

Supplementary Material for:

Improved Photoelectrochemical Performance of Chemically Grown Pristine Hematite Thin Films

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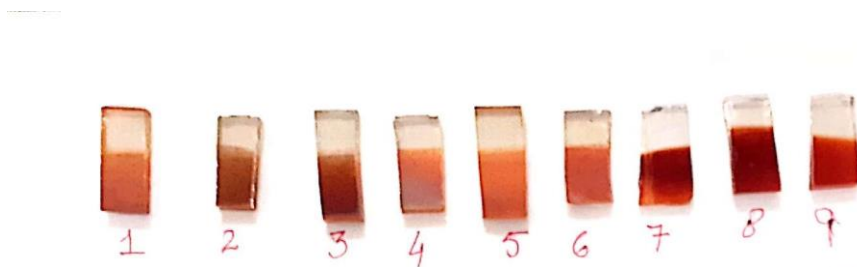


Fig. S1. Images of representative hematite films prepared by the SP method at 525 °C using FeCl_3 precursor; (1) in ethanol (2) in methanol using FeCl_3 , using $\text{Fe}(\text{NO}_3)_3$; in (3) ethanol and (4) methanol and using $\text{Fe}(\text{acac})_3$; in (5) ethanol and (6) methanol. (7) With FeCl_3 precursor in methanol by CVD at 500°C, and with FeCl_3 precursor by AACVD at 525°C in; (8) methanol and (9) ethanol.

Table SI. Thin films of iron oxides prepared using SP technique at different temperatures and conditions.

| Temperature/°C | Deposition Time/min | Precursor used/ 0.1M in Ethanol solvent | Precursor used/ 0.1M in Methanol solvent |
|----------------|---------------------|---|--|
| 450 | 20 | FeCl ₃ | FeCl ₃ |
| | 25 | Fe(NO ₃) ₃ | Fe(NO ₃) ₃ |
| | 30 | Fe(acac) ₃ | Fe(acac) ₃ |
| 475 | 20 | FeCl ₃ | FeCl ₃ |
| | 25 | Fe(NO ₃) ₃ | Fe(NO ₃) ₃ |
| | 30 | Fe(acac) ₃ | Fe(acac) ₃ |
| 500 | 20 | FeCl ₃ | FeCl ₃ |
| | 25 | Fe(NO ₃) ₃ | Fe(NO ₃) ₃ |
| | 30 | Fe(acac) ₃ | Fe(acac) ₃ |
| 525 | 20 | FeCl ₃ | FeCl ₃ |
| | 25 | Fe(NO ₃) ₃ | Fe(NO ₃) ₃ |
| | 30 | Fe(acac) ₃ | Fe(acac) ₃ |

Table SII. Thin films of iron oxide prepared using 0.1M FeCl₃ by CVD technique at different temperatures and deposition times.

| Temperature/°C | Deposition Time/min in Ethanol Solvent | Deposition Time/min in Methanol Solvent |
|----------------|--|---|
| 450 | 10 | 10 |
| | 15 | 15 |
| | 20 | 20 |
| | 25 | 25 |
| | 30 | 30 |
| 475 | 10 | 10 |
| | 15 | 15 |
| | 20 | 20 |
| | 25 | 25 |
| | 30 | 30 |
| 500 | 10 | 10 |
| | 15 | 15 |
| | 20 | 20 |
| | 25 | 25 |
| | 30 | 30 |

Table SIII. Thin films of iron oxide prepared using 0.1M FeCl₃ in different solvents by AACVD technique at different temperatures and deposition times.

| Temperature/°C | Deposition Time/min | Precursor FeCl ₃ (0.1M) / Solvent |
|----------------|---------------------|--|
| 450 | 20 | Ethanol |
| | | Methanol |
| | 25 | Ethanol |
| | | Methanol |
| | 30 | Ethanol |
| | | Methanol |
| 475 | 20 | Ethanol |
| | | Methanol |
| | 25 | Ethanol |
| | | Methanol |
| | 30 | Ethanol |
| | | Methanol |
| 500 | 20 | Ethanol |
| | | Methanol |
| | 25 | Ethanol |
| | | Methanol |
| | 30 | Ethanol |
| | | Methanol |
| 525 | 20 | Ethanol |
| | | Methanol |
| | 25 | Ethanol |
| | | Methanol |
| | 30 | Ethanol |
| | | Methanol |

Table SIV. Average crystallite size, from XRD data using Scherrer formula, of α -Fe₂O₃ films prepared by SP, CVD and AACVD methods, using a FeCl₃ precursor and a methanol solvent for a deposition time of 30 min at different temperatures.

| Temperature / °C | Crystallite size / nm | | |
|------------------|-----------------------|-----|-------|
| | SP | CVD | AACVD |
| 450 | 23 | 15 | 6 |
| 475 | 23 | 10 | 7 |
| 500 | 17 | 5 | 7 |
| 525 | 17 | 5 | 7 |

