Effect of TiO_y Stoichiometry on the Structure of TiO_y/HAP Nanocomposite

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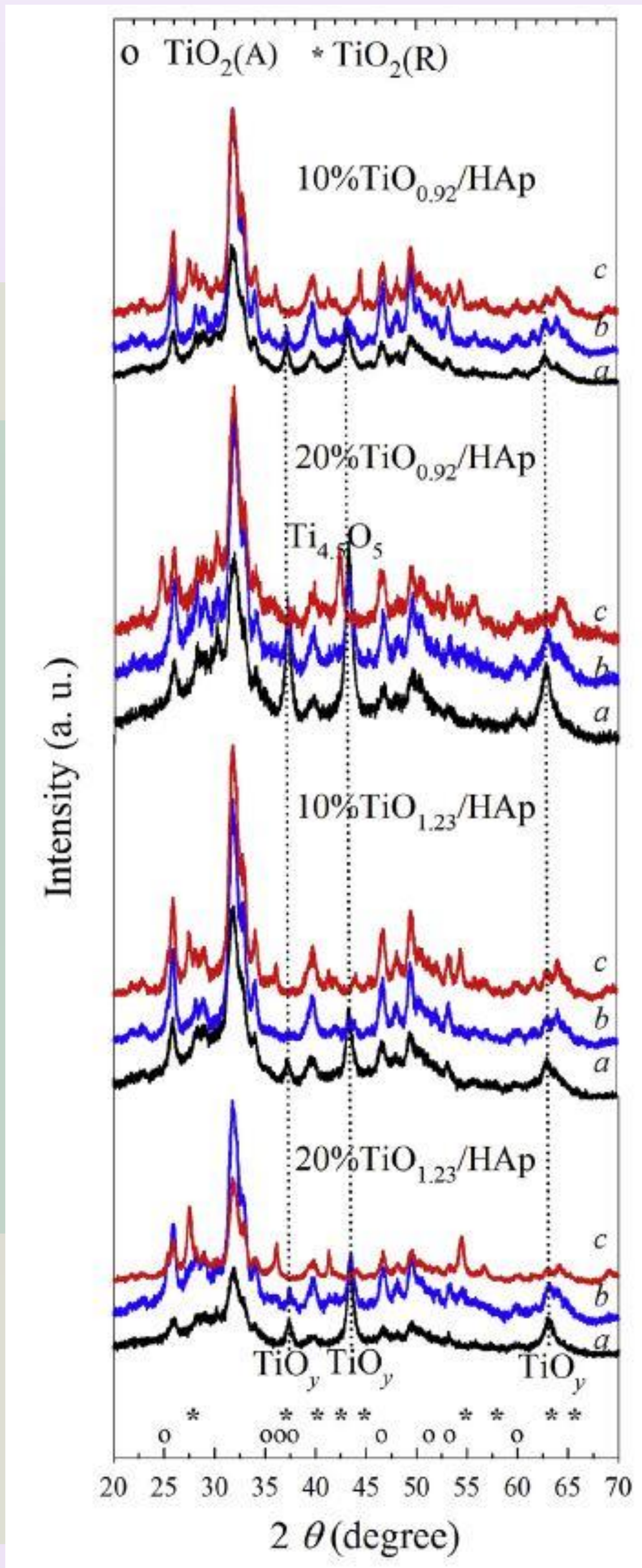
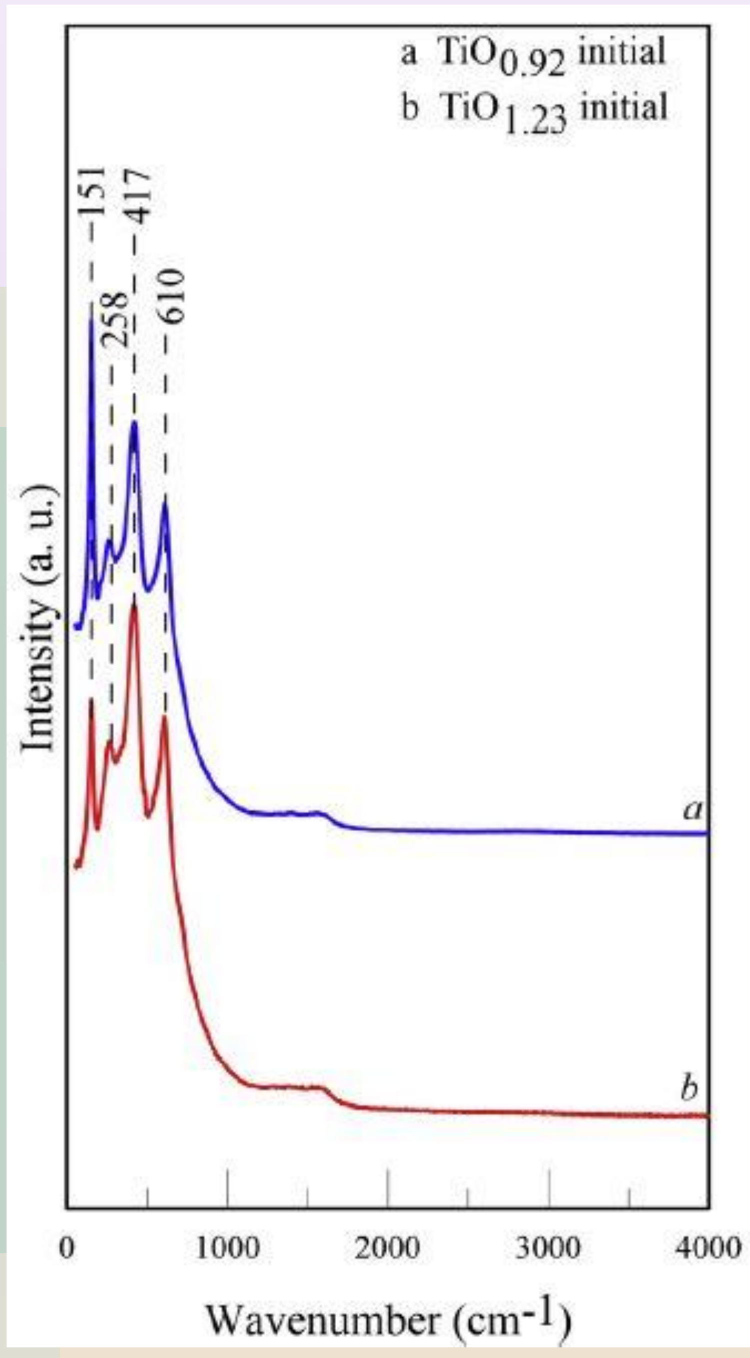
Composite materials based on hydroxyapatite (HAP) are of much interest for biology and medicine owing to their bioactivity. The advanced strength properties of HAP can be achieved by its reinforcement with dispersed titanium and titanium oxide particles. This makes it possible to combine biocompatibility with high mechanical strength and fracture toughness.

