Properties of nanostructured hematite prepared by various coating techniques for PEC water splitting

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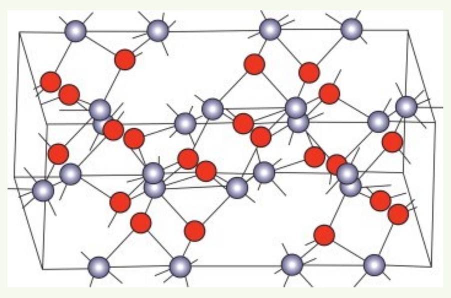
Introduction

Hematite (α-Fe_2O_3) is an abundant, n-type semiconductor which offers good thermal stability in aqueous mediums. It has a small indirect bandgap of 1.9~2.2eV which makes it favourable for applications in photoelectrochemical (PEC) water splitting [1]. Due to its stability and abundance, hematite has been used for various applications such as the manufacturing of gas sensors, lithium batteries, pigments, photocatalyst and as photo anodes in PEC water splitting for hydrogen production [2].



Structure

Hematite contains a rhombohedrally centered hexagonal shape of the corundum structure [2].

Various preparation techniques such as dip coating, spray-pyrolysis, spin coating, electron deposition and microemulsion-precipitation have been reported for preparing nanostructured hematite films [3]. In this study two colloidal solution-based techniques namely dip coating and spray-pyrolysis were used to synthesize hematite nanoparticles. This research was done to compare the structural and optical properties of hematite films prepared by different coating techniques.

Materials and Experimental Procedure

- Iron (III) nitrate nanohydrate ($Fe(NO_3)_3.9H_2O$, oleic acid ($C_{18}H_{34}O_2$), ethanol, deionized water.
- The substrate material was fluorine doped tin oxide (FTO)

Preparation of hematite nanoparticles

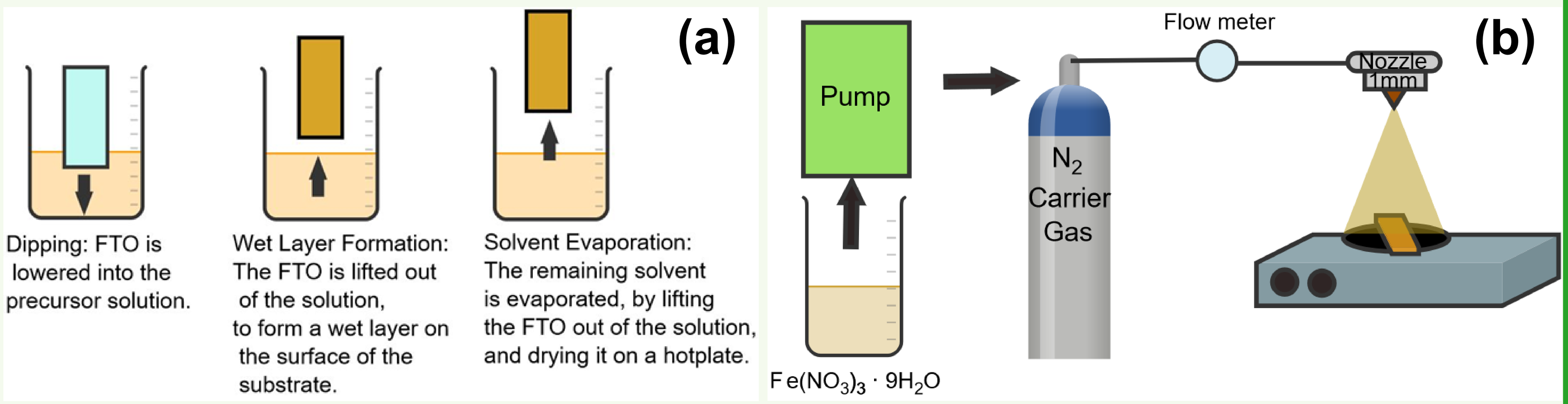


Fig.1. Schematic diagram for (a) dip coating and (b) spray-pyrolysis synthesis of hematite thin films.

- The precursor solution for dip coating was prepared by mixing a 2:1 mol ratio of iron(III)nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, Sigma Aldrich, AR, 99%) and oleic acid ($C_{18}H_{34}O_2$, Sigma Aldrich, GC, 99%); then heated at 110 °C for 2.5 hrs, forming a brick red mass of iron oleate ($C_{36}H_{66}FeO_4$).
- After each layer, the dip coated substrate was annealed at 500 °C for 1 hr, to form α-Fe_2O_3 crystals. The procedure was repeated four times in order to produce four layers of α-Fe_2O_3 thin film.