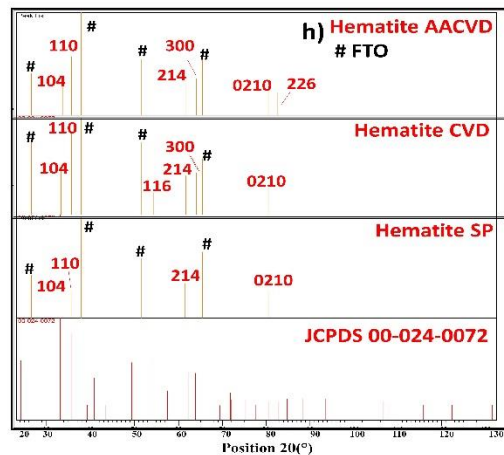
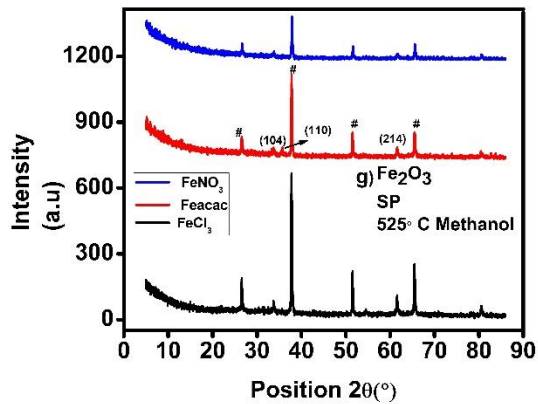
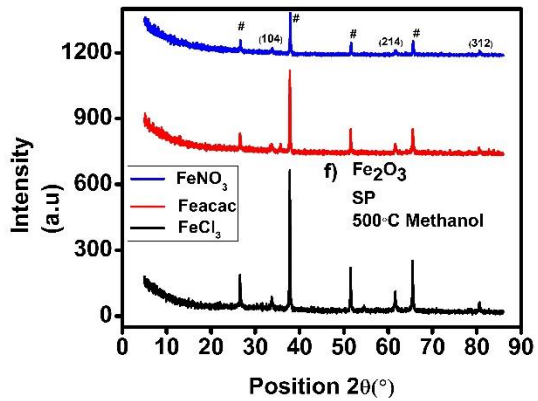
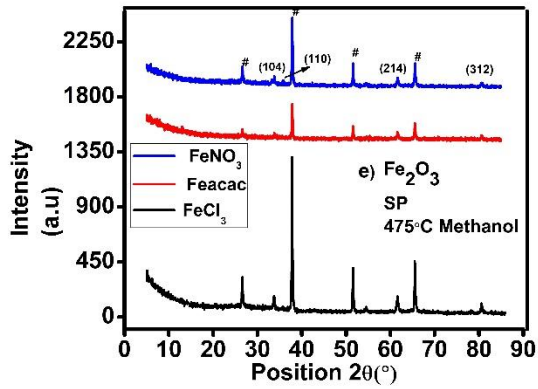
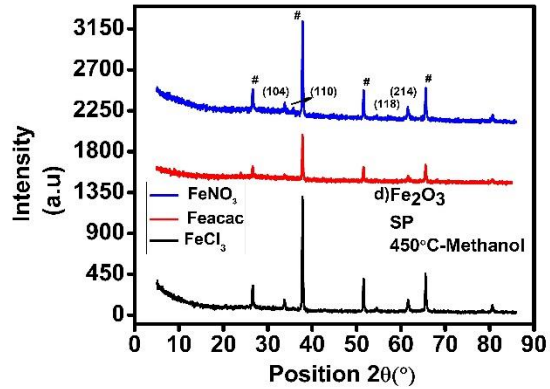
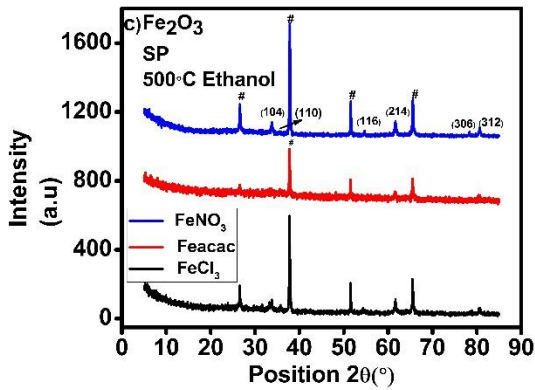
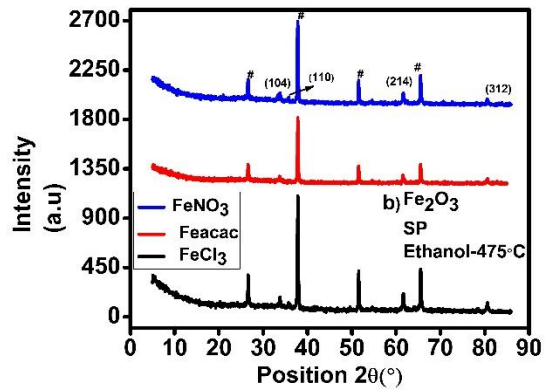
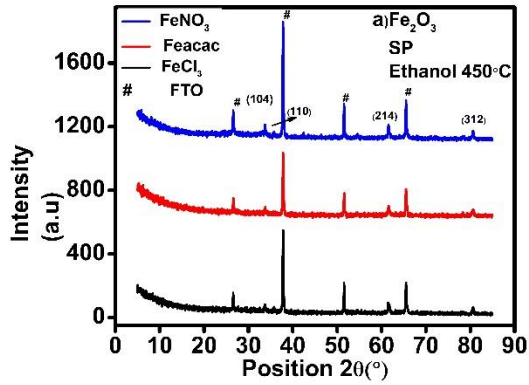


