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Effect of Zn^{2+} , Fe^{3+} and Cr^{3+} addition to hydroxyapatite for its application as an active constituent of sunscreens

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Abstract. Biocompatible phosphate materials are used in different applications like bone and dental implants, drug delivery systems and others, but could also be applied in inorganic sunscreens. Using sunscreens is extremely necessary, because long time exposure to sun can cause skin cancer. In this work chemical precipitation method has been used to produce hydroxyapatite. Cr^{3+} , Zn^{2+} and Fe^{3+} doped samples were characterized using powder X-Ray Diffraction (XRD) and Optical Absorption techniques. X-ray diffraction measurements confirmed the materials were in the expected crystalline structures. The crystallite size as measured from the X-ray pattern was 23–27 nm (± 1). The absorption spectra in the ultraviolet and visible ranges indicate that appropriately doped and sized hydroxyapatite particles may have potential applications as active constituents of sunscreens.

1. Introduction

The sun emits a wide spectrum of electromagnetic waves and ultraviolet light (UV) is the most aggressive to human tissues, mainly the skin. Large amounts of UVB and UVC are absorbed by earth's atmosphere. Solar UV radiation that reaches the earth as well as our skin, is composed by 5–10% energetic UVB (290–320 nm) and 90–95% UVA (320–400 nm) which is less energetic, but penetrates deeper the skin due to its longer wavelength [1]. Daily use of sunscreens became imperative in certain geographical regions to prevent damages caused to skin. The number of new cases of skin cancer is growing continually in the world, especially in Brazil; where this number is around 120 thousand a year [2]. Sunscreens might be capable to absorb or to reflect the incident UV radiation protecting the individuals [3].

The sunscreens are divided into two major classes: i- the so-called chemical filters, made of substances capable of absorbing solar UV converting it to less energetic photons that are emitted; and ii- the physical filters, composed by physical barriers, on the skin, reflecting radiation. The well known physical filters are zinc oxide and titanium dioxide [4].

In the case of long-term and frequent usage, particular attention must be paid to efficiency and safety. Many organic sunscreens penetrate into the skin causing photoallergies, phototoxic reactions and skin irritations [5]. Therefore, there is an urgent need for the development of a safer sunscreen system. This can be achieved by formulations with little penetration into the skin and using biocompatible materials. For these very reasons inorganic sunscreens represent one of the best means to protect the skin and are recommended for children and people with sensitive skins [6]. Titanium

dioxide and zinc oxide are popular inorganic sunscreen agents. Their high refractive indices, however, can make the skin look unnaturally white when incorporated into the products. Additionally, their high photocatalytic activity facilitates the generation of reactive oxygen species, which can oxidize and degrade other ingredients in the formulation, raising safety concerns [7-9].

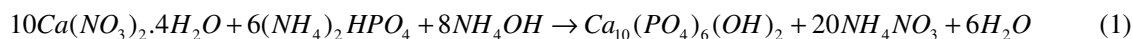
For solving problems described with titanium dioxide and zinc oxide, it is interesting to develop calcium phosphate that absorbs in the ultraviolet region. Calcium phosphates were already investigated and showed many possible applications in medicine [10,11], and, due to its chemical similarity with the mineral phase of the bones and teeth, they showed no toxicity [12-15]. Hydroxyapatite, $(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)$ actually used for highly stable and inert bone and teeth transplants, is also a promising candidate for advanced sunscreens. Furthermore, its UV absorption limit can be tuned to absorb in the desired range from UVB (290–320 nm) to UVA (320–400 nm) by simply introducing a doping.

Inorganic sunscreens must be constituted preferably with particles smaller than 400 nm, avoiding Rayleigh scattering, because the intensity of the scattering depends on the wavelength and it is proportional to the particle radius. Some sunscreens versions involve particles of 70–200 nm [2]. The objective of this study is to develop nanocrystalline HAP powders with appropriate absorption in the UV region, suitable as active components of inorganic sunscreens.

2. Experimental procedure

Hydroxyapatite (HAP) was produced using a precipitation route of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with $(\text{NH}_4)_2\text{HPO}_4$ [14,15].