Results

The XRD patterns of TiO_y/HAp nanocomposites at room temperature (a), after annealing at 400 (b) and 600 °C (c) (black, blue and red line respectively).

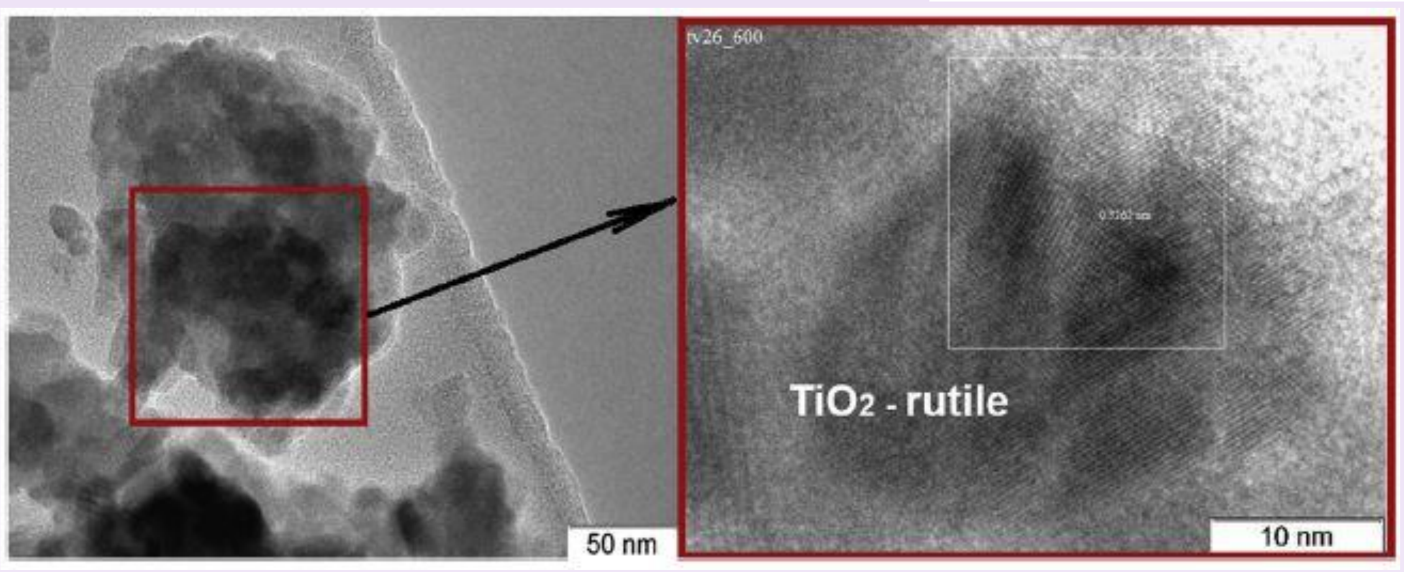
Annealing of nanocomposites gives rise to forming of different phases depending on the stoichiometry of additives the composition of the initial mixture: ordered $Ti_{4.5}O_5$, TiO_2 (anatase), TiO_2 (rutile).