Fig. S2. PXD patterns of hematite films fabricated at different temperatures in (a,b,c) ethanol and (d,e,f,g) methanol by SP methods; (h) line patterns of hematite thin films prepared by using FeCl_3 precursor in methanol annealed at 525°C by SP, CVD and AACVD methods with JCPDS card # 00-024-0072

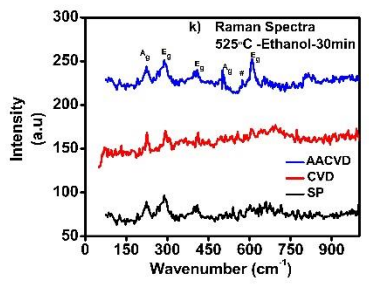
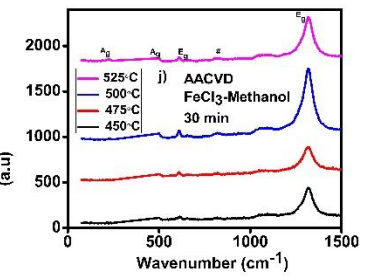
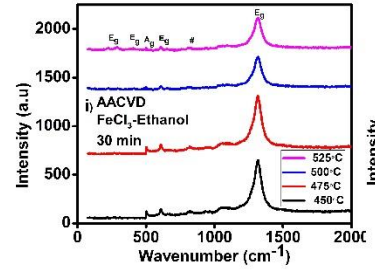
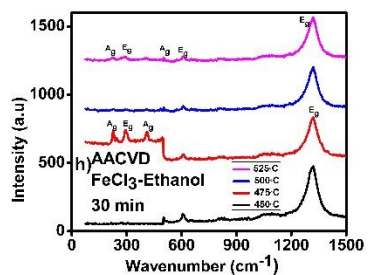
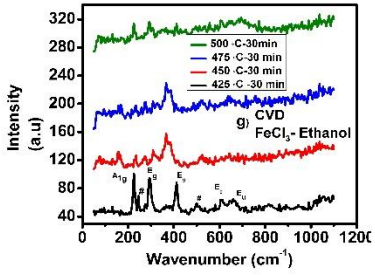
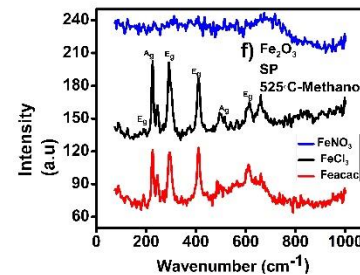
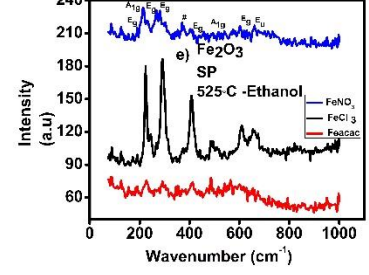
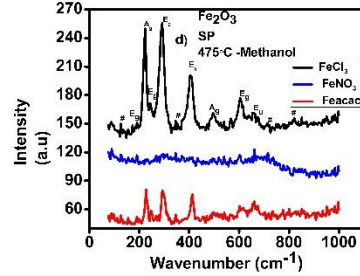
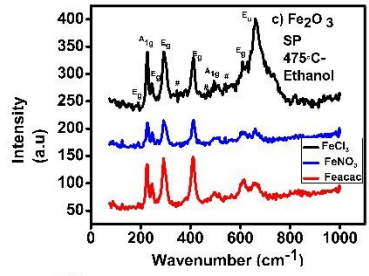
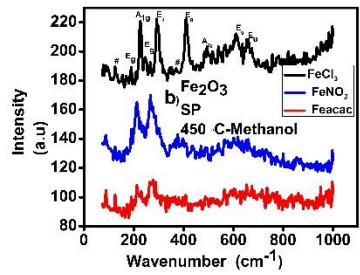
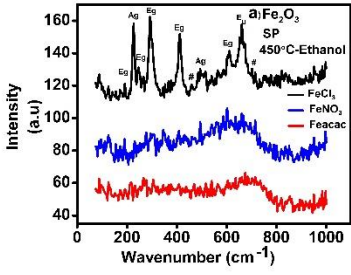