- The precursor solution was synthesized by dissolving 50 mM of iron(III)nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, Sigma Aldrich, AR, 99%) into 200 ml of deionized water.
- After four layers of spray-pyrolysis, the substrate was annealed at 500 °C for 1 h, forming four layers of α-Fe_2O_3 thin film.

Results and Discussion

* **Fig. 2,** shows the surface morphology of the α-Fe_2O_3 prepared by dip coating and spray-pyrolysis. Both samples showed a uniform morphology with the dip coating film indicating nanospheres and the spray-pyrolysis film indicating agglomerated nanoparticles. The grain size was determined with Average Grain Intercept (AGI) as 50.00 nm for the dip coated thin film as opposed to 45.82 nm for the spray-pyrolysis thin film.

* **Fig. 3(a),** shows the vibrational modes for α-Fe_2O_3. Both methods yielded polycrystal nanostructures presented by the strong vibrational modes of A_{1g} (230 cm^{-1}) and E_g (300 cm^{-1}) with high intensity. Five vibrational modes of two A_{1g} and three E_g were present in both films.

* **Fig. 3(b),** shows the diffraction patterns for α-Fe_2O_3. All peaks indexed at the 2 theta correlated with the JCPDS plot card no 33-0664. The two main peaks corresponding to the (104) and (110) Miller indices were present confirming the hexagonal rhombohedral structure of hematite. The remaining unlabeled intense peaks were due to the FTO substrate. The average crystal sizes of 11.5 nm and 15.45 nm were obtained from the Debye-Scherrer formula, for dip coating and spray-pyrolysis respectively.

* **Fig. 4(a),** shows the energy bandgap of α-Fe_2O_3 nanoparticles for the dip coating film. The onset bandgap was estimated as 2.08 eV.
* **Fig. 4(b),** shows the energy bandgap of α-Fe_2O_3 nanoparticles for the spray-pyrolysis film. The onset bandgap was estimated as 2.03 eV.
* Both films absorbed light in the visible region with the onset range of 590 nm to 610 nm.