The HAP reaction formation is expressed as follows:



The samples were prepared mixing a solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to a $(\text{NH}_4)_2\text{HPO}_4$ solution at a rate of 1.5 ml/min, keeping the pH constant at 10.4. The pH was adjusted during the mixing using a solution of NH_4OH . The mixture was then kept at room temperature for 50 hours. This period is called “maturation time”. The resulting suspension was filtered, repeatedly washed with distilled water and dried and calcined at 500 °C for 1 hour. At the end of the calcinations a ceramic in powder form is obtained, constituted by particles agglomerated due to weak bonds acting between them. After a light grinding in agate mortar these bonds are broken and we have hydroxyapatite in the form of a fine powder.

For the Cr^{3+} , Zn^{2+} and Fe^{3+} -doped samples, a 0.01 M solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively, were added to $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution.

The precipitated HAP powders was chemically and physically characterized using powder X-ray diffraction (XRD) and UV-vis diffuse reflectance. For characterization of the samples, the powders were drizzled and selected those between 75mm/μm and 150 mm/μm.

Powder XRD measurements were performed at room temperature in a Rigaku DMAX2000 diffractometer using $\text{CuK}\alpha$ radiation at 40 kV/40 mA with a spinning sample holder and a monochromator detector.

The UV-vis diffuse reflectance spectrum was measured on a UV-vis recording spectrophotometer (UV-2401, Shimadzu). Barium sulphate was used as reference to calibrate the spectrophotometer.

3. Results and discussions

X-ray powder diffraction (XRD) technique was used to study the effect of dopants on the phase identification of the samples. The typical XRD patterns of the pure and Zn^{2+} , Fe^{3+} , Cr^{3+} -doped HAP samples, which perfectly match with the JCPDS pattern 9-432 for HAP, are presented in figure 1. The incorporation of Cr^{3+} and Fe^{3+} into the material apparently leads to the formation of less crystalline HAP. This effect seems natural as the dopants assumed to substitute at Ca^{2+} sites (ionic radius 0.99 Å) have larger charge and smaller ionic radius (Cr^{3+} 0.63 Å, Fe^{3+} 0.64 Å). Several ions, usually with an ionic radius smaller than that of Ca^{2+} are known to inhibit the formation of HAP [17].

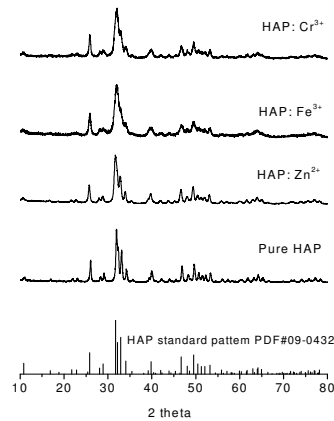


Figure 1. X-ray diffraction pattern of the pure HAP and Cr^{3+} , Fe^{3+} and Zn^{2+} -doped HAP compared to the HAP standard pattern PDF # 9-432.

Contradictory data are reported about zinc (ionic radius $0.74 \text{ \AA}$) incorporation into HAP structure. According to some authors [18-20] Zn^{2+} -doped HAP can be obtained without producing significant alterations in the structure of HAP. On the other hand, Le Geros et al [21] reported that incorporation of reduced amounts of Zn^{2+} into HAP structure induces an evident reduction of the degree of crystallinity of the HAP phase. In this work, HAP- Zn^{2+} exhibited high crystalline peak at about 33.11° ; almost identical patterns were recorded for pure and doped powders. The relatively broadening of the XRD peaks for Cr^{3+} , Fe^{3+} -doped HAP indicates that the sizes of the crystallite grains of those materials are smaller than the pure HAP and Zn^{2+} -doped HAP. Through Scherrer's equation, within the JADE Rigaku computer code, the medium crystallite sizes were estimated. The results are shown in table 1. Note that the effect of Zn^{2+} on the growth of HAP particles is more remarkable than those of Cr^{3+} and Fe^{3+} , although the reason for this difference remains unclear at the present. For Harry [22] the particle size of a powder for application as sunscreen should obey, in beginning, the size of the passage of a sieve 200 mesh. At the present work, the low values of crystallite sizes ($<30 \text{ nm}$) indicates the formation of nanoparticles.