Fig. S3. Raman spectra of hematite thin films by; SP method at 450°C in (a) ethanol , (b)in methanol, at 475°C (c) in ethanol (d) in methanol, at 525°C (e) in ethanol (f) in methanol, (g) CVD method in ethanol at various temperatures, (h) AACVD method in ethanol at various temperatures, (i and j) AACVD method in ethanol and methanol at various temperatures in extended frequency ranges (k) comparative Raman spectra of the films by SP, CVD and AACVD techniques at 525°C.

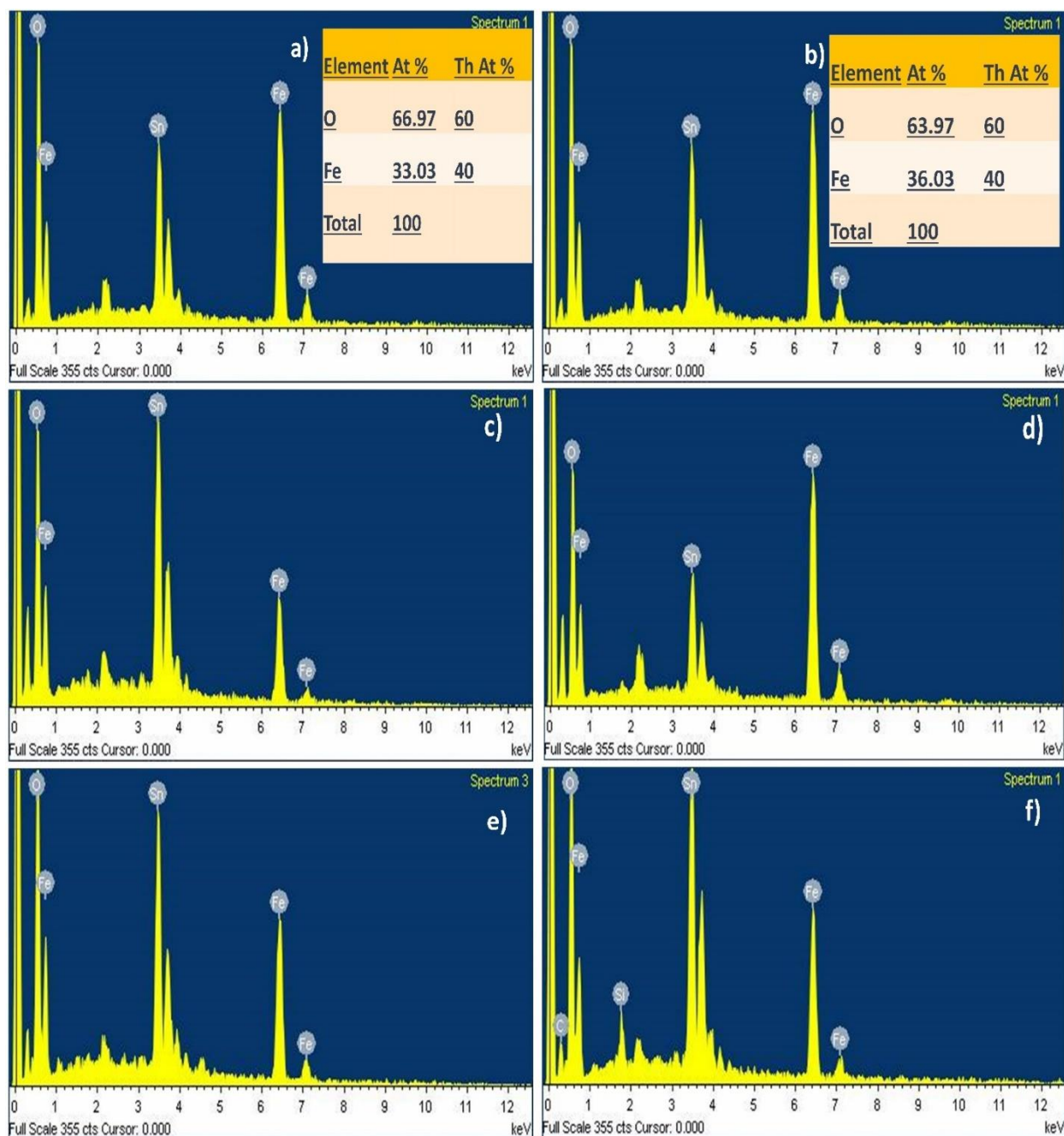


Fig.S4. EDX Spectra and elemental analysis data of pristine hematite formed by using $\text{Fe}(\text{NO}_3)_3$ by SP at 525°C in (a) methanol (b) in ethanol, (c) by using $\text{Fe}(\text{acac})_3$ and (d) FeCl_3 in ethanol, (e) using FeCl_3 in methanol (f) using FeCl_3 by CVD method.

