er}^{3+}$ films on Ti were measured as 2.95 GPa and 4.28 GPa, respectively, considerably exceeding that of the bare Ti substrate (2.12 GPa). In vitro cytocompatibility of CaTiO_3 and $\text{CaTiO}_3\text{:Er}^{3+}$ films were performed using BHK cells and the cell attachment on the films was reported.

1. Introduction

Titanium possesses for use in biomedical applications including low density, high ductility, and biocompatibility [1,2]. However, their mechanical performance, corrosion resistance, and biocompatibility further improved for the use in long term implants [3–5]. A previous study reported that TiO_2 nanotubes coatings could improve the corrosion resistance, and biocompatibility of the Ti substrates [6]. However, the surface hardness of the TiO_2 nanotubule coating is low which is limited for their long-term use of implants. Jingling Li et al. [7] reported that TiN-embedded TiO_2 nanotubes composite coating could enhance the mechanical properties, corrosion, tribocorrosion resistance, and antibacterial activity of the materials.

To date, most research on biomedical materials, particularly in bone implant applications, has focused primarily on biocompatibility, while systematic studies of mechanical properties remain limited. Calcium titanate (CaTiO_3), a perovskite-type oxide has attracted significant attention due to its chemical stability [8], bioactivity, and ability to promote apatite formation on implant surfaces [5,6,9]. Furthermore, the mechanical properties of CaTiO_3 can be modified by rare-earth doping. In particular, substitution of Ca^{2+} by Er^{3+} ions may induce lattice distortion and strengthen the material through solid-solution

strengthening.

Previous investigations have employed the Pechini method [6], plasma spraying [9], and other techniques to deposit CaTiO_3 and Er^{3+} -doped CaTiO_3 multilayer coatings with controlled film thickness for enhanced surface hardness. Additionally, hardness improvement of CaTiO_3 films through surface crystal structure modification has been reported [10]. However, the mechanical performance of these materials critically affects implant longevity and warrants further comprehensive investigation.

This study proposes a method for enhancing surface hardness of titanium through hydrothermal deposition of Er^{3+} -doped CaTiO_3 coatings with uniform cubic structure at 200 °C. The morphology and structure of CaTiO_3 and $\text{CaTiO}_3\text{:Er}^{3+}$ films were characterized by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). Hardness of the films were measured under 1 kgf load, and the biocompatibility of the films were evaluated using confocal laser scanning microscopy (CLSM).

2. Experimental procedure

CaTiO_3 and $\text{CaTiO}_3\text{:Er}^{3+}$ films were coated on the anodized Ti substrates using the hydrothermal method. Previously, TiO_2 nanotubes

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template created on the Ti substrates by anodizing using NH_4F (Merck, 99.9%), ethylene glycol (Merck, 99.9%) and water [11]. Calcium hydroxide [$\text{Ca}(\text{OH})_2$, Merck, 99.9%], sodium hydroxide (NaOH, Merck, $\geq 97.0\%$), TiO_2 nanotubes template, and erbium chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, Merck, 99.9%) were used as starting materials. The detailed coatings of CaTiO_3 and $\text{CaTiO}_3:\text{Er}^{3+}$ films were described in our previous publications [11,12].

The crystallographic properties of the obtained samples were investigated using X-ray powder diffraction (XRD, Siemens D500). Field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) was employed to investigate the morphology of samples. The bonding strength of the CaTiO_3 and $\text{CaTiO}_3:\text{Er}^{3+}$ films coating to the titanium substrate was measured using the TABER Multi-Finger Scratch/Mar-Tester-Model710, employing a tungsten carbide scratch tip with a diameter of 0.25 mm and a maximum load of 6 N. Microhardness measurement was performed on the sample surface using a Future Tech FM-100 Vickers microhardness tester. The Vickers microhardness (HV) of the coatings was evaluated using a microhardness tester with a square-based diamond pyramid indenter (face angle of 136°). A load of $F = 0.01$ kgf was applied on the sample surface. The lengths of the two diagonals (d_1 and d_2) of the indentation were measured under an optical microscope, and the average diagonal $d = (d_1 + d_2)/2$ was used. The HV values were calculated using the standard formula:

$$HV = 1.8544 \times \frac{F}{d^2} \quad (1)$$

where F is the applied load in kilogram-force (kgf) and d is the mean diagonal length.

In vitro cell attachment was evaluated using baby hamster kidney (BHK) cell cultures and cellular responses were characterized by a confocal laser scanning microscopy (CLSM, FV3000RS, Olympus).

