Effect of pH on the morphology and orientation of Fe_2O_3 nanostructures grown using aqueous chemical growth

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Abstract. Fe_2O_3 nanostructures were synthesized for various pH values on corning glass substrates by aqueous chemical growth (ACG) using a solution of ferric chloride ($FeCl_3$). It was found that increasing the pH from 1.15 to 3.0 of the solution significantly leads to a modification of the Fe_2O_3 morphology or orientation from randomly parallel needle shaped rod-like to randomly perpendicular rectangular structure on to a substrate.

1. Introduction

Hematite (alpha-Fe_2O_3) as an n-type semiconductor has a band gap of 1.9 - 2.2 eV which can absorb approximately 40% of solar incident radiation and stable in most electrolytes with wide range of pH > 3 [1], has a high content of iron and is natural abundance, non-toxic, environmental friendly, photo-corrosive resistance and photo-catalytic [2], which makes it an ideal candidate for water splitting using sunlight compared to alternatives which are abundant and inexpensive such as TiO_2, ZnO, and WO_3 with wide band gaps and are therefore limited in general to terrestrial solar energy efficiency to less than ~4% [3]. The disadvantages of this material is that it has a high resistivity for a single crystal, Low electron mobility and very short hole diffusion length of 2 to 4 nm which exhibit high rate of charge carrier recombination and therefore poor charge transfer.

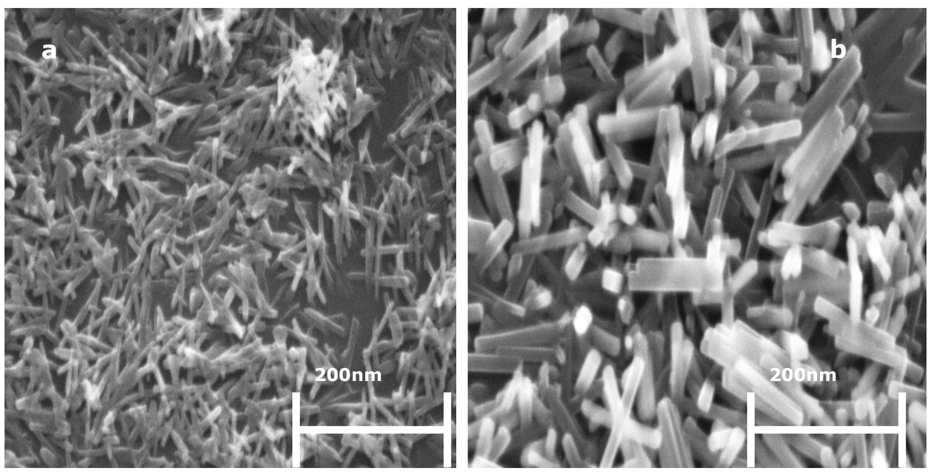
The efficient photo-voltaic properties have been demonstrated through designing a thin film of hematite consisting of crystalline arrays of oriented nanorods [4]. These designs exhibited substantial photo-current efficiency due to a better transport and collection of photo-generated electrons through a designed path. Hematite has a conduction band gap edge which is too low than the chemical potential for hydrogen gas (H_2/H^+) evolution [5,6] without an external bias, although the valence band edge is located at a lower energy level, which is in correspondence with the chemical potential for oxygen gas (H_2O/O_2) evolution. Therefore this energy position of the band edge level can be modified using the electronegativity of the dopants and solution pH [7]. ACG [7,8,9] is a quite simple technique for the deposition of nanostructures at relatively low temperatures, presenting several advantages such as the use of non-expensive equipment, the requirement of cheap and non-toxic reagents and the presence of non-hazardous by-products. Moreover, the morphological and structural characteristics of the grown samples can be controlled by adjusting parameters such as the concentration of the solution, the reagents stoichiometry, the temperature and the pH [10,11]. In this work, we investigate the possibility of controlling the nanostructures morphology grown using ACG by adjusting the pH of the solution. Towards this scope, results are presented related to the deposition of Fe_2O_3 nanostructures on corning glass, at a deposition temperature of 95 °C, for a range of growth periods and various pH values. In this work we report on the effect of various pH values on surface morphology of the deposited of Fe_2O_3 nanostructures on glass substrate grown by aqueous chemical growth technique.

2. Experimental approach

Hematite (alpa-Fe_2O_3) nanostructures was grown by employing aqueous chemical growth technique, using 0.1 M aqueous solution of ferric chloride ($FeCl_3$) as precursors at various values of pH adjusted using a concentrated hydrochloric acid (HCl) solution. The solution and the glass substrate was placed in Pyrex glass bottles with polypropylene autocleavable screw caps and heated at a constant temperature of 95°C for 24 h in a regular laboratory oven. After this generation period, the samples were taken out and washed thoroughly with MilliQ de-ionized water to reduce residual salts. The homogeneous films of akaganiete (FeOOH) was obtained first on the substrate and annealing it on air at 500^{o}C for 1hr to transform FeOOH to alpa-Fe_2O_3. The morphology investigation was studied using a Leo-Stereo Scan 440 Scanning Electron Microscope (SEM).