Table SV. Grain size of hematite particles prepared by different methods.

| <u>Method</u> | <u>Temperature/°C</u> | <u>Precursors</u> | <u>Solvent</u> | <u>Average particle size/nm</u> |
|----------------------|------------------------------|--------------------------|-----------------------|--|
| CVD | 500 | FeCl ₃ | Ethanol | 133 |
| SP | 525 | FeCl ₃ | Methanol | 182 |
| AACVD | 525 | FeCl ₃ | Methanol | 126 |

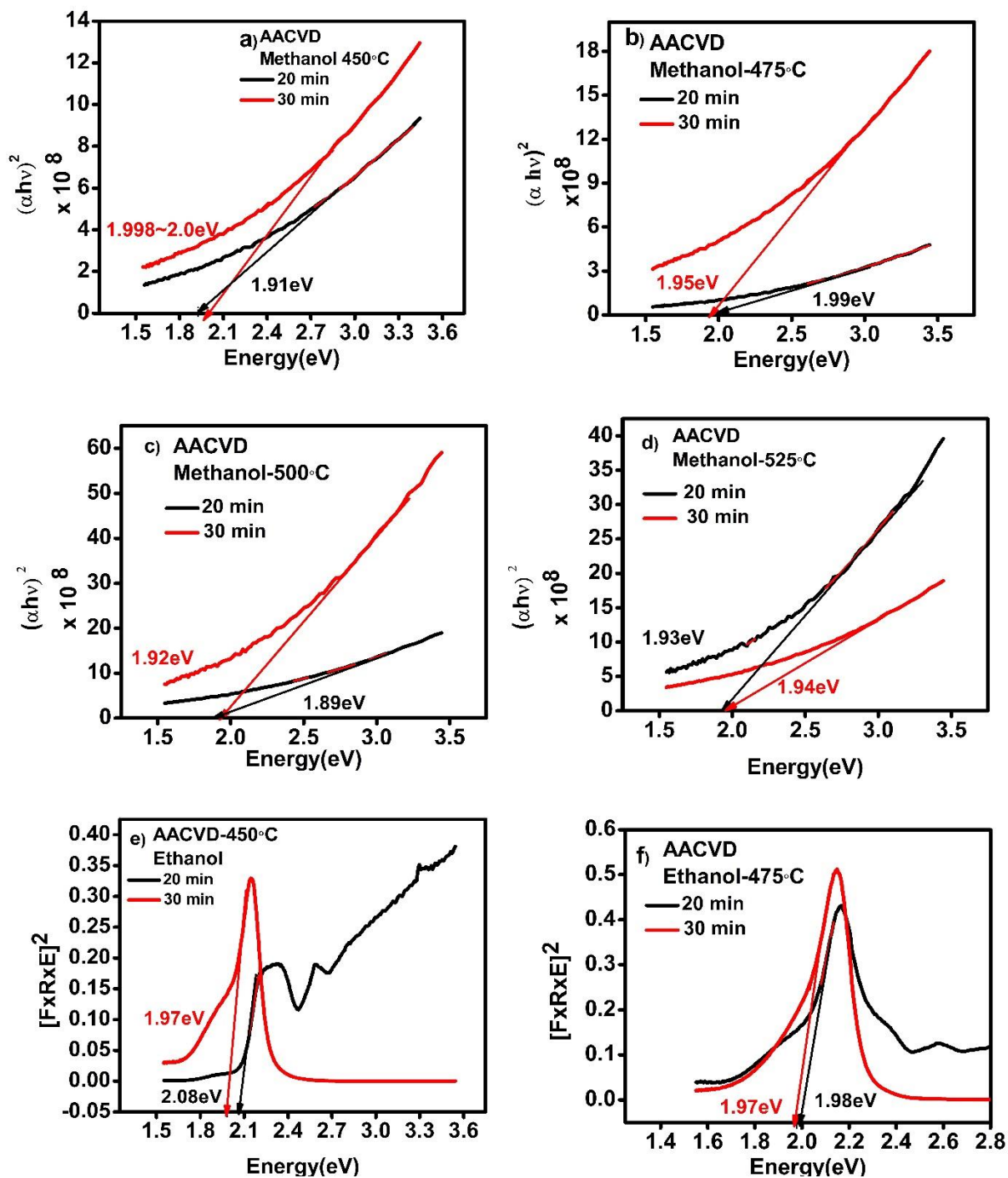


Fig.S5. UV-Vis (a-d) absorbance spectra in methanol solvent and (e-f) reflectance spectra in ethanol solvent of pristine hematite films prepared by AACVD at different temperatures for different times.

