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Oxygen vacancies, the optical band gap (E_g) and photocatalysis of hydroxyapatite: Comparing modelling with measured data

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ABSTRACT

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is a calcium phosphate employed both in biomedicine and for environmental remediation. It is known that HAp can also be photocatalytic under UV light, probably due to oxygen deficiencies, but the mechanism is unclear, and reported optical band gap energies vary greatly. For the first time we propose the mechanisms and precise kinds of vacancies which may cause the photocatalytic activity of HAp, and compare these theoretical data with our measured data on both samples of marine origin and commercial HAp powders. Density functional theory (DFT) (from first principles calculations and Density of States (DOS) modelling) was used to calculate the optical band gap energy (E_g) created by various possible oxygen vacancies in the HAp lattice: O from PO_4, O from OH, the loss of an entire OH group, or the simultaneous loss of O from PO_4 and an entire OH group. The modelled values match the measured values very closely, suggesting that in non-photocatalytic HAp, if any vacancies exist, they are O atoms from the OH group, resulting in a band gap of ~5 eV in the UVC region (not present in solar light at the Earth's surface). However, in photocatalytic HAp, reduction from the combustion of an organic component at 1000 °C led to oxygen deficiency in the phosphate groups, probably in the O15 position, giving an E_g of ~3.45 eV, in the UVA region (present in sunlight). Heating HAp with no organic component to 1200 °C also led to vacancies, of both an entire OH group and oxygen from PO_4 groups, which led to an intermediate E_g value of ~4 eV, on the boundary of the UVA-UVB regions. Absorption peaks were also predicted in the visible-light region with some types of vacancy.

1. Introduction

Pollution of the environment is one the key challenges for our modern industrial society; the increasing level of toxic compounds, both in air and waters, requires effective methods and techniques for their degradation and/or conversion into harmless species [1]. Photocatalysis is an important methodology for environmental remediation; through which it is possible to degrade hazardous chemicals both in liquid and in the gas phase [1,2].

Photocatalysts are semiconductors, i.e. materials with an energy band gap (E_g). When irradiated with energy $\geq E_g$, a negatively charged electron (e^-) can be promoted to the conduction band from the valence band; this leads to the formation of a positively charged hole (h^+) in the valence band. These two charged species can react with molecules adsorbed on the surface of the material, and such reactions can eventually lead to the degradation of these molecules [3]. Examples of the degraded molecules include dyes and pharmaceuticals in the liquid phase, while species such as nitrogen oxides (NOx), volatile organic compounds (VOCs) and alcohols/alkanes can be decomposed in the gaseous phase [4].

Beyond being used for pollution degradation, photocatalysts can also be employed for bacteria inactivation. Microorganisms can be killed by interactions with the e^-/h^+ couple or with other Reactive Oxygen Species (ROS), such as radicals, which are generated with light irradiation [5].

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Table 1
Unit cell parameters *a*,*b*,*c* [Å] (from [31]).

Phase	Group	*a*, Å	*b*, Å	*c*, Å
Hexagonal	$P6_3/m$	9.417	9.417	6.875
Monoclinic	$P2_1/b$	9.48	18.96	6.83

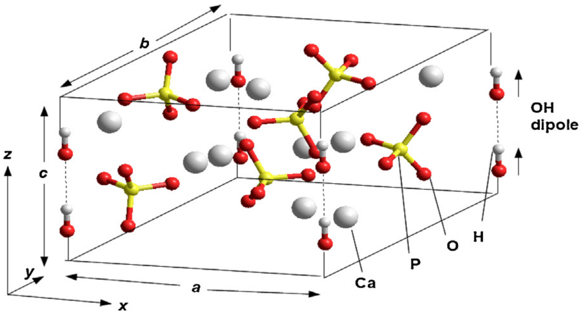

Fig. 1. Hexagonal HAp unit cell ordered structure. All OH groups are oriented in the same direction. They are positioned at the four corners of the unit cell, but only one pair in one corner belongs to this unit cell, the other three pairs belonging to neighbouring unit cells (e.g., one OH per unit cell).

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is a calcium phosphate employed both in biomedicine and for environmental remediation. Its use in biomedicine as a material for bone implants is due to its high biocompatibility and bioactivity [6]. In environmental remediation, HAp can be used for heavy metals absorption and removal, especially for bivalent cations such as Pb (II), Cd (II) and Zn (II) [7].

In recent years, the use of HAp as a photocatalyst has also been investigated, and several studies reported some forms of HAp as being photocatalytically active. Biphasic HAp-TiO_2 materials, for instance, showed greater photocatalytic activity compared to either single phase HAp or TiO_2 [8,9]; titanium-doped HAp has also exhibited photocatalytic behaviour. In the latter case, the insertion of the Ti^{4+} ion into the HAp lattice led to light absorption in the UV region, with the absorption being stronger for higher Ti^{4+} concentrations [10,11]. Different band gap values were measured for Ti-doped HAp; generally they were between 3.0 and 3.2 eV (around the values for anatase and rutile TiO_2) [12], and higher values up to 3.65 eV were also measured [13].

