Redox Reaction in Water Splitting

Oxidation: \[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \] (1.23 V vs. SHE)

Reduction: \[ 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \] (0.0 V vs. SHE)

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2 \]

- $\Delta G$ of water splitting reaction is positive
- Energy intensive process
- Oxidation of water involves 4e\(^-\) and is thermodynamically more challenging

$\Delta G^0 = 238 \text{ kJ mol}^{-1}$
Classification of Water Splitting Processes

Energy
- Light => Photo-catalytic
- Electrical => Electrochemical
- Light + Electrical => Photo-electrochemical

Mechanism
1. Artificial Photosynthesis
2. Water splitting using – semiconductors etc.
Natural photosynthesis

i. Absorption of light by PSII & generation of e⁻
ii. Cascade of downhill movement of e⁻ along very closely spaced energy levels to PSI and h⁺ used up for H₂O oxidation -100% charge separation
iii. Photoexcitation of PSI
iv. Downhill movement of e⁻ and donation of e⁻ to NADP⁺
v. 2 photons give one e⁻ and one h⁺
Mechanism of Photosynthesis

- Photons excite Chl to Chl*
- Chl* donates an electron (e⁻) to CO₂, forming (CHO)n
- CO₂ oxidation results in the formation of (CHO)n
- WOC (Water Oxidation Complex)
- WOC accepts electrons from Chl⁺ and 2H₂O, producing 4H⁺ and O₂

WOC = Water Oxidation Complex
Mechanism of Artificial Photosynthesis

Ru(II)* → Ru(II)

S₂O₈²⁻ → SO₄²⁻ + SO₄⁻

Catalyst

Photons

Ru(II) → Ru(III)

Catalyst =⇒ Mⁿ⁺ / Mⁿ⁺₁⁺

2H₂O → 4H⁺ + O₂
Photosynthetic center in plants

\[ \text{Mn}_4\text{CaO}_4 \]

*core main component of PSII*
Photocatalytic activity in oxide with Mn$_4$O$_4$ cubane

Greenbaltt and coworkers, J. Am. Chem. Soc., 2010, 132, 11467
LiMn$_2$O$_4$ and effect of delithiation

LMO = LiMn$_2$O$_4$ ; Mn(III/IV)
DLMO = Delithiated LMO ; Mn(IV)

- $O_2$ evolution increases only slightly on delithiation
- $O_2$ evolved per unit surface area is higher for LMO
- Rate of $O_2$ evolved is slightly high for LMO
- Turn over frequency (TOF)

$LMO = 2.2 \times 10^{-5}$ s$^{-1}$ & $DLMO = 2 \times 10^{-5}$ s$^{-1}$

Importance of Co (III) and Mn (III)

All samples with Co (III) and Mn (III) & $e_g^1$, irrespective of crystal structure show good catalytic activity for $O_2$ evolution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure</th>
<th>TOF ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$Co$_2$O$_4$</td>
<td>Spinel</td>
<td>$9 \times 10^{-4}$</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>Perovskite</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>Bixbyite</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>Perovskite</td>
<td>$4.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>MgMn$_2$O$_4$</td>
<td>Spinel</td>
<td>$8.2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
O$_2$ evolution by LnMnO$_3$

![Graph showing O$_2$ evolution over time for different Ln elements.]

All orthorhombic perovskites with Co (III) show comparable catalytic activity for O$_2$ evolution.

LaCoO$_3$ shows slightly higher activity.

TOF is comparable to other perovskites.
Conclusions

- All Mn and Co oxides in +3 oxidation state show good catalytic activity irrespective of their crystal structure.
- Trivalency ensures easy electron transfer from the metal ion
- For good catalytic activity B site transition metal ions must have 1 electron in antibonding $e_g$ orbital (e.g. $d^4$ and $d^6$ systems).
- Localized $e_g$ electron in the antibonding $\sigma^*$ can readily be donated during the photocatalytic OER
- Presence of a single electron in the antibonding $e_g$ orbital is expected to yield just the appropriate strength of interaction between $O_2$ and the catalyst.


Both LaCoO$_3$ and LaMnO$_3$ shows increase in activity with Pt loading.

LaCoO$_3$:Pt (2 wt%) shows twice the activity compared to LaCoO$_3$ ($O_2$ evolved per mole of Co) after 20 min.