3. Results and discussion

Fig. 1 (A) showed the XRD diffraction patterns of the Ti substrate, the CaTiO_3 films, and the $\text{CaTiO}_3:\text{Er}^{3+}$ films. As shown in Fig. 1.(a), all of the films displayed diffraction peaks at 27.4° , 33.1° , 39.4° , 41.2° , 47.03° , 59.1° , and 69.8° correspond to the (111), (121), (031), (220), (040), (042), and (242) planes of the characteristic orthorhombic phase of the CaTiO_3 (JCPDS 86-1393) with additional peak of Ti substrates. The XRD patterns of the $\text{CaTiO}_3:\text{Er}^{3+}$ films also showed the same diffraction peaks of the pure perovskite CaTiO_3 structure with no significant impurity phases were detected except for peaks from the Ti substrates. These results demonstrated that CaTiO_3 and $\text{CaTiO}_3:\text{Er}^{3+}$ films were successfully coated on the Ti substrates.

Figs. 1 (B)-(D) showed the microstructure of the Ti substrate, the CaTiO_3 films and the $\text{CaTiO}_3:\text{Er}^{3+}$ films. As shown in Figs. 1(B)-(D), the distinct structural changes can be clearly observed on the Ti substrates, the CaTiO_3 films and the $\text{CaTiO}_3:\text{Er}^{3+}$ films. As shown in Fig. 1 (C), the CaTiO_3 films exhibited a uniform columnar structure with diameters of approximately 100 nm. The Er^{3+} -doped CaTiO_3 films (Fig. 1D) showed cubic structure with dimension ranging from 2 to 5 μm and remarkable uniformity. EDS analysis Figs. 1 (E)-(F) and Table 1 showed the presence of Ca, Ti, O, and Er^{3+} in the CaTiO_3 films and $\text{CaTiO}_3:\text{Er}^{3+}$ films. The atomic composition of Er^{3+} was 1.8% which suggested that the Er^{3+} ion was successfully doped into the CaTiO_3 films.

Table 1

EDS analyses for the concentration element of CaTiO_3 , and $\text{CaTiO}_3:\text{Er}^{3+}$ films.

Elements	O	Ca	Ti	Er
CaTiO_3 films	47.8%	14.4%	37.8%	0%
$\text{CaTiO}_3:\text{Er}^{3+}$ films	50.0%	24.1%	24.0%	1.8%