Table. SVI. Band gap data for the prepared hematite films as taken from the Tauc plots (see Fig 4b) for methanol solvent and by K-M plots for ethanol solvent.

| Temp/o C | Time/<u>min</u> | Eg/eV in Methanol | Eg/eV in Ethanol |
|-----------------|------------------------|--------------------------|-------------------------|
| 450 | 20 | 1.91 | 2.08 |
| | 30 | 1.99-2.0 | 1.97 |
| 475 | 20 | 1.99 | 1.98 |
| | 30 | 1.95 | 1.97 |
| 500 | 20 | 1.89 | - |
| | 30 | 1.92 | - |
| 525 | 20 | 1.93 | 2.05 |
| | 30 | 1.94 | 2.08 |

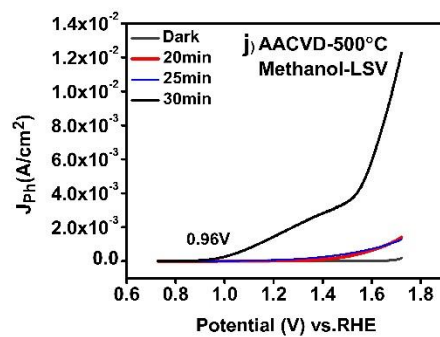
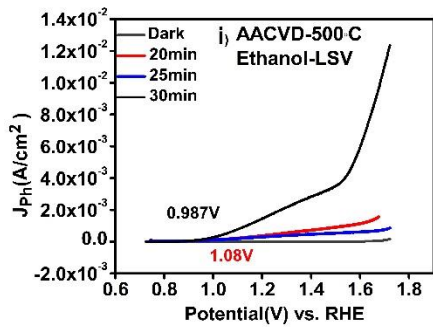
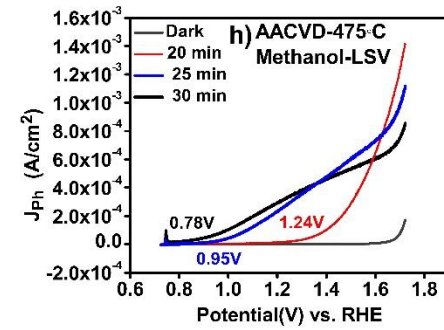
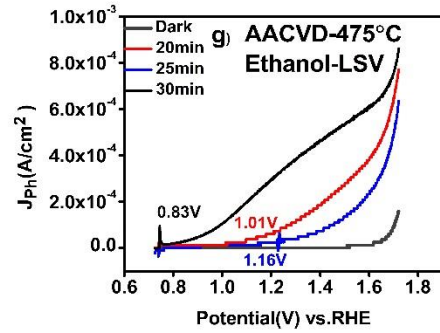
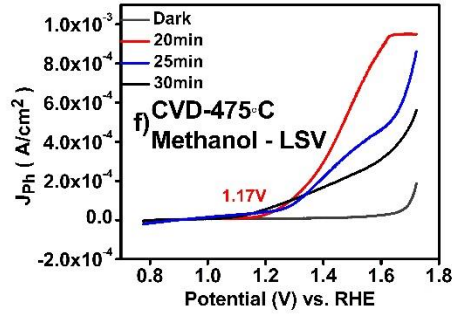
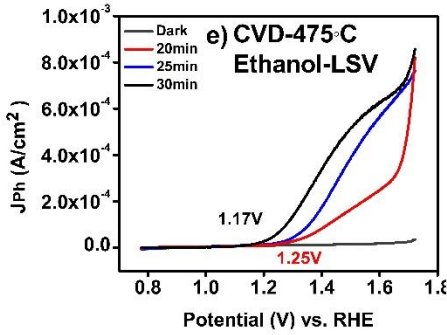
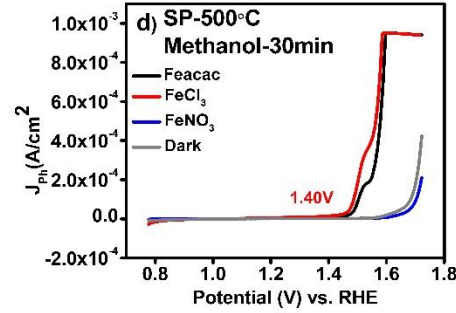
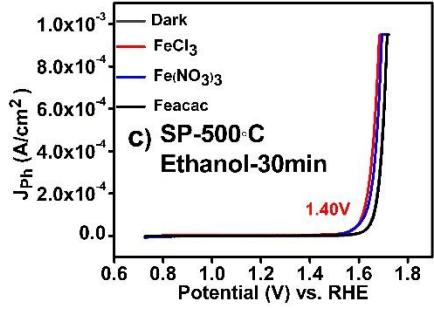
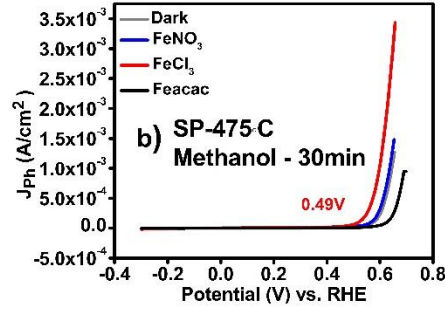
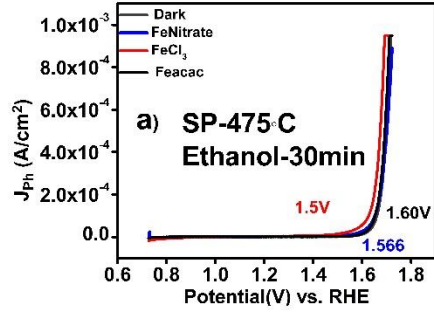


