











Hybridization of Fe-O in iron doped hydroxyapatite for superior electrochemical charge storage

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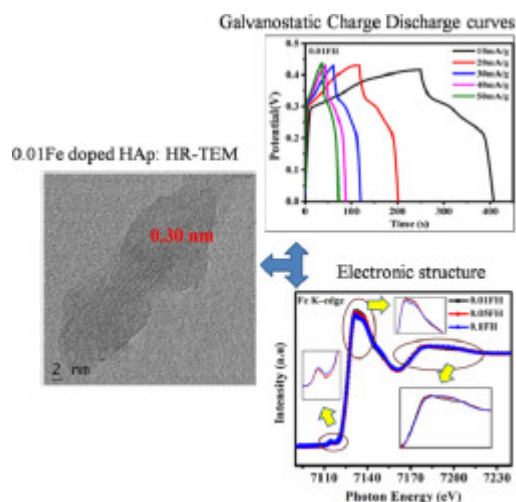
Highlights

- First report on strong hybridization of Fe-O in FeHAp for supercapacitor application.
- High unoccupied density of states of Fe at 0.01FH compared with the other samples.
- Reduction of coordination of Fe-O and its interatomic distance at 0.01FH.
- The specific capacitance of asymmetric supercapacitor cell is 90F/g at 30mA g^{-1} .

Abstract

Hydroxyapatite (HAp) is an interesting phosphate candidate with a weak electrical conductivity that can be tuned by doping metal ions to enhance the active sites for electrochemical charge storage. HAp and Fe-doped HAp were prepared by a wet chemical method. On doping, the crystallite size reduces to 9.56nm. The surface area of 0.01FH (0.01% Fe) is 152.17m²/g which is ~3 times higher compared to PH. The 0.01FH sample shows the highest specific capacitance of 351.3F/g at 30mA/g. While X-ray photoemission spectroscopy shows the oxidation states of Fe in 2⁺ and 3⁺, X-ray absorption indicates (i) the enhancement of unoccupied density of states of Fe, and (ii) reduced interatomic distance of Fe-O in 0.01FH. These results show that the augmentation of surface properties and hybridization of Fe-O and the modification of its local atomic structures are responsible for high electrochemical charge storage in 0.01FH.

Graphical abstract



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Introduction

The industrial revolution is predominantly dependent on non-renewable fossil resources like oil, gas, coal, etc. The drastic depletion of these resources triggers the need for alternative green energy resources to harness solar, wind, and tidal energy [1], [2], [3], [4]. There is a greater demand for reliable technical platforms for power storage systems such as batteries [5], fuel cells [6], and supercapacitors [7,8]. Supercapacitor possesses intriguing merits such as high-power density, long life expectancy, wide-temperature operation range (up to 70°C), environmental friendliness, and exclusively high energy efficiency (90%–95%) [9]. From a mechanistic perspective, the oppositely charged ions stored within the layers of the interface of electrode/electrolyte are known as Electric Double-Layer Capacitors (EDLC) [10], [11], [12]. Materials such as metal oxides/hydroxides [13,14], metal phosphates [15,16], metal sulphides [17,18], and conductive polymers [19,20] display multiple oxidation states by redox and stores energy at the electrode surfaces are known as pseudocapacitors [21]. The capacitive behavior of pseudocapacitors is found to be more effective than the EDLCs. In terms of pseudocapacitors, oxides, and conductive polymers were examined owing to their higher electrochemical activities that lead to a very high capacitance. However, they suffer from a lack of stability and electrical conductivity [22]. Metal phosphate is one of the promising electrodes for supercapacitors owing to its exceptional layered structures and higher specific capacitance [23]. Besides, the metal phosphates possess a framework structure consisting of huge channels/cavities and their high redox behavior provides elevated ionic conductivity and the capability to store charges [24]. Furthermore, the covalent bonds of P-O in phosphates relate to a highly steady structure and a tiny diffusion