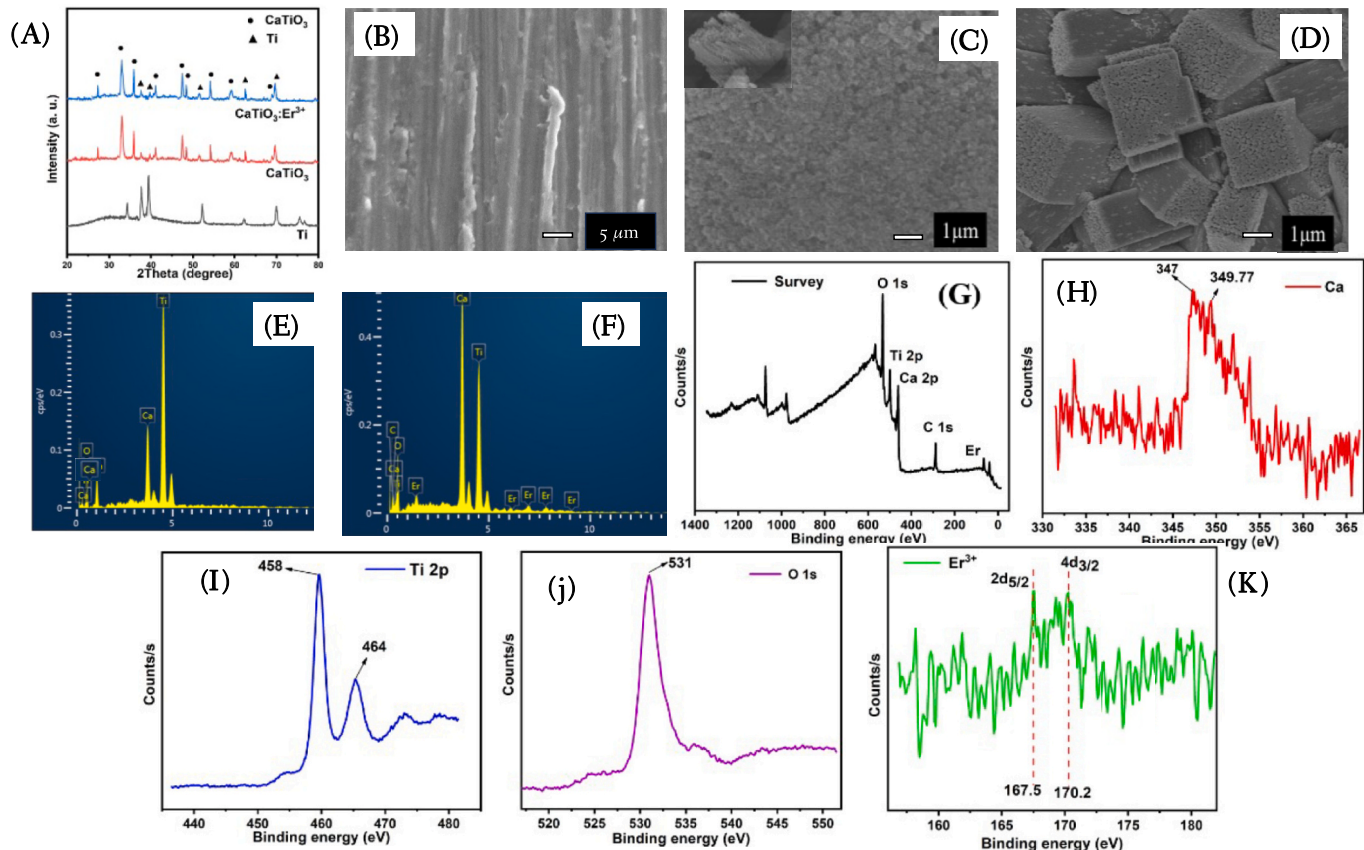


Fig. 1. (A) XRD patterns of Ti substrates, CaTiO_3 , and $\text{CaTiO}_3:\text{Er}^{3+}$ films; FE-SEM images of samples: (B) Ti substrates, (C) CaTiO_3 films, (D) $\text{CaTiO}_3:\text{Er}^{3+}$ films; (E) EDS of CaTiO_3 films, (F) EDS of $\text{CaTiO}_3:\text{Er}^{3+}$ films and (G-K) XPS of $\text{CaTiO}_3:\text{Er}^{3+}$ films.

To elucidate the exact role of the dopant on the mechanical properties, the chemical states and lattice incorporation of Er^{3+} were investigated using high-resolution XPS, Fig. 1(G)–(K). Fig. 1(G) displayed the XPS survey spectrum of CaTiO_3 films for identification the surface elements of Ti, O, and Ca. The C 1 s peak at 285.5 eV corresponding to adventitious carbon was used to calibrate the peak positions of all elements. Fig. 1(H) showed the high-resolution XPS spectrum of the chemical state of Ca^{2+} located at approximately 346.21 and 349.77 eV. These peaks corresponded to Ca 2p_{3/2} and Ca 2p_{1/2}. These measurements were consistent with the previously works for the CaTiO_3 films, confirming the existence of the CaTiO_3 [13]. The presence of Ti^{4+} in CaTiO_3 was confirmed by two main peaks in the Ti XPS spectrum, located at 458.09 and 463.8 eV which correspond to Ti 2p_{3/2} and Ti 2p_{1/2}, Fig. 1(I). The peak at 529.26 eV in Fig. 1(J) could be fitted to the O 1 s configuration, while the minor peak at 531.1 eV could be attributed to chemisorption of oxygen caused by hydroxyl (OH) groups on the surface. As shown in Fig. 1(K), the presence of erbium ions in the Er^{3+} state was successfully identified by the Er 4d_{5/2} peak at 167.5 eV and the Er 4d_{3/2} peak at 170.2 eV. Interestingly, the binding energy of Er 4d_{5/2} (167.5 eV) was lower than the values commonly assigned to pure bulk Er_2O_3 (~ 168.0–168.5 eV). This noticeable chemical shift provides strong evidence that Er^{3+} ions are effectively incorporated into the CaTiO_3 which indicates that Er^{3+} ions successfully substituting at the Ca^{2+} sites rather than forming a segregated oxide phase. The substantial ionic radius mismatch between the substituting Er^{3+} ($r \approx 0.89 \text{ \AA}$) and the host Ca^{2+} ($r \approx 1.12 \text{ \AA}$) caused the localized lattice distortion and strain fields. These fields act as effective obstacles against dislocation glide, thereby it could be expected for enhancing the film hardness.