Fig.S6. LSVs of hematite thin films fabricated by SP for 30 min using three precursors in (a) ethanol at 475 °C , (b) methanol at 475 °C, (c) ethanol at 500 °C, (d) methanol at 500 °C, using FeCl₃ precursor for 20, 25 and 30 min at 475 °C by CVD in; (e) ethanol and (f) methanol, under same conditions by AACVD in; (g) ethanol, (h) methanol, and by AACVD at 500 °C in; (i) ethanol, (j) methanol.

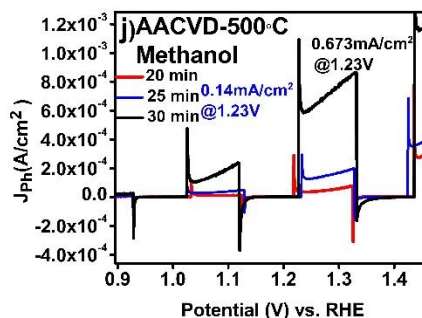
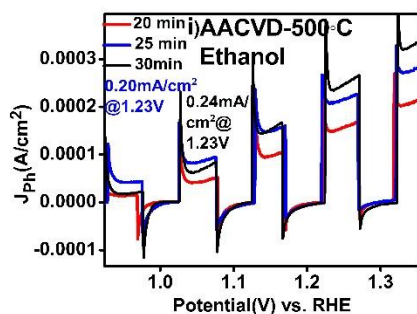
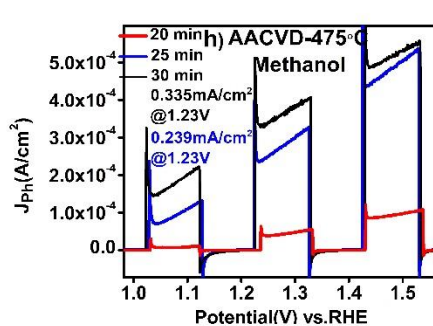
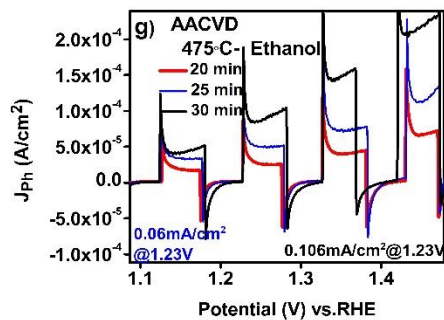
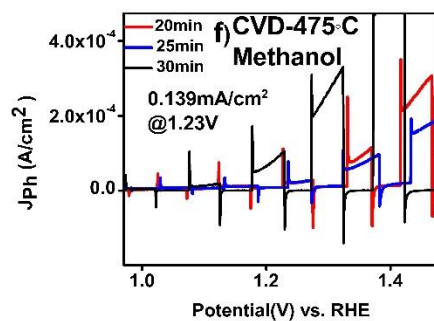
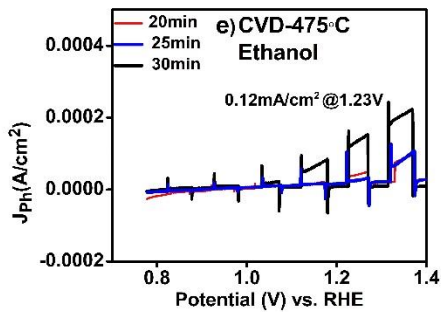
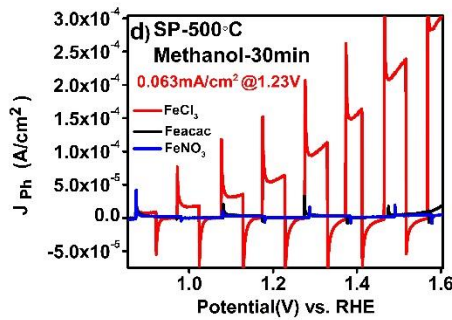
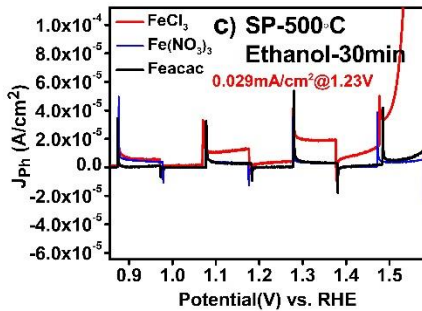
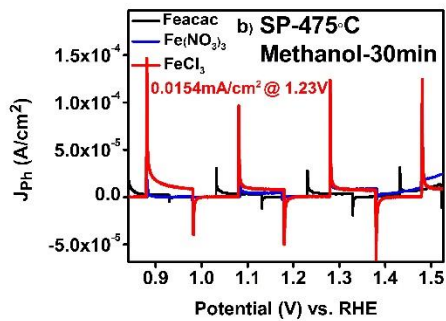
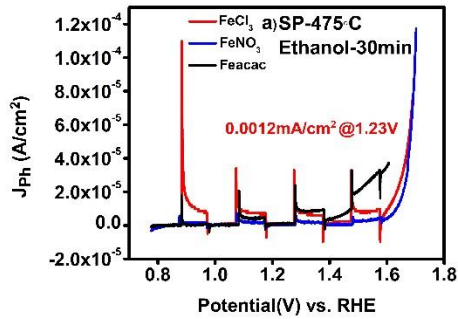


