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Candle Flame-Treatment as an Effective Strategy to Enhance the Photoelectrochemical Properties of Ti-doped Hematite Thin Films

Marjan Saeidi [1], Amin Yourdkhani[1*], Seyed Ali Seyed Ebrahimi[2] and Reza Poursalehi[1]

[1] Materials Engineering Department, Faculty of Engineering, Tarbiat Modares University, Tehran, Iran

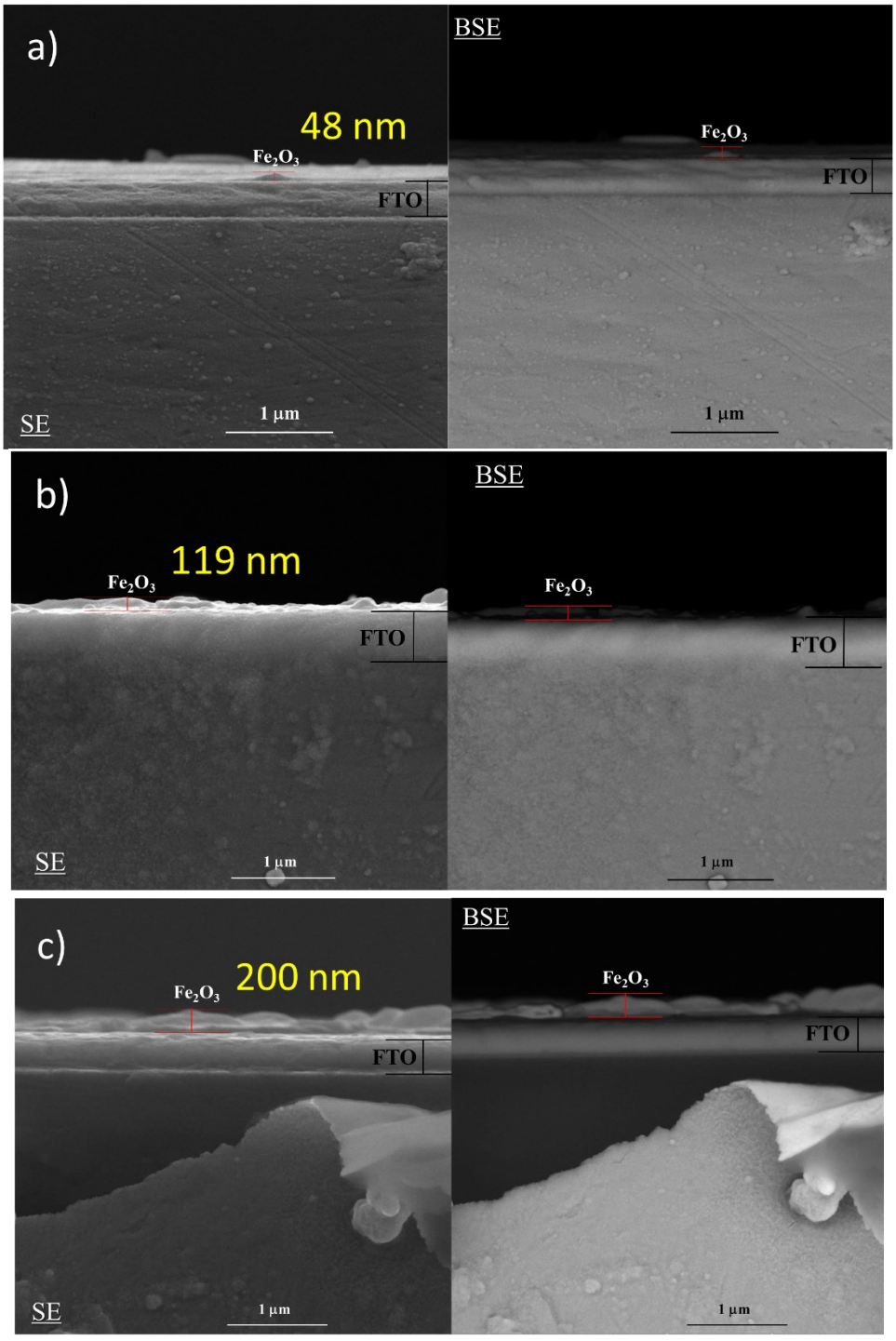
[2] University of Tehran, Advanced Magnetic Materials Research Center, School of Metallurgy and Materials, College of Engineering, Tehran, Iran

Corresponding Author:

*Email: a.yourd@modares.ac.ir ; Tel: +98 21 8288 – 3348, Fax: +98 21 8288- 4390

Supporting Information:

Figure S.1.a-d shows FE-SEM cross-sectional views of 4% Ti-doped samples with different thicknesses in both secondary and back-scattered modes.