The average Vickers hardness values of the CaTiO_3 films and the $\text{CaTiO}_3:\text{Er}^{3+}$ films were presented in Fig. 2 and Table 2. The deposition of the CaTiO_3 films and $\text{CaTiO}_3:\text{Er}^{3+}$ films on the Ti substrates resulted in a significant increase in the hardness of Ti. The highest value of 4.28 GPa was achieved for the $\text{CaTiO}_3:\text{Er}^{3+}$ films, while the lowest value of 2.12 GPa was obtained from the Ti substrates. The CaTiO_3 films showed the hardness value of 2.95 GPa. The enhanced hardness of CaTiO_3 and $\text{CaTiO}_3:\text{Er}^{3+}$ films compared to that of the Ti substrates originates from their crystalline structure and chemical bonding. The CaTiO_3 films exhibited a rigid perovskite structure (ABO_3) with high symmetry and

Table 2Vickers hardness (HV) of the Ti substrates, CaTiO_3 films and $\text{CaTiO}_3:\text{Er}^{3+}$ films.

Sample	Applied load, F (kgf)	d ₁ (μm)	d ₂ (μm)	Average d (μm)	Vickers hardness (GPa)
Ti substrates	0.01	9.06	9.45	9.255	2.12
CaTiO_3 films	0.01	8.12	7.57	7.845	2.95
$\text{CaTiO}_3:\text{Er}^{3+}$ films	0.01	6.47	6.56	6.515	4.28

minimal deformation, contrasting with the hexagonal close-packed (HCP) Ti structure where metallic bonding facilitates atomic plane slippage [14]. Notably, the $\text{CaTiO}_3:\text{Er}^{3+}$ films demonstrated superior hardness to undoped CaTiO_3 films. This enhancement resulted from Er^{3+} ions ($r \approx 0.89 \text{ \AA}$) preferentially substituting Ca^{2+} sites ($r \approx 1.12 \text{ \AA}$) at A-positions due to their intermediate ionic radius [15,16]. The ionic radius mismatch induces local lattice distortion and elastic strain fields, impeding dislocation motion and strengthening the material through solid solution hardening.

Fig. 2 (D)–(E) illustrated the scratch test to assess the bonding strength of the CaTiO_3 , and the $\text{CaTiO}_3:\text{Er}^{3+}$ films on the Ti substrates. Typically, the critical scratch force for perovskite coatings falls within the range of 1–10 N, depending on the synthesis method and conditions. The critical loads for the CaTiO_3 and $\text{CaTiO}_3:\text{Er}^{3+}$ films ranged from approximately 4.85 to 4.97 N. These results suggested that the films has relatively good scratch resistance.

For biomedical applications, cytocompatibility assessment is an important factor. The Ti substrates, the CaTiO_3 films, and the $\text{CaTiO}_3:\text{Er}^{3+}$ films were subjected to baby hamster kidney (BHK) cell culture for 48 h, as presented in Fig. 3. All the films and Ti substrates demonstrated good cell adhesion capability. However, it can be observed that cells on the $\text{CaTiO}_3:\text{Er}^{3+}$ films displayed the highest cell density compared to that of the CaTiO_3 and the Ti substrates. These results confirmed that the CaTiO_3 films, and the $\text{CaTiO}_3:\text{Er}^{3+}$ films were cytocompatibility coatings.