Results and Discussion

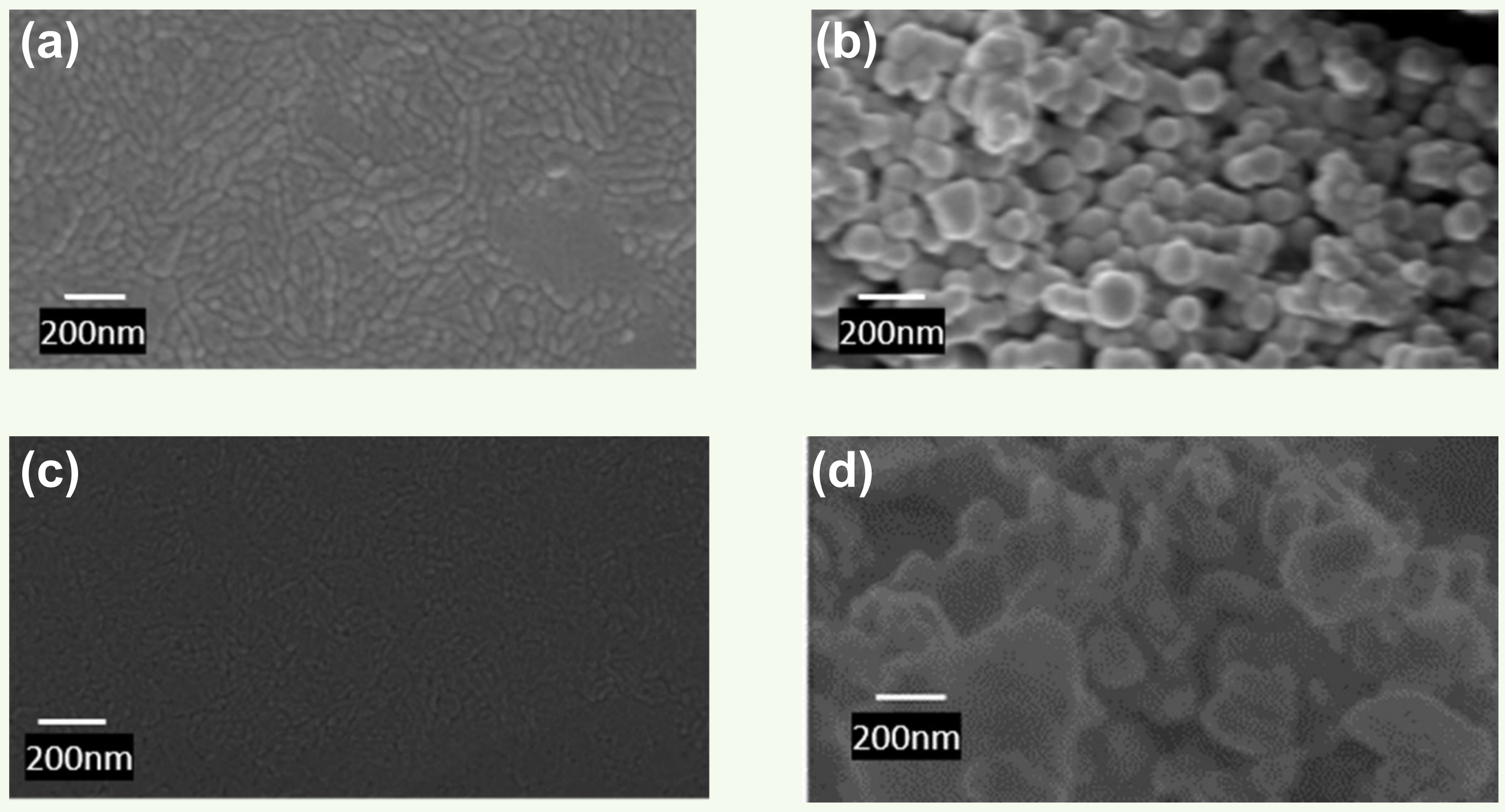


Fig.2. (a) Morphology of hematite thin film prepared by dip coating, (b) Morphology hematite nanoparticles prepared by dip coating, (c) Morphology of hematite thin film prepared by spray-pyrolysis, (d) Morphology hematite nanoparticles prepared by spray-pyrolysis.

