Correlation of Surface Structure and Water Oxidation Photocurrent in Oxygen Plasma-treated Iron Oxide Photoanode

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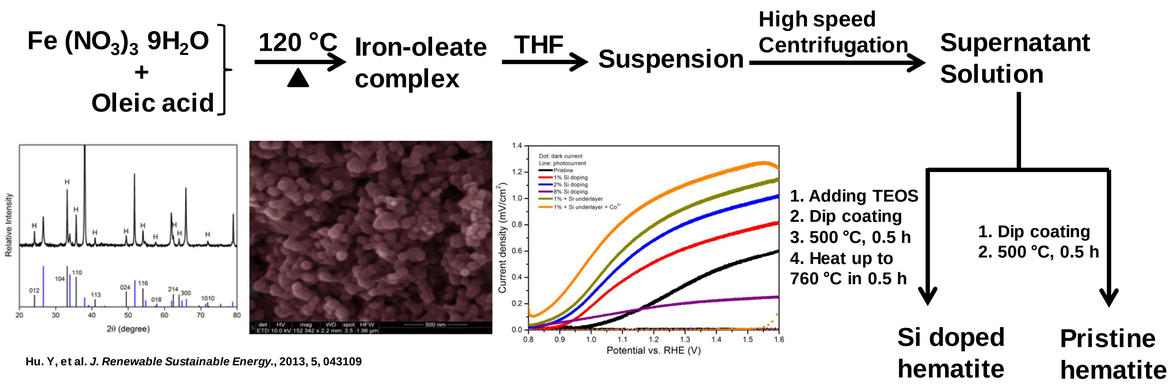
Introduction

Hematite (α-Fe_2O_3) is a prospective photoanode material for the oxygen evolution reaction upon water splitting. The surface states of hematite have been under scrutiny for several decades. However, their origin and influence on the photoelectrochemical performance is still poorly understood. In the present study, hematite films were prepared by dip-coating fluorine-doped tin oxide coated glass substrate followed by surface modification via oxygen plasma treatment. O 1s core level X-ray photoelectron spectra and resonant valence band photoemission at Fe 3p edge suggested the filling of oxygen vacancies and oxidation of Fe^{2+} upon oxygen plasma treatment. Electrochemical impedance spectroscopy was employed to determine the degree of charging of surface states. An existence of strong correlation between oxygen vacancies, surface states and photocurrent density was demonstrated.

Dip coating method for hematite preparation



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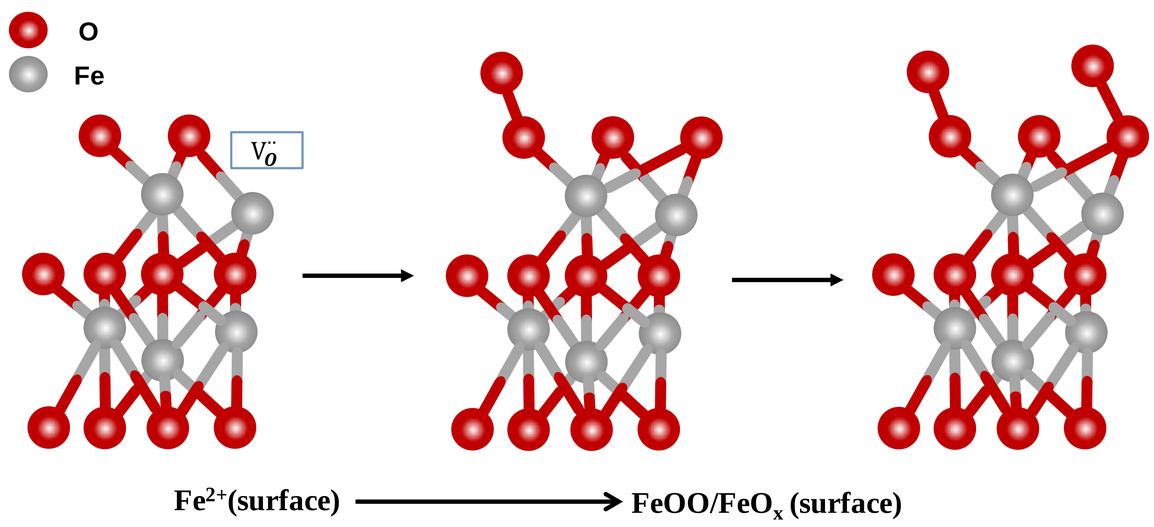
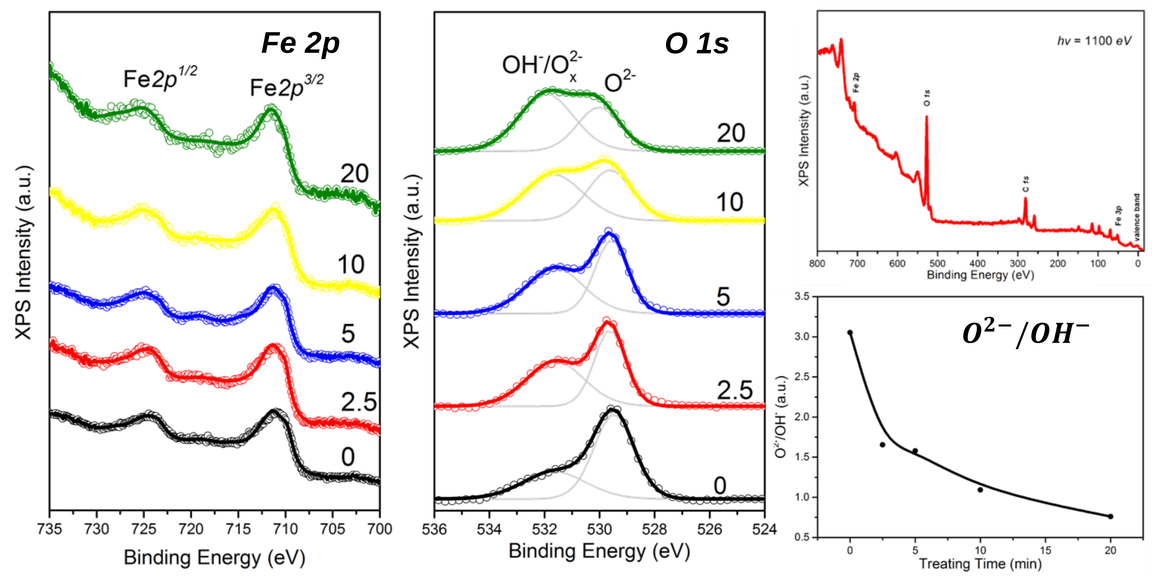
- Photocurrent density over 1 mA/cm^2 at 1.23 V_{RHE} achieved for Si doped hematite sample
- Undoped hematite samples were post-treated *via* oxygen plasma for this study