Fig. S7. Chopped light LSVs of the hematite thin films fabricated from FeCl_3 by SP, CVD and AACVD methods at different preparation temperatures; (a,c) SP films using ethanol (b,d) SP films using methanol (e) CVD films using ethanol, (f) CVD films using methanol, (g,i) AACVD films using ethanol (h,j) AACVD films using methanol.

Table SVII. PEC performance of the prepared hematite photoanodes under various set of conditions with 30 minutes deposition period, by the three methods.

| Technique | Precursor | Solvent | Annealing Temperature / °C | Photocurrent-Density / mA cm ⁻² | Onset Potential / V |
|-----------|--|----------|-------------------------------|--|------------------------|
| CVD | FeCl ₃ | Ethanol | 475 | 0.129 | 1.17 |
| CVD | FeCl ₃ | Ethanol | 500 | 0.123 | 1.01 |
| CVD | FeCl ₃ | Methanol | 475 | 0.139 | 1.07 |
| CVD | FeCl ₃ | Methanol | 500 | 0.29 | 0.99 |
| SP | FeCl ₃ | | 475 | 0.0012 | 1.5 |
| | FeCl ₃ | | | | 1.56 |
| | Fe(NO ₃) ₃ . 9H ₂ O | | | | 1.60 |
| | Feacac | | | | |
| SP | FeCl ₃ | Ethanol | 500 | 0.0029 | 1.4 |
| | FeCl ₃ | | | | 1.49 |
| | Fe(NO ₃) ₃ . 9H ₂ O | | | | 1.6 |
| | Feacac | | | | |
| SP | | | 525 | 0.05 | 1.58 |
| | FeCl ₃ | | | 0.01 | 1.5 |
| | Fe(NO ₃) ₃ . 9H ₂ O | | | - | 1.6 |
| | Feacac | | | | |

| | | | | | |
|-------|--|----------|-----|--------|------|
| SP | | Methanol | 475 | 0.0154 | 0.48 |
| | FeCl ₃ | | | - | 0.55 |
| | Fe(NO ₃) ₃ . 9H ₂ O | | | - | 0.61 |
| | Feacac | | | | |
| SP | | | 500 | 0.063 | 1.45 |
| | FeCl ₃ | | | - | 1.62 |
| | Fe(NO ₃) ₃ . 9H ₂ O | | | - | 1.47 |
| | Feacac | | | | |
| SP | | | 525 | 0.12 | 1.39 |
| | FeCl ₃ | | | - | 1.4 |
| | Fe(NO ₃) ₃ . 9H ₂ O | | | - | 1.54 |
| | Feacac | | | | |
| AACVD | | Ethanol | 475 | 0.106 | 0.83 |
| - | FeCl ₃ | | 500 | 0.24 | 0.98 |
| | | | 525 | 1.13 | 0.89 |
| AACVD | | Methanol | 475 | 0.335 | 0.78 |
| | | | 500 | 0.673 | 0.96 |
| | FeCl ₃ | | 525 | 1.23 | 0.76 |

Table SVIII. Amount of the gases evolved on the ACACVD fabricated hematite photoanode, using methanol solvent at 525°C, in a hydrogen generation device as measured by coupled gas chromatograph.

| Time / h | H ₂ produced / $\mu\text{mol cm}^{-2}$ | O ₂ produced / $\mu\text{mol cm}^{-2}$ |
|----------|---|---|
| 1 | 0 | 0.721 |
| 2 | 0.045 | 0.956 |
| 3 | 0.121 | 0.977 |
| 4 | 0.215 | 1.063 |
| 5 | 0.328 | 1.174 |
| 6 | 0.402 | 1.225 |