



Surface fluorination of α -Fe₂O₃ using selectfluor for enhancement in photoelectrochemical properties



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ABSTRACT

Fluorinated α -Fe₂O₃ nanostructures are synthesized via a facile hydrothermal route using Selectfluor™ (F-TEDA) as a fluorinating as well as growth directing agent. The addition of incrementally increasing amount of F-TEDA to Fe precursor under hydrothermal conditions resulted in preferential growth of α -Fe₂O₃ along (110) orientation with respect to (104) direction by ~35%, the former being important for enhanced charge transport. On increasing fluorination, the hierarchical dendritic-type α -Fe₂O₃ changes to a snow-flake type structure (F-TEDA-20%) anisotropically growing along the six directions however, at higher F-TEDA concentrations (\geq 30%), loosely held particulate aggregates are seen to be formed. The X-Ray Photoelectron Spectroscopy (XPS) suggest the maximum fluorination of α -Fe₂O₃ at 1.21 at% in 30% F-TEDA. Further, optical absorption studies reveal reduction in optical band gap from 2.10 eV in case of pristine to 1.95 eV for fluorinated α -Fe₂O₃. A photoanode made by taking 20% fluorinated α -Fe₂O₃ in a ratio of 10:90 with respect to TiO₂ (P-25) showed improved performance in dye sensitized solar cells with an increase in efficiency by ~16% in comparison to that of pristine Fe₂O₃ and TiO₂. Furthermore, anode consisting of thin films of fluorinated α -Fe₂O₃ on FTO also exhibit enhanced current density on illumination of ~100 W/m². The increase in photoelectrochemical activity seems to be due to the combination of two factors namely preferential growth of α -Fe₂O₃ along (110) direction resulting in an improved charge transfer efficiency and reduced recombination losses due to the presence of fluorine.

1. Introduction

Hematite or α -Fe₂O₃ is widely used in a variety of applications such as electrode in lithium batteries [1,2], production of magnetic materials [3], visible-light photocatalysis [4–6], water treatment [7], gas sensors [1,8], electromagnetic devices, paints and pigments [9]. High-quality hematite films are mainly fabricated by various techniques such as atmospheric pressure chemical vapor deposition (APCVD), atomic layer deposition, electron-beam, pulse laser deposition, reactive DC magnetron sputtering and metal organic decomposition for use in photoelectrochemical cells [10–13]. Being a highly abundant, low cost and non-toxic material with a low bandgap of 2.1–2.2 eV, α -Fe₂O₃ has attracted immense attention in the recent past. However, there are certain drawbacks that limits the use of α -Fe₂O₃ in solar application such as low mobility of carriers ($< 0.1 \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$) [14] high recombination rates, short diffusion length (2–4 nm) [15], short excited state lifetime ($< 10 \text{ ps}$) [16], poor light absorption [17], and improper band

position [18] for unassisted water splitting that limit its application in solar applications. There is lot of impetus in improving its properties by structural modification, variation in morphology and by doping [19,20].

Recently, extrinsic fluorine anion doping of semiconducting metal oxides such as SnO₂, TiO₂, Co₃O₄ and Fe₂O₃ have turned out as an important route for surface passivation of metal oxides that inhibits e^-/h^+ recombination and improves charge carriers mobility. Additionally, fluorine doping is expected to achieve tunable optical absorption and modified band position for enhancement in photoelectrochemical activity. Theoretical studies also suggest that the partial replacement of O²⁻ by aliovalent anion such as F⁻ can effectively reduce the electrical resistivity of Fe₂O₃ [21]. For example, Tondello et al. synthesized F-doped Co₃O₄ by plasma enhanced chemical vapor deposition method using fluorinated β -diketonatecobalt derivative as a single fluorine and cobalt precursor and observed a significant improvement in hydrogen production. Similarly, Choi et al. carried out fluorination of TiO₂ using

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sodium fluoride for enhanced photo catalytic action [22,23]. The enhancement in catalytic activity is understandable due to increase in Lewis acidity of Fe-centers by substitution of surface oxygen atoms with fluorine. For example, Zhu *et al.* observed rapid photo catalytic degradation of Rhodamine dye using fluorinated SnO₂ [24,25]. Several fluorine-doped metal oxides have been synthesized in order to enhance the electrochemical performance of energy storage devices. Lee *et al.* synthesized F, N-doped Fe₂O₃ using ammonium fluoride and urea and used it for supercapacitor application [26].