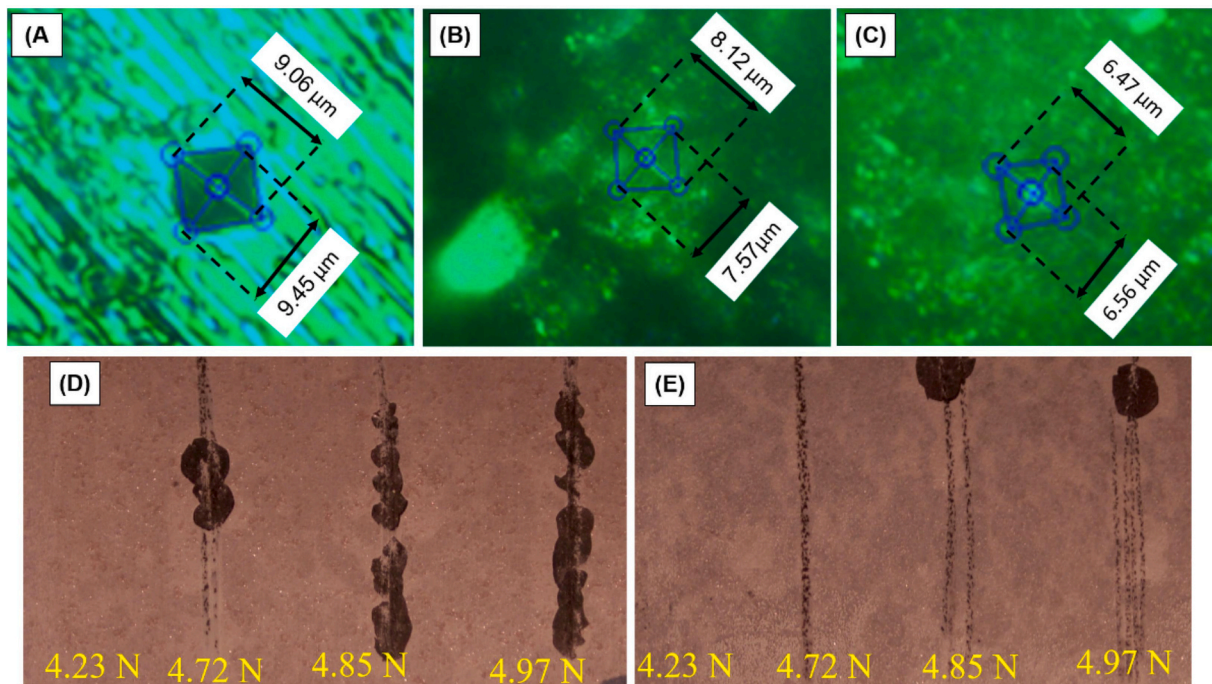


Fig. 2. Vickers hardness image of (A) Ti substrates, (B) CaTiO_3 films, (C) $\text{CaTiO}_3:\text{Er}^{3+}$ films, (D) scratch of CaTiO_3 films and (E) $\text{CaTiO}_3:\text{Er}^{3+}$ films.

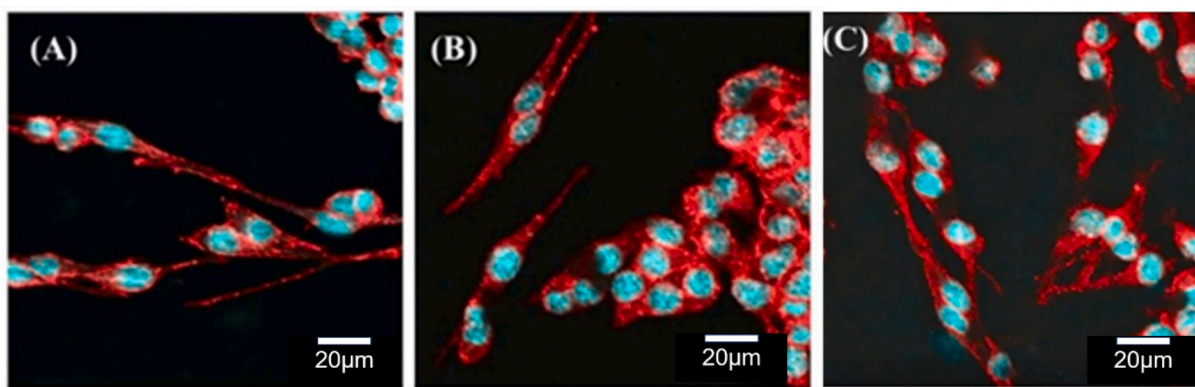


Fig. 3. CLSM images of the cell attachment with blue (DAPI for nuclei), and red (phalloidin 555 for actin) on (A) Ti substrates, (B) CaTiO_3 films, and (C) $\text{CaTiO}_3:\text{Er}^{3+}$ films. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

CaTiO_3 and $\text{CaTiO}_3:\text{Er}^{3+}$ films were successfully coated onto the Ti substrates via a hydrothermal route to enhance the surface hardness properties of the Ti substrates. The enhancement in surface hardness was attributed to the presence of perovskite structure (ABO_3) and preferentially substituting Ca^{2+} by Er^{3+} ion in CaTiO_3 and $\text{CaTiO}_3:\text{Er}^{3+}$ films, respectively. The present study also demonstrated that the films exhibited good cytocompatibility compared to that of the bare Ti substrates. These findings demonstrate the valuable use of the CaTiO_3 and the $\text{CaTiO}_3:\text{Er}^{3+}$ coatings in biomedical applications.

CRediT authorship contribution statement

Nguyen Thi Thanh Tuyen: Writing – original draft, Validation, Data curation. **Tran Thi Trang:** Visualization, Formal analysis, Conceptualization. **Le Thi Tam:** Methodology, Investigation, Formal analysis. **Hoang Van Vuong:** Validation, Resources, Methodology. **Nguyen Van Toan:** Visualization, Resources, Formal analysis. **Nguyen Ngoc Thang:** Resources, Methodology, Conceptualization. **Le Thi Bang:** Validation, Investigation, Data curation. **Ta Quoc Tuan:** Validation, Resources, Methodology. **Cao Xuan Thang:** Visualization, Software, Resources. **Vuong-Hung Pham:** Writing – review & editing, Supervision, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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