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Review

Calcium hydroxyapatite-based photocatalysts for environment remediation: Characteristics, performances and future perspectives

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ABSTRACT

Calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) is a material widely used in biomedicine, for bone implants manufacture, due to its biocompatibility. HAp has also application for environmental remediation, as it can be employed as metal removal; moreover, it has the capability of effectively adsorbing organic molecules its surface.

In recent years, the photocatalytic properties of HAp have been investigated; indeed several studies report of HAp used as photocatalyst, either on its own or combined with other photocatalytic materials. Although in the majority of cases the activity was induced by UV light, some reports of visible light-activated materials were reported.

Here we present a critical review of the latest developments for HAp-based photocatalysts; the materials discussed are undoped single phase HAp, doped HAp and HAp-containing composites.

For undoped single phase HAp, the possible surface treatment and lattice defects which can lead to a photoactive material are discussed.

Considering doped HAp, the use of Ti^{4+} (the most common dopant) is described, with particular attention to the effects that this metal have on the characteristics of the material (i.e. crystallinity) and on its photocatalytic behaviour. The use of other dopants is also discussed.

For the multiphasic materials, the combination of HAp with other photocatalysts is discussed, mainly but not only with titanium dioxide TiO_2.

Overall, HAp is a compound with high potential as photocatalyst; this property, combined with its capability for heavy metal removal, makes it a multifunctional material for environmental remediation.

As future perspectives, further studies, based on the results obtained until present, should be performed, to improve the performance of the materials and/or shift the band gap into the visible. The use of other dopants and/or the combination with other photocatalysts, for instance, are features which is worth exploring.

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1. Heterogeneous photocatalysis

Photocatalysis is a general term which refers to a photoreaction whose rate is increased due to the action of a catalyst (Castellote and Bengtsson, 2011). Photocatalytic reactions can be homogeneous or heterogeneous. In homogeneous photocatalysis, both the reactants and the photocatalyst are in the same phase; in the heterogeneous, on the contrary, the phases are different, the photocatalyst being generally in solid phase with the reactants being liquids or gases.

Heterogeneous photocatalysis processes, in particular, gained increasing attention in latest years, due to the interesting applications in several areas, which include environment remediation, energy production and catalysis of chemical reactions (Lee, 2016; Matsuoka et al., 2007; Colmenares and Luque, 2014). Generally heterogeneous photocatalysts are inorganic semiconductors (SC), titanium dioxide TiO_2 being the most common example. To act as photocatalyst, such semiconductor should have a full valence band and an empty conduction band. When irradiated with light whose energy is equal or higher to that of the band gap, an electron will be promoted from the valence band to the conduction band; this will generate a hole-electron pair, according to the reaction:

$$SC + h\nu \rightarrow e^- + h^+$$

Both charged species can then react with other chemical compounds they are in contact with; a reaction with water or molecular oxygen, for instance, are reported below (Hashimoto et al., 2005).

$$H_2O + h^+ \rightarrow HO\bullet + H^+$$

$$O_2 + e^- \rightarrow O_2^-$$

The radicals and/or ionic species formed can react further, to form more species, which are referred to as Reactive Oxygen Species (ROS).

$$O_2^- + H^+ \rightarrow HO_2\bullet$$

$$h^+ + O_2^- \rightarrow 2O\bullet$$

The full reaction scheme is shown in Fig. 1. Considering the application for environment remediation, ROS can then react with other molecules, such as organic contaminants or toxic gaseous species; such reactions can eventually lead to a partial or full degradation of these molecules.

A photocatalyst should have several characteristics to be usable in technological applications; a very important parameter is the efficiency in photogenerating the (e^-- h^+) charges under appropriate light irradiation. Also, once the charges are generated, it is important to avoid their recombination; fast recombination is in fact one of the main drawbacks of the heterogeneous photocatalysis (Xu et al., 2014). Several parameters, further than the nature of the photocatalyst, can affect both these properties; the morphology of the material, for instance, can be determinant. In the case of nanomaterials, on the other hand, the dimensions and the shape of the particles are also crucial, while for deposited coatings, preferred orientation can play a role (Hu et al., 2016; Jo and Natarajan, 2015; Lyandres et al., 2012). The photocatlysts should also be stable in the environment(s) they will be used in; moreover, considering in particular the use for environment remediation, the photocatalyst should also be non-toxic.

As already mentioned above, TiO_2 is the most used photocatalyst to date. TiO_2 can exist in three structures – anatase, rutile and brookite; although the anatase is the most effective photocatalyst, materials containing a combination of different TiO_2 phases, anatase and rutile in particular, showed the highest photocatalytic activity (Di Paola et al., 2012; Tobaldi et al., 2013). In recent years, however, there has been increasing interest in the development of other photocatalysts, using different semiconductor materials. One of the reasons for finding alternative materials is that TiO_2 has a band-gap in the ultraviolet region (about 3.2 and 3.0 eV for anatase and rutile respectively); therefore, it uses only a small fraction (3–5%) of the solar light (Mo and Ching, 1995). Indeed several visible-light photocatalysts were developed, some examples being zinc and tungsten oxides or silver phosphate (Di Paola et al., 2012; Martin et al., 2015).

At the same time, however, composite photocatalysts were also considered; several combinations using different materials were studied, many of which were still based on TiO_2. The presence of more than one compound can increase the efficiency in the charges' generation and reduce their combination, hence leading to materials with higher photocatalytic activity; moreover, photocatalysts with different band gap values can be obtained (Marschall, 2014).

Hydroxyapatite was one of the materials studied while searching for alternative photocatalysts. The sections below will describe the structure and the most important properties of this compound; subsequently a review of the hydroxyapatite application as photocatalyst will be presented.

2. Hydroxyapatite structure and properties

Calcium hydroxyapatite (HAp) is a phosphate with the formula $Ca_{10}(PO_4)_6(OH)_2$. HAp can have two possible structures, as it can be either monoclinic or hexagonal (space groups $P2_1/b$ and $P6_3/m$ respectively); the most common form is the hexagonal one, shown in Fig. 2. It can be seen that calcium has two possible positions, Ca1 and Ca2 (Chiatti et al., 2012).

Hexagonal HAp is the main component of human and animal bones (Figueiredo et al., 2010); because of this, synthetic HAp is widely used in biomedicine. HAp, in fact, it replicates the composition and behaviour of human bones; it is therefore used to fabricate bone implants. For this particular application, carbonated HAp is used, to mimic more closely the composition of human bones (Boutinguiza et al., 2012). HAp is very biocompatible and osteoconductive, as it favours the formation of new bone through osteoblast cells' growth (Nathanael et al., 2016). Other applications in biomedicine include drug delivery (Cole et al., 2016) and bioimaging (Xu et al., 2016).

HAp has very low solubility at neutral pH; in literature, however, very different acidity constants were reported. According to Bertazzo, in fact, pK values in the range between 84 and 120 were measured (2010); these differences can be due to different parameters. The stoichiometry of the compound, for instance, can have a significant effect; the presence of carbonate in the HAp