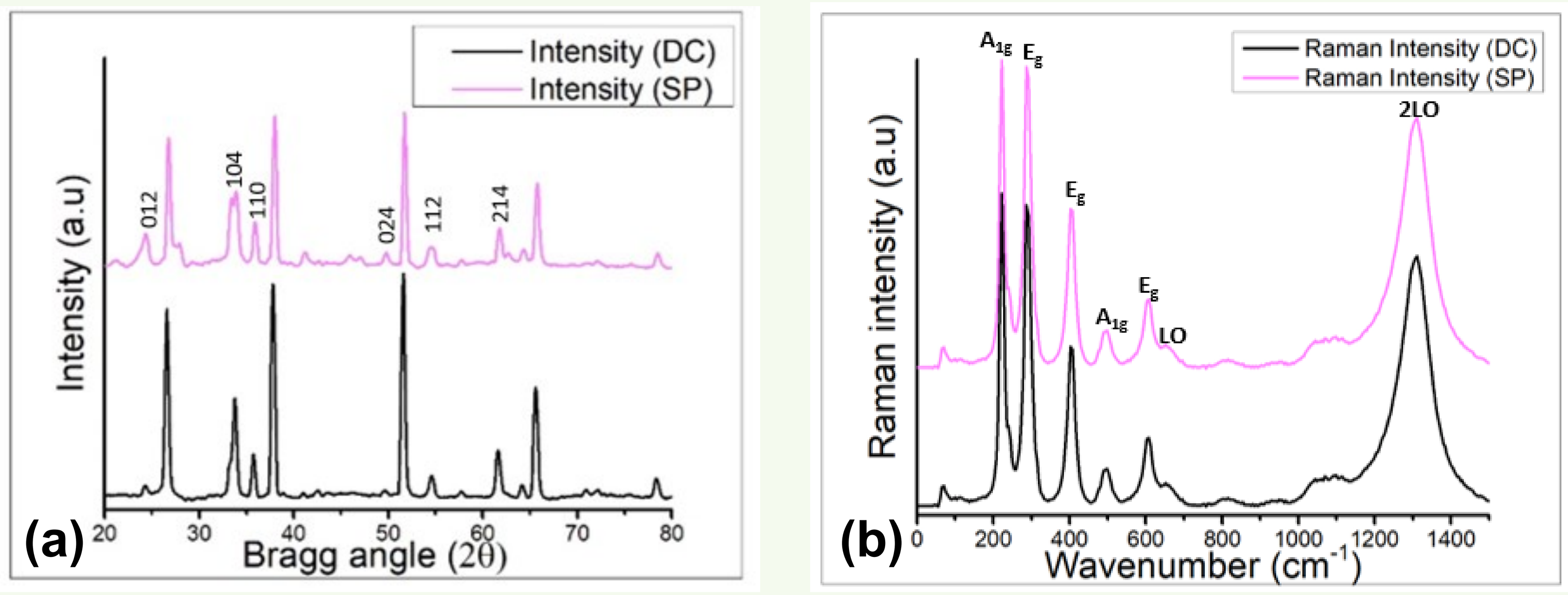


Fig.3. (a) XRD planes of α-Fe_2O_3 films prepared by dip coating and spray-pyrolysis, (b) Raman spectra of α-Fe_2O_3 nanoparticles prepared by dip coating and spray-pyrolysis.

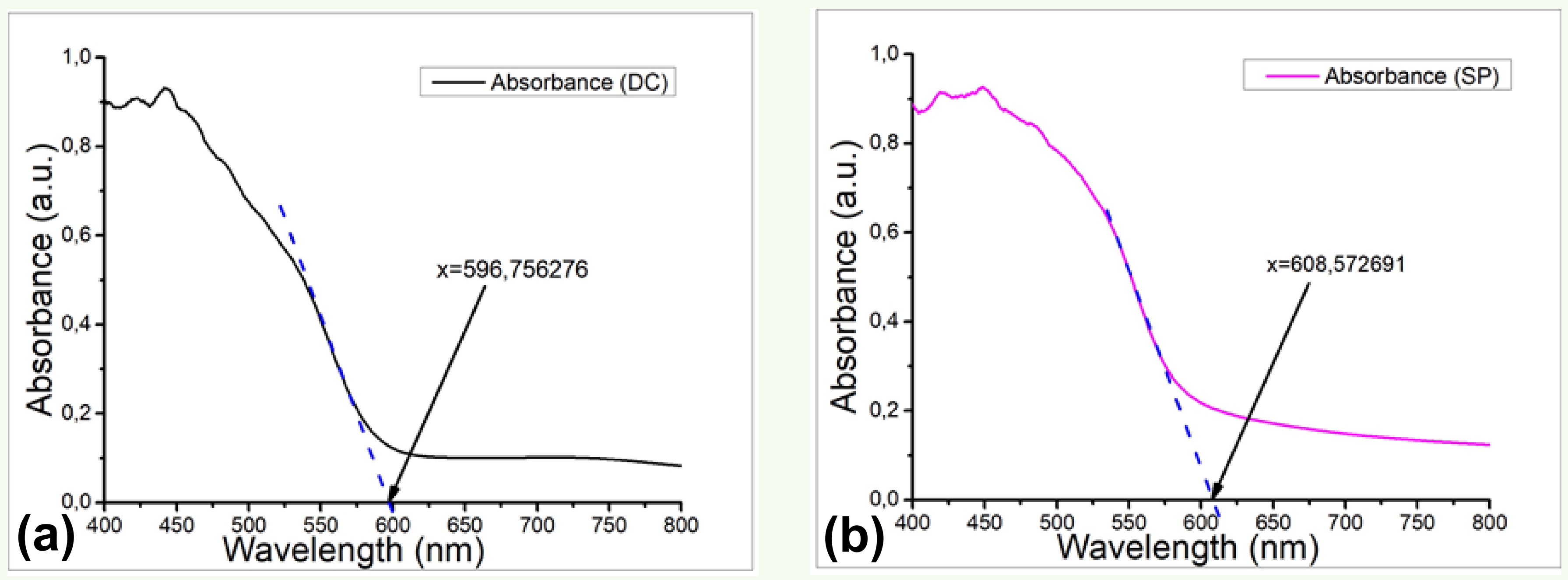


Fig. 4. Absorbance spectra of films prepared by (a) dip coating and (b) spray-pyrolysis. The inset shows the absorbance of both the α-Fe_2O_3 samples.

Conclusion

- Optical studies performed by UV-Vis indicated that samples prepared by spray-pyrolysis showed slightly better absorbance.
- This could be attributed to grain size, as smaller grain size reduces grain boundaries which reduces the distance that light needs to travel in order to be absorbed.
- It was also noted that the spray-pyrolysis samples had a smaller bandgap which is indicative of better absorption.
- This study suggests that the various nanoparticle production methods, as well as annealing repetition can influence the structural integrity of hematite thin films.

Acknowledgements

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References

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