path length for the charge carrier, which is responsible for the superior electrochemical charge storage in the system. Among metal phosphates, nickel, and cobalt-based phosphates are widely studied due to their abundance and high conductivity [25], [26], [27]. HAp is an inexpensive and eco-friendly material with high biocompatibility and bioactivity. Micro and nanometre-sized HAp are of boundless interest in various areas such as adsorption/separation of protein, bone tissue engineering, etc., [28], [29], [30]. Moreover, a layer of HAp provides numerous P-OH groups that act as adsorption sites for several analytes like dyes [31], proteins [32], and drugs [33]. Its physical and chemical properties mainly depend upon crystallinity. Hydroxyl ions (OH^-) are located at the center of Ca^{2+} triangles that orient in the c-axis direction in HAp. Since, the distance between two adjacent OH^- ions are too large (0.344 nm), charge transfer happens via an OH^- ion that interacts with O of $-\text{PO}_4$ [34,35]. The ions with structure would be responsible for the passage of electrons and energy storage [36]. Nevertheless, the conductivity of HAp is too low for electrochemical applications without further modification. Hence, doping bivalent/trivalent ions into the HAp system enhances the conductivity by affecting the hydroxyl (OH^-) groups that result in electrical charge compensation [37,38].

In the current study, the Fe^{3+} ions are incorporated in the HAp matrix and their impact on structural, functional, morphological, and electrochemical properties is investigated. For the first time, the electronic and atomic structures of the developed samples are examined by using synchrotron-based X-ray Absorption Spectroscopy and Extended X-ray Absorption Fine Structure spectroscopy to understand the mechanism of electrochemical charge storage. Here, a strong hybridization between Fe and O, the reduction of the coordination number (Fe-O), and the interatomic distance of Fe-O are disclosed that responsible for the enhancement of specific capacitance at the low concentration of Fe ions (0.01FH) in comparison with the other samples.

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Section snippets

Chemicals

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ and ammonia solution (25%) were procured from Merck, Mumbai, India and were used without any further purification....

Synthesis of HAp

To synthesize pure HAp, calcium nitrate tetrahydrate and diammonium hydrogen phosphate were taken as the source for calcium (Ca^{2+}) and phosphate (PO_4) respectively. 0.5M of calcium nitrate tetrahydrate and 0.3M of diammonium hydrogen phosphate were...

Characterization

The structure of the samples is examined by Powder X-Ray Diffraction (PXRD) using a Panalytical diffractometer (D8 Advance Bruker) with $\text{CuK}_\alpha = 1.5406 \text{ \AA}$ radiation in the 2θ range of $10^\circ - 80^\circ$ with a step size of 0.02. The functional groups of the samples were collected in the mid-IR region of $4000\text{cm}^{-1} - 400\text{cm}^{-1}$ by FTIR (JASCO FT/IR6300). The Raman spectrum was recorded using a laser source of wavelength $\sim 488\text{nm}$ and excitation power of 50mW in the Lab Ram-HR 800 Raman spectrometer. The particle...

X-ray diffraction

X-ray diffraction patterns of the PH and FH samples are shown in Fig.1 and the average crystallite sizes D (nm) of the samples were calculated using Scherrer's Eq.(1) and mentioned in Table 1. $D = k\lambda / \beta \cos\theta$ where λ is the wavelength of CuK_α radiation ($\lambda = 0.1541 \text{ nm}$), β is the full width at half maximum intensity for the diffraction peak under consideration (radian), θ is the diffraction angle of the corresponding reflection, and k is the broadening constant that varies with the crystal structure.

The ...

Conclusions

HAp and Fe-doped HAp were prepared by the chemical co-precipitation route. XRD patterns confirm that there is no formation of minor phases on doping of Fe^{3+} ions (0.01M and 0.05M) in the HAp matrix. However, the crystallite size reduces to 9.56nm. The addition of Fe ions results in agglomerated spherical and rod-like nanoparticles. Enhanced surface area

(152.17 m²/g) and pore volume (0.649 cc/g) and the reduction of pore size (9.56 nm) are also achieved in the 0.01FH. The XPS results confirm ...

CRedit authorship contribution statement

Kurinjinathan Panneerselvam: Conceptualization, Methodology, Software, Data curation, Writing – original draft. **Anita R Warriar:** Supervision, Writing – review & editing. **Thileep Kumar K:** Visualization, Investigation. **Roselin Ranjitha Mathiarasu:** Visualization, Investigation. **Raghu Subashchandrabose:** Visualization, Investigation. **Yu-Cheng Huang:** Visualization, Investigation. **Thanigai Arul Kumaravelu:** Conceptualization, Methodology, Software, Data curation, Writing – original draft, Supervision,...

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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