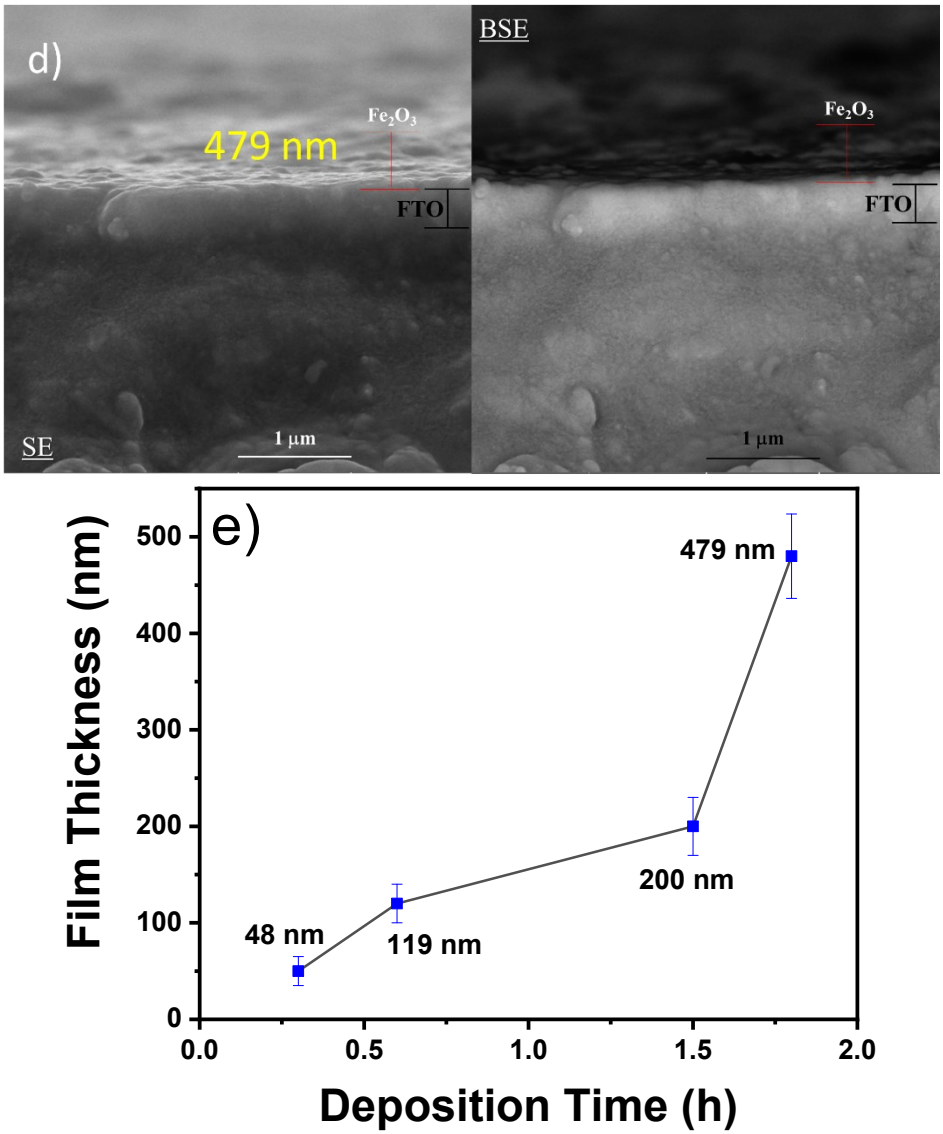
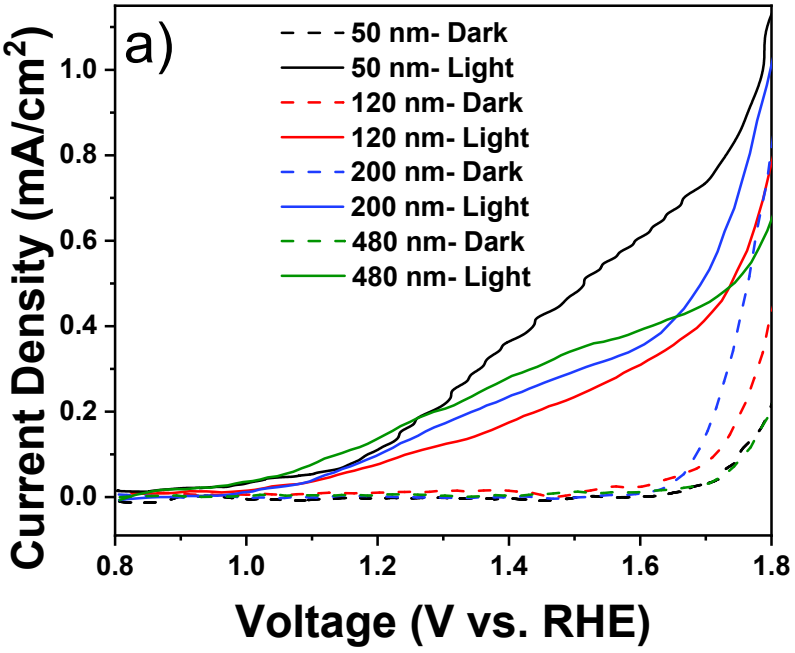