Among solution-based fluorinating agents, HF and NH₄F are generally used, however, these act preferentially as growth directing agents with no evidence for fluorination in the growth of metal oxides [27]. Herein, we for the first time, utilized F-TEDA as a fluorinating agent that provides electrophilic fluorine in solution as the reactive species. In this work, we developed a facile yet effective hydrothermal strategy for the in-situ preparation of F-Fe₂O₃ by modifying the known method for dendritic growth of α -Fe₂O₃ [28]. In order to understand the interaction of fluorine with α -Fe₂O₃, we focussed on the interplay between the fluorine content (varying F-TEDA concentration 0–40%) and resulting structural, optical and photoelectrochemical properties together with study on its application in visible light photo-electrochemical and dye sensitized solar cells.

2. Experimental section

2.1. Synthesis of pristine and F-Fe₂O₃

Aqueous solution of (15 mM) of K₃[Fe(CN)₆] was heated in Teflon hydrothermal vessel (200 mL) at 140 °C for 48 h following the literature method [28]. The precipitate was obtained and washed with de-ionized (DI) water followed by ethanol wash to get rid of the by-products. It was further centrifuged and dried in hot air oven at 70 °C for 4h. *In-situ* fluorination was carried out using Selectfluor™ (N-Chloromethyl-N'-fluorotriethylenediammoniumbis(tetrafluoroborate), F-TEDA, Sigma Aldrich) as the fluorinating agent. F-TEDA was mixed in different weight percent with respect to the principal reactant before the start of reaction.

2.2. Characterization

Bruker D8 Advance diffractometer equipped with Cu-K α radiation having 1.54 Å wavelength was used for X-ray diffraction (XRD) analysis. ¹⁹F NMR spectra were collected from the reaction mixture before and after reaction (supernatant) in D₂O using Bruker 500 spectrometer operating at 500 MHz. TEM imaging was performed by transmission electron microscope (FEI Technai G2 T20 ST) equipped with energy-dispersive X-ray spectroscopy (Burker X-100). For imaging, ~10 mg of sample was dispersed in ethanol and drop casted on a copper grid and allowed to dry before imaging. HRTEM images were analyzed using Image J and Gatan digital micrograph software. Field Emission Scanning Electron Microscope (FESEM) imaging was performed using Nova NanoSEM 600 instrument (FEI Co., The Netherlands). Diffuse reflectance spectra were recorded in solid state using UV–vis spectrophotometer (Varian Cary 4000) with polytetrafluoroethylene (PTFE) as the reference material. Surface composition and chemical states were measured with an Omicron nanotechnology (Oxford instruments) X-ray photoelectron spectroscopy (XPS) instrument equipped with monochromatic Al K α radiation. Specific surface area was analyzed by N₂ adsorption–desorption isotherms (Quntachrome autosorb iQ3). Solar Simulator (model number SS50AA, Photoemission Tech) was used to illuminate the devices.