Some forms of single-phase HAp, with no dopant, also showed photocatalytic activity; indeed, Nishikawa reported the degradation of pollutants such as methyl mercaptane and dimethyl sulphate by HAp under UV irradiation [14,15]. Some HAp of natural origin has also exhibited photocatalytic behaviour – HAp derived from both cod fish bones and mussel shells has been used to degrade methylene blue [16,17].

Despite these interesting results, however, it is not yet clear which are the structural features affecting and/or imparting the photocatalytic behaviour to some forms of HAp. According to Nishikawa, UV irradiation can lead to an oxygen vacancy in the HAp lattice. This causes an electron transfer from the HAp vacancy to the atmospheric oxygen which, in turn, leads to the formation of the charged $O_2^{\bullet-}$ species, and indeed, $O_2^{\bullet-}$ was observed with EPR spectroscopy [14,18]. $O_2^{\bullet-}$ can then react with liquid/gaseous molecules and degrade them.

Although the detection of $O_2^{\bullet-}$ can be linked to the photocatalytic activity of HAp, it does not explain why some HAp forms are photocatalytic while others are not, i.e. why some forms can generate $O_2^{\bullet-}$ when irradiated while others do not. Piccirillo *et al.*, for instance, made two single-phase HAp materials from cod fish bones; of these two, only one showed photocatalytic activity, while the other did not [16]. According to the authors, a possible explanation for such a difference was the existence of an oxygen vacancy present in the photoactive HAp material, whose formation was due to the more reducing environment the material was prepared in.

In this work we present a density functional theory (DFT) modelling study of HAp, which correlates various possible oxygen vacancies in the HAp lattice (in PO_4, OH, and PO_4 + OH sites) with the variations in the value of the optical band gap E_g. To achieve this, first principles calculations of the HAp lattice and Density of States (DOS) modelling of defects in this system, specifically oxygen vacancies, were used [19]. The modelling results are compared with the band gap (E_g) values measured by the authors in actual HAp samples, of both marine origin and commercial products, using the Tauc plot method [20].

2. Materials and methods

2.1. Sample preparation

The preparation of HAp samples of marine origin was as previously described [16]. Briefly, the clean and dried cod fish bones were treated in solution containing an excess of either calcium chloride or calcium acetate (samples indicated with the symbols **B_Ac** and **B_Cl** respectively). After the solution treatment, the bones were dried and calcined at temperatures of 1000 °C (**B_Ac_1000** and **B_Cl_1000**) or 1200 °C (**B_Cl_1200**), using a heating rate of 5 °C/min and an annealing time of 1 h. Commercial HAp samples (Biotal, samples indicated by the letter **C**) were also studied as comparison; the powder was analysed as purchased (**C**) and after annealing at 1200 °C (**C_1200**), using the same conditions described above. Previous analysis of these samples showed that they all were single-phase HAp [21].

2.2. UV spectra measurement and band gap calculation

UV–vis spectra were acquired using a Shimadzu UV 3100 JP spectrometer equipped with an integrating sphere made of $BaSO_4$, in the range 250–825 nm, with a 0.2 nm in resolution. $BaSO_4$ was used as a white reference material. To calculate the optical band gap values, the Kubelka–Munk function [22] was applied with the aim of converting the diffuse reflectance into the absorption coefficient α:

$$\alpha \approx \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \equiv F(R_\infty) \qquad (1)$$

In Eq. (1) *K* and *S* are the absorption and scattering coefficients, respectively, whilst the reflectance R_∞ is equal to: $R_{\text{sample}}/R_{\text{standard}}$ [22]. Afterwards, the Tauc plot was applied [20]. This method assumes that the absorption coefficient α in (1) can be expressed as follows:

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \qquad (2)$$

where *A* is a material constant, *h* is the Planck's constant, is the frequency of the light, E_g is the (optical) energy band gap of the allowed transitions, and γ is the power coefficient, characteristic for the type of transition. For HAp the value of γ is accepted to be equal to 1/2 because for such materials, the transition is assumed to be indirectly allowed [23]. So, by plotting $[F(R_\infty)h\nu\nu]^{1/2}$ against $h\nu$, we can estimate the optical E_g of the material from the *x*-axis (α = 0) intercept of the line that is tangent to the inflection point of the curve. This was found by fitting the transformed Kubelka–Munk equation *versus* the photon energy with a sigmoidal Boltzmann function. The optical E_g value was then obtained from the *x*-axis intercept of the line that is tangent to the inflection point of said curve.