Table 1. Medium size crystallite obtained via XRD measurements using Scherrer's equation to HAP prepared with different dopant at room temperature.

HAP	Crystallite size $\pm 1 \text{ (nm)}$
Pure	27
Zn^{2+}	25
Fe^{3+}	23
Cr^{3+}	23

An inorganic sunscreen which functions well when absorbing or reflecting the UV light, but, tends to be opaque and white on the skin is unacceptable for cosmetic use. The higher refractive index of titanium dioxide compared with zinc oxide (2.6 vs 1.9) [23] explains its whiter appearance. The still lower refractive index of HAP (around 1.6 [24, 25]) leads to a transparent appearance and a higher cosmetic acceptability.

For a composition to be an efficient sunscreen two main characteristics are necessary: (I) absorption in the UV region (II) to dissipate the energy absorbed with the minimum impact to skin, impeding,

therefore, the formation of reactive species. The particle size is of great importance for the effectiveness of the sunscreen, nanoparticles improve the absorption in the UV region and increase the absorption intensity [26]. Production of doped HAP in nano scale has been developed, exploring its absorption capability and its intense scattering of the solar radiation in the UV region. To evaluate the photoprotection action of that material the technique of diffuse reflectance was used.

For the sake of comparison diffuse reflectance measurements were performed in titanium dioxide (TiO_2) commonly used in sunscreens formulations in cosmetics industry. As can be seen in figure 2, TiO_2 showed one large absorption around 268-419 nm.

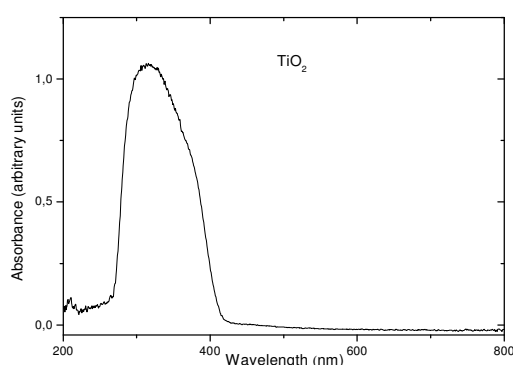


Figure 2. UV-Vis absorption spectrum of TiO_2 .

Even if they have a good performance in optical absorption, TiO_2 and ZnO catalyze the formation of superoxide and hydroxyl radicals which can initiate oxidations, putting at risk people's health. TiO_2 is a semiconductor that can absorb light and, under certain conditions, generates free radicals. The band gap of 3 eV for TiO_2 is a measure of the minimum energy required to promote an electron from its valence band to its conduction band [27]. A compound with this kind of band gap can be excited by radiation at wavelengths below ~ 380 nm. Thus, TiO_2 may be susceptible to excitation by UVB and UVA in sunlight. Photoexcitation of TiO_2 could promote a single electron from the valence band to the conduction band, leaving a positively charged space (a hole) behind. Usually, the electron recombines with the hole, but sometimes the hole migrates to the particle surface, where it can react with absorbed species. In an aqueous environment it can react with water or hydroxyl ions, forming hydroxyl radicals [28]. Such processes are well known for aqueous preparations of TiO_2 , exposed to either artificial UV light or natural sunlight. In this capacity, the photocatalytic potential of TiO_2 has been used experimentally to degrade suspensions of organic materials and purify drinking water.

In literature it was found that zinc oxide blocks mostly UVA radiation and has an attenuation maximum around 380 nm, but this can vary slightly with particle size [21, 29]. Its photocatalytic mechanism has been proven to be similar to that of TiO_2 [30].

In 1993, FDA (Food and Drug Administration) defined that a sunscreen should retain UVA around 360 nm to allege to be anti-UVA and the material used in the formulation should be able to present absorption in this spectrum region.