Surface during O_2 plasma treatment



- We found that the surface of hematite was oxidized after oxygen plasma treatment, suggesting filling of oxygen vacancies. Combined results from O 1s XPS, formation of iron oxyhydrate is hypothesized.
- Based on previous theoretical and DFT studies on hematite surface, oxygen vacancy is necessary during water oxidation. It suggests that filling oxygen vacancy after plasma treatment may negatively affect photoelectrochemcial properties of hematite photoanode.

XPS analysis on plasma treated hematite samples



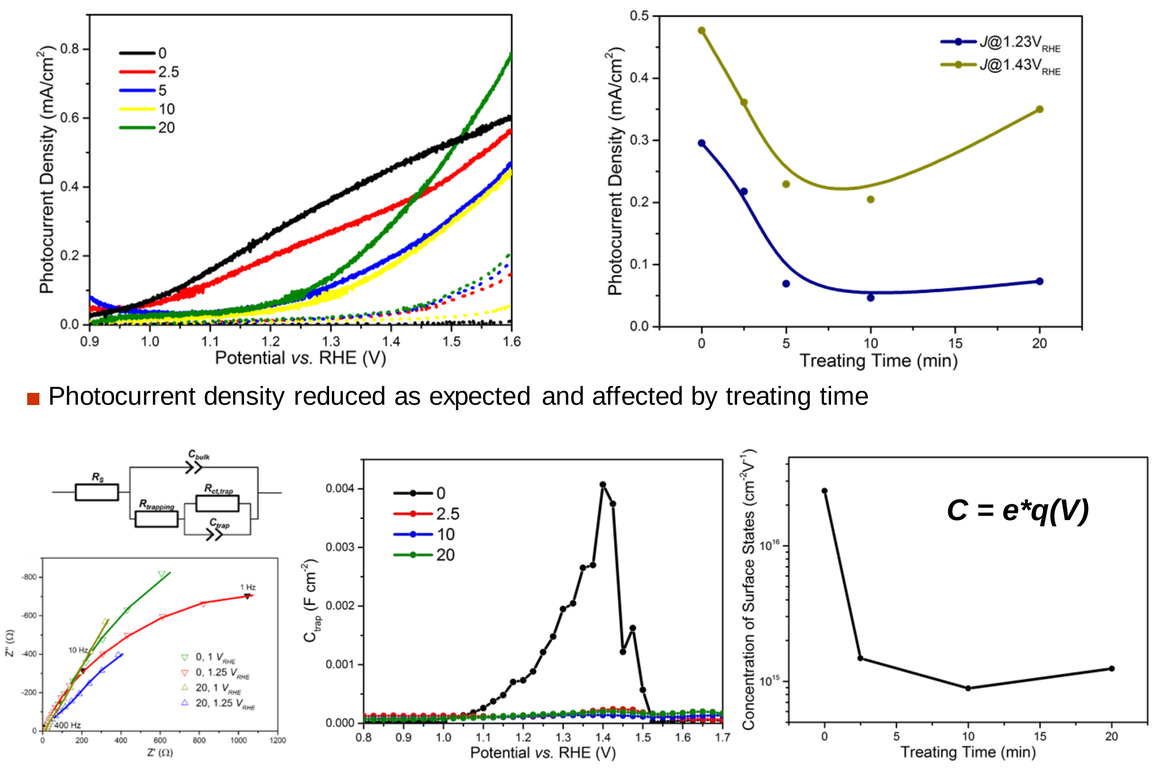
O 1s core level XPS after O_2 plasma treatment