3. Results and discussion

Scanning Electron Microscope (SEM) images of Fe_2O_3 hematite nanostructures grown for 24 h on corning glass using an aqueous solution at 95 °C and for various pH values ranging from 1.15 to 3.0 are presented in Figure.1.



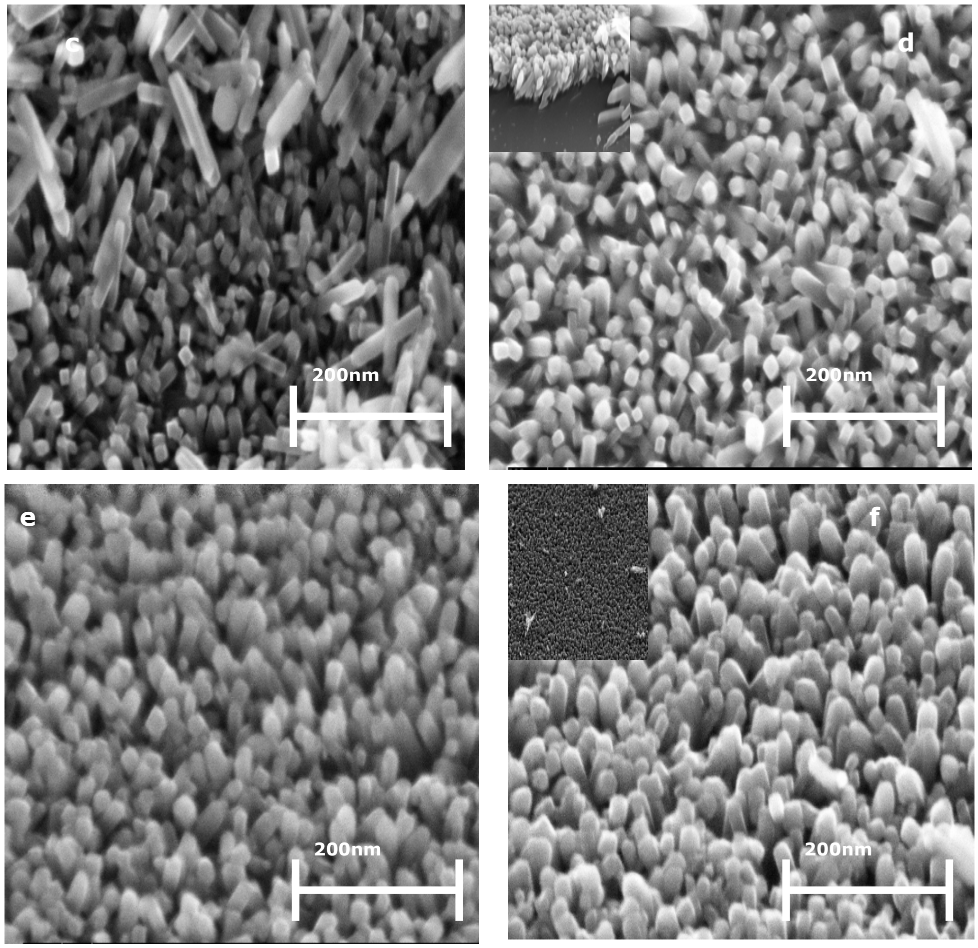


Figure 1 SEM images of Fe_2O_3 deposited on corning glass using ACG for a deposition time of 24 h at various pH values, (a) pH 1.15, (b) ph1.5, (c) pH 1.75, (d) pH 2.0, (e) pH 2.5, (f) pH 3.0, which presenting the morphology and the orientation of the nanostructures all the images were taken at a scale of 200nm.

As can be seen, the morphology and orientation of the obtained Fe_2O_3 nanostructures strongly depends on the pH of the solution. At a pH of 1.15 needle like random oriented nanorods are observed. At a pH of 1.5 the nanorods are cubic at the tip and the orientation is mixed random and perpendicular oriented on to a substrate. Therefore this shows that the perpendicular orientation of cubic nanorods starts at pH 1.5. Increasing the pH to a value of 1.75, a most observed orientation of the nanorods is perpendicular on the substrate, while only cubic structured perpendicular nanorods are observed at the pH of 2.0. At the pH of 2.5 to the pH of 5.0, nanorods with a spherical shape at the tip are observed. Finally, at pH 5.0, the random oriented nanorods structures are observed. Following the above observations, it is clear that the morphological characteristics of as-prepared Fe_2O_3 nanorods arrays are controlled by the concentrated hydrochloric acid.