In figure 3 is presented the UV-Vis absorption spectra of pure and Cr^{3+} , Zn^{2+} , Fe^{3+} -doped HAP produced in this work and the maximum absorption wavelengths for TiO_2 , pure and doped HAP are shown in the table 2. Pure HAP presents optical absorption in UV region (200-340 nm), with a strong band below 247 nm. Similar results for pure HAP were found by Nishikawa [31] when producing HAP by an aqueous precipitation procedure from $\text{Ca}(\text{OH})_2$ and H_3PO_4 at temperature 1150°C .

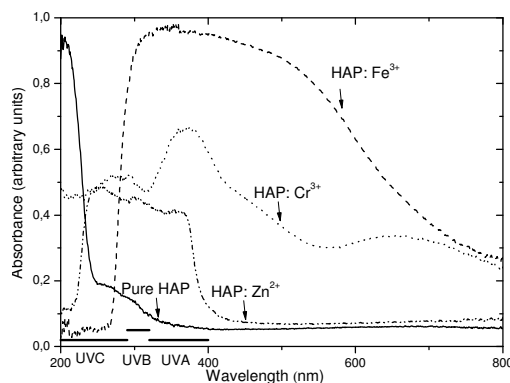


Figure 3. UV-Vis absorption spectra of Zn^{2+} , Fe^{3+} , Cr^{3+} -doped HAP.

Table 2. Maximum absorption wavelengths of the powders.

Powders	Maximum Absorption (nm)
Pure HAP	207
Zn^{2+}	240-372
Fe^{3+}	310-427
Cr^{3+}	368
TiO_2	316

As can be seen in figure 3, the optical absorption of HAP had suffered significant changes with the introduction of Cr^{3+} , Fe^{3+} and Zn^{2+} . Cr^{3+} -doped HAP generates absorption bands from UV to the visible (231-315, 318-542, 579-800 nm). Fe^{3+} -doped HAP showed a wide absorption from UV to the visible (267-800 nm) regions. The absorption bands in the visible region can induce the possibility of an undesirable visual color effect in sunscreens. During sunscreen production care has to be taken to avoid the agglomeration of particles, because the final effect of the product will decrease and the bad dispersion will generate a colored film. This problem can be healed if there is a good dispersion of the sunscreen on the skin and thus, a colored sunscreen will have transparent appearance when correctly applied on the skin [2].

Even if the Fe^{3+} and Cr^{3+} -doped HAP had good results in their absorption spectrum, the Zn^{2+} -doped HAP is the highlighted sample, because it showed absorption features in the spectral interval of 213-420 nm, which is similar to that obtained for TiO_2 . Moreover, it is known that an excellent sunscreen should have maximum absorption capacity in relationship the UV radiations in wavelengths between 296.7 and 320 nm [22]. With this aim, the most promising sample produced in this work is the Zn^{2+} -doped HAP.

4. Conclusions

Sunscreen efficiency is directly related to the physical and chemical properties of the ingredients, in particular their absorption and/or dispersion capabilities with respect to solar radiation. The present work contributes information on the production and optical absorption of Zn^{2+} , Fe^{3+} or Cr^{3+} -doped HAP as possible active components of sunscreens.

A simple and low cost technique to produce doped HAP has been worked out, resulting in single-phase samples as shown by XRD powder analysis. The doped HAP samples display absorption bands in the ultraviolet region as required, similarly to TiO₂ powders frequently used in sunscreen formulations. The observed absorption bands in the visible region may result in some visual color of the products, however, no damage to the success of the application is expected if the HAP component is appropriately incorporated in the sunscreen formula leading to its sufficient dispersion on the skin. Due to the excellent biocompatibility of HAP combined to the low toxicity of the Zn²⁺ ions, the Zn²⁺-doped HAP has a promising potential to be applied as a sunscreen. However, the long road from the sunscreen's elaboration to its commercialization necessitates several further studies by specialists of different areas in order to guarantee the protection against the undesirable effects of the ultraviolet radiation.

5. References

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