The Raman spectra of TiO0.92 (a) and TiO1.23 (b) nanopowders after high-energy milling for 8 h.

- The dependence on the stoichiometry of additives manifests itself in the presence of a phase with variable titanium valence ($Ti_{4.5}O_5$) and anatase in $TiO_{0.92}$/HAp and of TiO_2 (anatase and rutile)
- in $TiO_{1.23}$/HAp after annealing, as well as in the possibility of partial substitution of titanium ion of different valence (Ti^{3+} and Ti^{4+}) for Ca^{2+} positions.
- This causes different positions of the bands related to Ti-O vibrations and different distortion of positional symmetry of PO^{3-}_4 ion resulting in different broadening of its vibration bands.



HRTEM images of the TiO_2 nanoparticles formed during annealing of nanocomposites TiO_y/HAp at 600 °C.

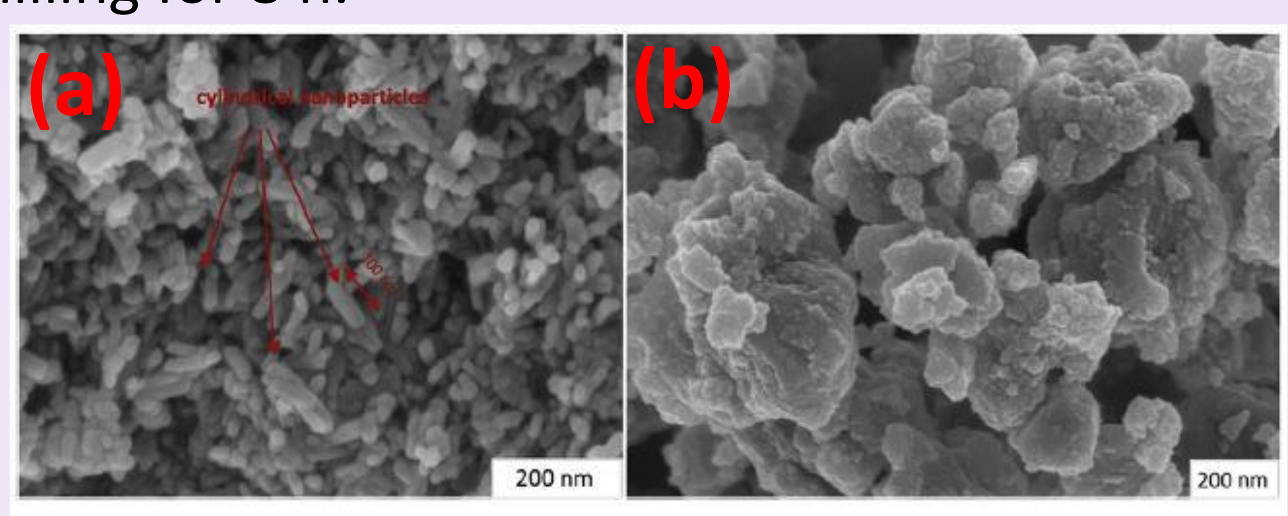


Fig. 4. SEM images: (a) cylinder nanoparticles in initial HAp; (b) $TiO_{0.92}$/HAp powders after high energy milling.

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Conclusion

1. Initial HAp and HAp after milling during 8 h contained cylinder nanoparticles, which were not observed in the mixes of TiO_y/HAp.

2. The shift and value of the relative intensity of the band in the region of 144-151 cm^{-1} in the Raman spectrum indicated changes in the relative concentration of vacancies and bond length in the TieO system.

3. In the process of annealing of TiO_y/HAp nanocomposites from room temperature to 600 °C, new phases $Ti_{4.5}O_5$ and TiO_2 were formed (depending on the stoichiometry of additives). At the first stage (400 °C), the surface groups $[Ti(OH)_2]^{2+}$ and $[TiHPO_4]^{2+}$ were formed, and partial cation heterovalent substitution of Ti^{3+} and Ti^{4+} for Ca^{2+} took place, which was accompanied by vacancy formation and anion substitution. Terminal carbonyls were formed. As the annealing temperature raised to 600 °C, the surface groups disappeared.