Furthermore, the shape and the orientation of the nanostructures changes with increasing pH. The diameter of the nanorods increases with an increase in the pH values while the lengths decrease. For the diameter, it shows that the best engineered rods are found at pH 1.5 to pH 2 where the length is long. All these changes observed are due to the pH of the solution. To summarize the changes in the morphology of the Fe_2O_3 nanostructures, the graphs of length and diameter as a function of the pH value are showed in Figure.2 (a, b).

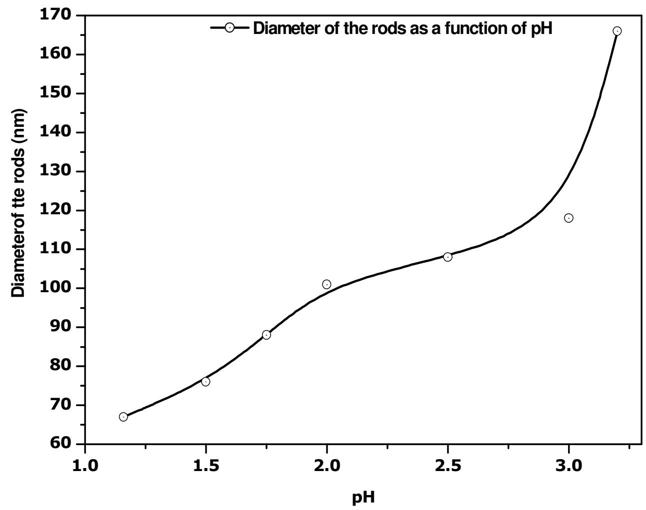


Figure 1 (a) present the diameter as a function of the pH values

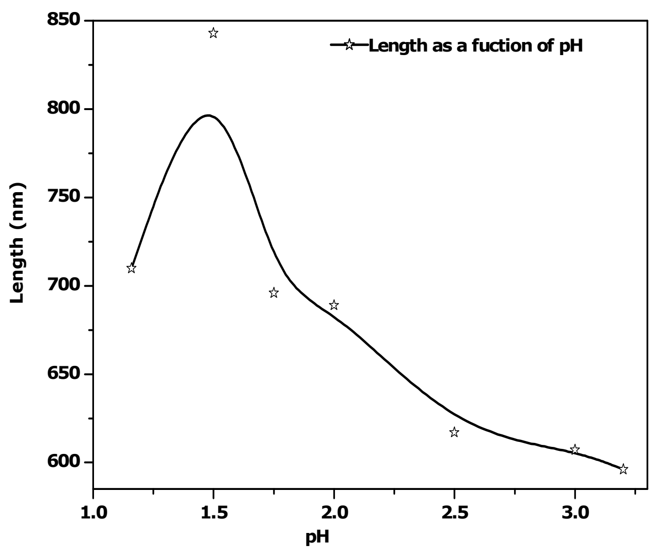


Figure 2(b) presents the Length of the rods as a function of pH values

4. Conclusions

The pH effect on the morphological and orientation characteristics of hematite nanostructures grown by ACG using aqueous solution of $FeCl_3$ as precursors at 95 °C for various deposition times was examined. It was found that pH significantly influences the shape of the Fe_2O_3 nanostructures, leading to a modification of the morphology orientation from randomly parallel oriented rod-like to perpendicular oriented nanorods structures on the substrate. Therefore, one can control the shape of the Fe_2O_3 nanostructures by adjusting the pH of the solution.

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References

[1] Kleiman S A, Huda M N, Walsh A, Yan Y, Stucky G D, Hu Y S, Al-Jassim M M and McFarland E W 2010 *Experiment and Theory Chem. Mater.* **22** 510–17

[2] Vayssieres L 2006 *C. R. Chimie* **9** 691–701

[3] Kleiman S A, Hu Y-S, Forman A J, Stucky G D and McFarland E W 2005 *J.* Com. *Chem.* **7** 264

[4] Matsumoto Y 1996 *J. Solid State Chem.***126** 227-34

[5] Vayssieres L 2006 *Solar Hydrogen and Nanotechnology, SPIE Proceedings* **6340**, 1-336

[6] Glasscock J A., Barnes P R F, Plumb I C, Bendavid A and Martin P J 2006 *Solar Hydrogen and Nanotechnology, SPIE Proceedings* **6340**, 1-336

[7] Beermann N, Vayssieres L, Lindquist S E, Hagfeldt A, 2000 *J. Electrochem. Soc.* **147** 2456-61

[8] Vayssieres L 2003 *Adv. Mater.* **15** 464

[9] Li Q 2005 *Chem. Mater* **17** 1001.

[10] Liu X, Jin Z, Bu S, Zhao J and Yu K 2006 *Mater. Sci. Eng., B, Solid-State Mater.Adv. Technol.* **129** 139

[11] Zhang H 2005. Mater. Lett. 59 1696