LaMnO$_3$:Pt (2 wt%) shows 1.5 times the activity compared to LaMnO$_3$ ($O_2$ evolved per mole of Mn) after 20 min.
Water Splitting with Semiconductors

1. Absorption of light by semiconductor
2. Separation of photo-generated electron and hole pair
3. Redox reactions at co-catalysts on the semiconductor

- Band gap > 1.23 eV (=1100 nm)
- CB more –ve than reduction potential of \( H^+/H_2 \) (0 V vs SHE)
- VB more +ve than oxidation potential of \( O_2/H_2O \) (1.23 V vs SHE)
Some semiconductors for water splitting

Absorption of light

Charge separation

Redox reactions

Heterostructures

\[ \text{Z-Scheme} \]

- Spatial separation of charges
- Reduced recombination of e\(^-\) and h\(^+\)

Alivisatos and co-workers J. Phys. Chem. Lett. 2010, 1, 1051–1054
Schemes of Photocatalytic Hydrogen Production

I) Use of Na₂S and Na₂SO₃ as sacrificial agents

II) Use of Benzyl alcohol as sacrificial agent
H₂ evolution and benzyl alcohol oxidation

[Diagram showing the process of H₂ evolution and benzyl alcohol oxidation with visual representations of ZnO/Pt/Cd₀.₈Zn₀.₂S and ZnO/Pt/CdS catalysts.]

- **ZnO/Pt/Cd₀.₈Zn₀.₂S**
  - **λ > 395 nm**
  - Activity (mmol h⁻¹ g⁻¹): 50
  - AQY (%): 18

- **ZnO/Pt/CdS**
  - Activity (mmol h⁻¹ g⁻¹): 37
  - AQY (%): 34

**GC-MS Data:**

- **Benzaldehyde**
  - Retention Time: 5.48 min
  - Mass Spectrum: 12.5

- **Benzyl alcohol**
  - Retention Time: 5.63 min
  - Mass Spectrum: 11

**Benzaldehyde and Benzyl alcohol**

[Graph showing GC-MS data with peaks for benzaldehyde and benzyl alcohol at specific retention times and mass spectra.]
<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Activity (mmolh(^{-1})g(^{-1}))</th>
<th>AQY (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/Pt/CdS(^a)</td>
<td>11.2(^c) (17.4(^d))</td>
<td>11.9(^c) (11.1(^d))</td>
<td>Present work</td>
</tr>
<tr>
<td>ZnO/Pt/CdS(^b)</td>
<td>31.6(^c)</td>
<td>34.5(^c)</td>
<td>Present work</td>
</tr>
<tr>
<td>ZnO/Pt/Cd(<em>{0.8})Zn(</em>{0.2})S(^a)</td>
<td>12.5(^c) (31.2(^d))</td>
<td>18.0(^c) (23.1(^d))</td>
<td>Present work</td>
</tr>
<tr>
<td>ZnO/Pt/Cd(<em>{0.8})Zn(</em>{0.2})S(^b)</td>
<td>36.5(^c)</td>
<td>50.4(^c)</td>
<td>Present work</td>
</tr>
<tr>
<td>ZnO/Pt/CdS(<em>{0.5})Se(</em>{0.5})(^a)</td>
<td>16.0(^c) (19.0(^d))</td>
<td>9.3(^c) (8.1(^d))</td>
<td>Present work</td>
</tr>
<tr>
<td>RGO-Zn(<em>x)Cd(</em>{1-x})S</td>
<td>1.8(^d)</td>
<td>23.4(^c)</td>
<td>J. Zhang, J. Yu, M. Jaroniec, J. R. Gong, <em>Nano Lett.</em> <strong>2012</strong>, <em>12</em>, 4584.</td>
</tr>
</tbody>
</table>

\(^a\) Na\(_2\)S and Na\(_2\)SO\(_3\) are used as hole scavengers. \(^b\) Benzyl alcohol is used as hole scavenger. \(^c\) Visible radiation. \(^d\) UV-visible radiation. \(^e\) Light sources for reaction and AQY calculations are different.
The ZnO/Pt/CdS nanostructures were prepared by a simple solution process. ZnO/Pt/CdS nanostructures exhibited a good H$_2$ evolution properties.

ZnO/Pt/Cd$_{0.8}$Zn$_{0.2}$S and ZnO/Pt/CdS$_{0.5}$Se$_{0.5}$ nanostructures were also prepared by a simple solution process. These nanostructures exhibited improved H$_2$ evolution properties.

The use of organic molecule such as benzyl alcohol shows excellent results in H$_2$ evolution in addition to oxidation products such as benzaldehyde.

ZnO$_{1-x}$(N,F)$_x$/Pt/Cd$_{1-y}$Zn$_y$S nanoheterostructures

\[
\text{ZnO} \xrightarrow{\Delta \text{NH}_3, \text{NH}_4\text{F}} \text{ZnO}_{1-x}(N,F)_x
\]


- Atomic content of N 18 % and F 20 %
- Absorption spectrum extended to visible light due to band structure modifications

Formation of heterostructures with visible light sensitive ZnO and CdS is an interesting strategy for the visible light induced hydrogen evolution.