2.3. DSSC fabrication

All solar cells were prepared according to the typical procedure as mentioned in our previous study [29]. Briefly, pristine and F-Fe₂O₃

(20%) were mixed with TiO₂ (P25) powders in 5:95, 10:90, 20:80 and 40:60 ratios in the form of a paste and uniformly grinded with ethyl cellulose in α -terpinol and ethanol (wt% ratio: 2.7:1:3.38). The paste was screen printed on the fluorine doped tin oxide (FTO) substrates and dried at 120 °C for 6 min and repeatedly printed 5 times to increase the layer thickness. The electrodes were sintered at 450 °C for 30 min in the air resulting in film of ~15 μ m thickness with active area of 1 cm². The platinum sol was deposited onto the FTO counter electrode and then calcined at 450 °C for 30 min. The photoanodes were soaked in 0.5 mM N719 dye solution for 18 h. Finally, these were assembled along with Pt counter electrode using a Surlyn spacer (thickness of 25 μ m) and Iodolyte Z 50 (Solaronix) as the electrolyte resulting in a sandwich structure as shown in supporting information, Fig. S2a. The fabricated DSSC device was then illuminated under solar simulator 1000 W/m² (1 Sun) for J-V and EIS measurements. All the fabricated DSSCs were averaged over three cells.

2.4. Photoelectrochemical measurements

The films of α -Fe₂O₃ and F-Fe₂O₃ were prepared by three layer screen printing on FTO glass for photoelectrochemical measurements. The paste of appropriate viscosity was prepared by mixing 0.05 g of ethyl cellulose, 0.3 mL of α -terpinol and 0.02 mL glacial acetic acid in a mortar and pestle for 30 min. Upon complete dissolution of ethyl cellulose, 0.1 g of hematite was added and mixed for 10 min. Further, appropriate amount of ethanol was added for viscosity adjustment. The prepared paste was layer by layer coated on FTO glass using 100 mesh screen and squeegee. Every layer was dried before coating successive layer. The prepared films were further annealed at 500 °C for 5 h before using for electrochemical measurements. Electrochemical workstation (CHI6600) was used for I-V measurements and impedance spectroscopy (EIS) analysis in a three-electrode set up using Pt mesh as counter electrode and Ag/AgCl (3 M KCl) as reference electrode. The potential were converted to the reversible hydrogen electrode (RHE) scale using the standard Nernst equation. The graphs were plotted from a frequency range of 1–10⁵ Hz. Chronoamperometry experiments were performed at 0.6 V versus Ag/AgCl (1.6 V versus RHE). The measurements were performed under illumination of 100 W/m² (one-tenth of 1 Sun) while the light source was switched on and off after every 5 s. The photocurrent value at the end of the chronoamperometry measurement was taken as the steady-state photocurrent and was used to compare different samples.

3. Results and discussion

F-TEDA is a well-known, commercially available, stable fluorinating reagent that acts as a source of *electrophilic fluorine* in organic synthesis [30–32]. In this study, we have employed it for fluorination of an inorganic material, α -Fe₂O₃ not only due to its high reactivity but also for its ease of handling as compared to the other sources of fluorine such as HF, XeF₂ and F₂ [33,34]. Synthesis is scaled up in different-sized Teflon vessels of 100, 200 and 800 mL capacity as shown in Fig. 1a. The hydrothermal reaction for K₃[Fe(CN)₆] was carried out with and without F-TEDA at an optimized reaction condition of ~140 °C for 48 h as detailed in experimental methods. The pH changes in the reaction medium were monitored before and after reaction completion to gain better insight in the process of fluorination (Fig. 1c). The pH of the reaction mixture containing Fe precursor and F-TEDA (10 wt% – 40 wt%) is comparatively lower (pH = 3.4 – 4.0) than Fe precursor in water (pH = 6.2) as the F-TEDA is a salt of strong acid and weak base. However, after the hydrothermal reaction, pH of the supernatant becomes higher due to CN⁻ assisted dissociation of water that result in formation of OH⁻ ions [35]. For higher concentrations of F-TEDA, the pH of supernatant after the reaction decreases gradually. As seen from Fig. 1c (bottom curve), the overall pH change for the reaction is higher in presence of fluorinating agent (10, 20 and 30 wt% of F-TEDA) as

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