Figure S.1 a-d) FE-SEM cross-sectional views of 4% Ti-doped samples with different thicknesses in both secondary and back scattered modes and e) The variation of film thickness versus deposition time.

The thickness-dependent PEC properties of 4% Ti-doped samples were measured under dark and illumination conditions and their J-V and chronoamperometry plots are shown in Figure S.2.a and b, respectively.

The thinnest film (~50 nm) showed the highest photocurrent density while the thickest one (~480 nm) showed the lowest photocurrent density. Two effects oppositely act on the thickness-dependent PEC properties of thin films. First, as the film thickness increases, the light absorption also increases. Second, the series resistance increases as the film thickness increases as well as the recombination of photo-generated electron-hole pair [1, 2]. The depletion layer created by the charge transfer between the hematite electrode and electrolyte is extended from the surface of the electrode through the film thickness. The depletion layer is an active area for PEC charge separation. Since the thickness of the thinnest film (50 nm) is most likely comparable with the depletion layer, it is expected that this film offers better electron-hole charge separation. Our results indicate that the PEC properties are thickness-dependent in such a way that the thinnest film showed improved PEC properties suggesting that it favors the charge separation. The lower PEC properties of thicker films are attributed to the considerable electron-hole recombination as a result of short diffusion length as well as the negative effect of the grain boundaries.