- OH^-/O_x^{2-} peak (~532 eV) enhanced compared to O^{2-} peak (~ 529.5 eV)
- O^{2-} peak shifted to high binding energy due to OH^-/O_x^{2-} peak
- Possible reason: Formation of OOH or OH group on surface. Investigation on oxidized state of Fe needed

Fe 2p core level XPS

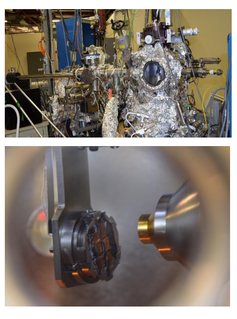
- Differences are small between samples thus difficult for analysis
- Other analysis method needed

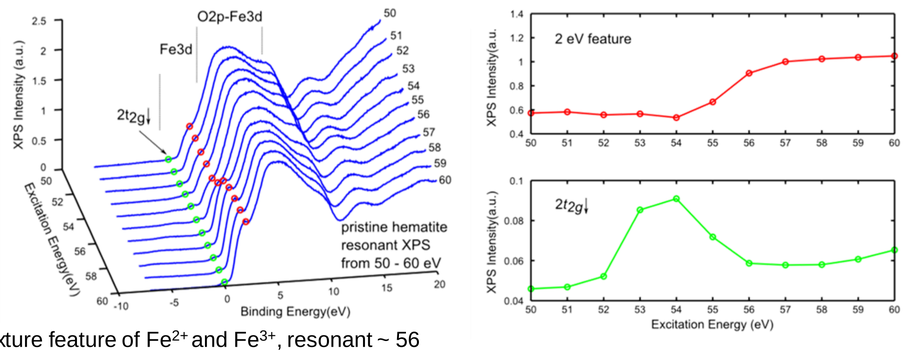
Photoelectrochemcial properties and surface states



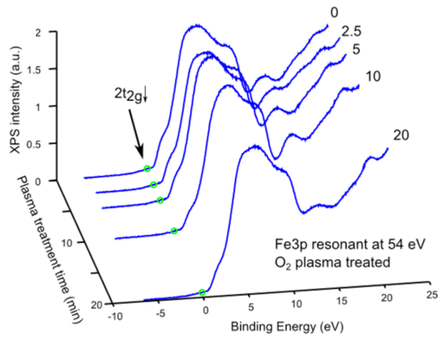
- Photocurrent density reduced as expected and affected by treating time
- Surface states were studied by impedance spectroscopy under illumination. The capacitance of trapped states suggests the charging/discharging process on surface states. It decreased after oxygen plasma treatment, indicating less photoexicted holes accumulating on surface states for water splitting
- Reduced concentration of surface states around 1.4 V_{RHE} on surface after treatment
- Combined with surface structure study by O 1s XPS and resonant valence band XPS (O^{2-}/OH^- and $2t_{2g}\downarrow$ vs. treating time), an obvious correlation between surface structure, surface states and photoelectrochemcial performance was demonstrated

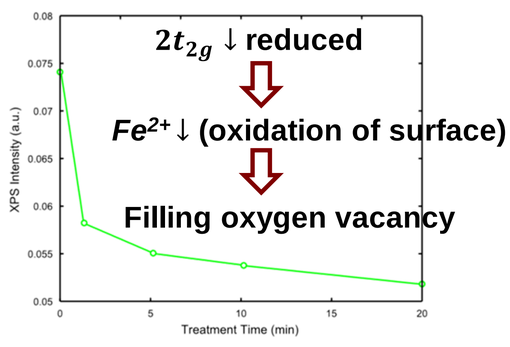
Resonant valence band XPS





- 2 eV feature is a mixture feature of Fe^{2+} and Fe^{3+}, resonant ~ 56
- According to band theory, 0 eV feature is from and **ONLY** from $2t_{2g}\downarrow$ state of Fe^{2+}. The undoped hematite contains Fe^{2+} on surface and its resonant energy is around 54 eV
- Resonant energy of 54 eV was selected for best contrast. Intensity of $2t_{2g}\downarrow$ feature vs. treatment time suggests reduced Fe^{2+} concentration after oxygen plasma treatment (oxidation of sample surface)





Conclusion

- Oxygen plasma treatment strongly modified hematite surface
- From XPS and resonant valence band XPS, plasma treatment filled oxygen vacancies on hematite surface. Formation of iron oxyhydrate sites were hypothesized.
- Photoelectrochemcial properties of treated hematite samples reduced as expected. Electrochemcial impedance spectroscopy suggest decreasing the concentration of surface states of hematite sample.
- Obvious correlation between surface structure, surface states and photocurrent density was demonstrated.

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