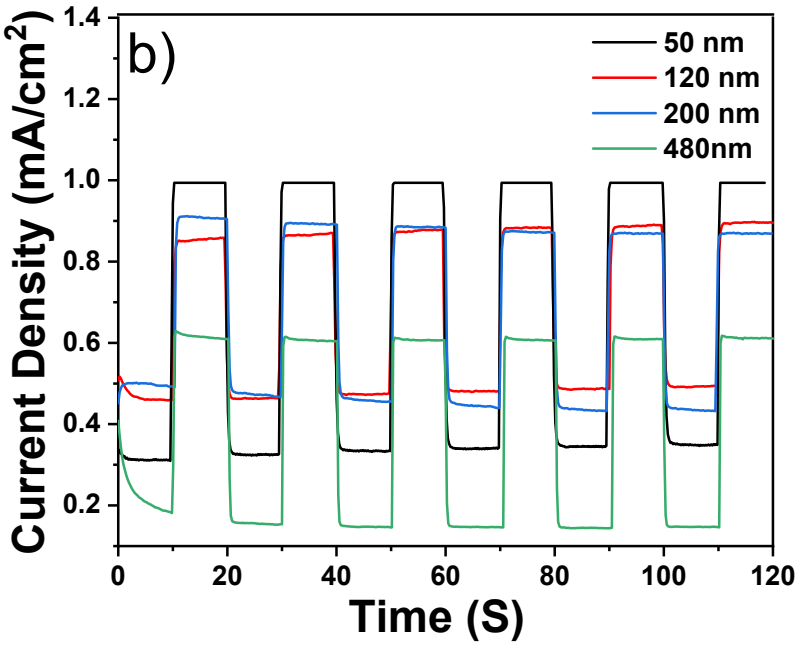


Figure S.2. a) J-V and b) chronoamperometry plots of 4% Ti-doped samples with different thicknesses (the dashed curves in J-V plot correspond to dark current densities)

We flame-treated the samples for 120 seconds and the substrates started flowing and deforming. Therefore, the time for the flame-treatment was chosen 90 seconds. We extended the flame treatment process in four periods and measured the PEC properties after each period.

The chronoamperometry results obtained at 1.8 V vs. RHE under light-off and light-on conditions are shown in Figure 1.a and b. The PEC data show that the current densities were improved under light-off and light-on conditions for the flame-treated sample after two periods. Further extending the flame-treatment process resulted in decreasing the current density. The photocurrent density after the fourth time became lower than that sample flame-treated for the first time.

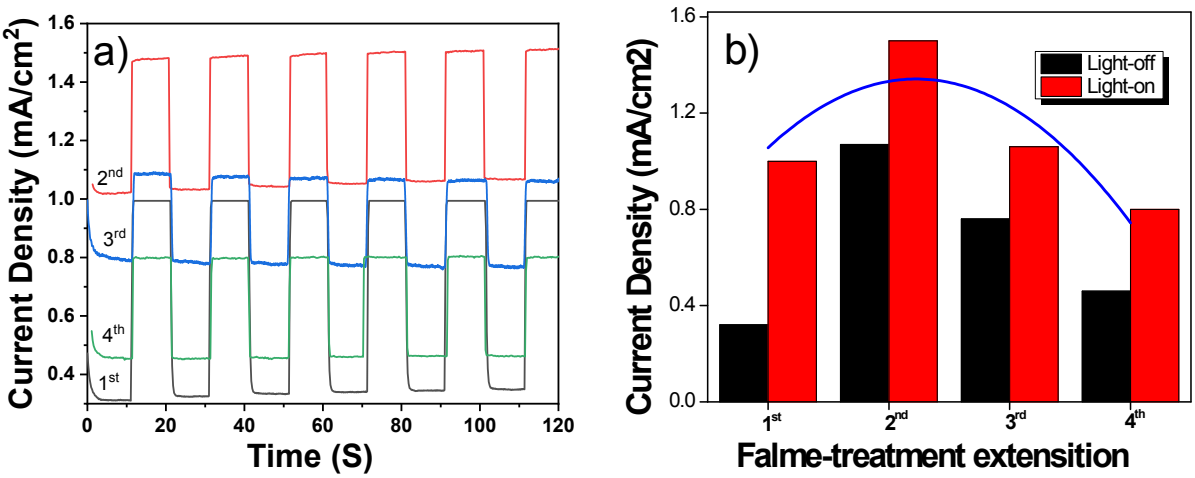


Figure 1. a) The chronoamperometry plots for the candle flame-treatment extensions up to four times at 1.8 V vs. RHE and b) current density at light-off and light-on conditions versus the flame-treatment extension.

Upon candle flame-treatment, the oxygen vacancy defects are introduced into the lattice of hematite [3,4]. It is well understood that oxygen vacancies in hematite improve the bulk conductivity and facilitate surface electrocatalytic reactions [5-8]. Oxygen vacancy defects activate the Ti-doping and as a result, weakly bound electrons are released [9]. Based on the obtained data, the increase in the current density after the second flame-treatment is more likely relates to the complete activation of Ti-doping which increases the concentration of weakly bound electrons. However, the current density was decreased upon extending the flame-treatment process for the 3rd and 4th times. Wang *et al.* [10] suggested that oxygen vacancies on the surface act a traps states which has a negative side effect with increasing the interfacial charge recombination. Therefore, the maximum photocurrent can be achieved by balancing the positive and negative effects of oxygen vacancies.

References

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