TEM Image of ZnO$_{1-x}$(N,F)$_x$/Pt/CdS
Comparison of hydrogen evolution studies on ZnO/Pt/CdS and ZnO(N,F)/Pt/CdS

ZnO(N)/Pt/CdS and ZnO(N,F)/Pt/CdS have shown excellent hydrogen evolution with a rate of 35 mmol/h/g with and AQY of 30% in the presence of benzyl alcohol as sacrificial agent under visible light irradiation.

Effect of substitution of Zn as in ZnO_{1-x}(NF)_x/Pt/Cd_{0.8}Zn_{0.2}S

Substitution of Zn in CdS has further improved the hydrogen evolution with an evolution rate of 43 mmol/h/g (AQY 44%).

H₂ evolution by N,F codoped TiO₂

N, F co-doped TiO₂ - maximum H₂ evolution of 400 μmoles/g rate of ~ 60 μmoles/g/h without the loading of any noble metal or other co-catalyst.

N-doped TiO₂ - 37 μmoles/g

Use of NiO as a co-catalyst in ZnO/NiO/CdS type heterostructures

Vectorial ordering of conduction band minimum in this system allows efficient charge-separation and the reduction of proton to hydrogen.

**Advantages**

- Noble-metal free
- Highly efficient
- Easy to synthesize
Comparison of $\text{H}_2$ evolution activities

- ZnO/NiO/Cd$_{1-x}$Zn$_x$S ($x=0.0$, 0.2) heterostructures are highly active under visible as well as UV-visible irradiation.
- Activities of ZnO/NiO/Cd$_{1-x}$Zn$_x$S ($x=0.0$, 0.2) are comparable or superior to those obtained with Pt and Au co-catalysts.
- Activities and quantum yields of ZnO/NiO/Cd$_{1-x}$Zn$_x$S ($x=0.0$, 0.2) are superior to many of the literature reports using NiO as a co-catalysts.

H₂ evolution on (TiO₂)₁₋ₓ(NiO)ₓ/Cd₀.₈Zn₀.₂S (x = 0-1) heterostructures

MoS$_2$ for Photocatalytic H$_2$ evolution

**Colloidal MoS$_2$ nanoparticles**

- $[\text{Ru(bpy)}_3]^{2+}$ sensitized
- TON of 93

Chem. Comm. 2009, 0, 4536

**RGO-MoS$_2$ composite**

- Eosin Y sensitized
- Yield 2 mmoles.g$^{-1}$.h$^{-1}$

Mechanism of H₂ evolution in Graphene-MoS₂ composites

\[ EY = \text{Eosin Y (sensitizer)} \]
\[ \text{TEOA} = \text{Triethanol amine (sacrificial electron donor)} \]

1. EY on photoexcitation goes to triplet excited state that takes e⁻ from TEOA and forms EY anion
2. EY⁻ being highly reactive donates an e⁻ to Graphene which then transfers this e⁻ to MoS₂ for water reduction

Photocatalytic H₂ evolution by MoS₂-graphene composites

NEG-MoS₂ > EG-MoS₂ > MoS₂

* MoS₂ prepared at high temperature.

- Graphene acting as electron channel.
- N doped (electron rich) favors electron transfer from graphene to MoS₂

**Sample** | **Yield/h (mmoles g⁻¹ h⁻¹)** | **TOF (h⁻¹)**
--- | --- | ---
MoS₂ | 0.05 | 0.008
EG-MoS₂ | 0.54 | 0.21
NEG-MoS₂ | 0.83 | 0.45

NEG = 5% N doped graphene
NRGO-MoS$_2$ > RGO-MoS$_2$ >> MoS$_2$

- **NRGO is highly $e^-$ rich and thus transfers $e^-$ easily to MoS$_2$**
- **Greater stacking of MoS$_2$ thus higher density of edges**
- **MoS$_2$ grows perpendicular to NRGO (the electron donating substrate) thus better electron transfer.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield/h (mmoles g$^{-1}$ h$^{-1}$)</th>
<th>TOF (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>0.05</td>
<td>0.008</td>
</tr>
<tr>
<td>RGO-MoS$_2$</td>
<td>3</td>
<td>0.68</td>
</tr>
<tr>
<td>NRGO-MoS$_2$</td>
<td>10.8 (42(400W))</td>
<td>2.9 (11.5(400W))</td>
</tr>
</tbody>
</table>
Chemically exfoliated MoS$_2$ prepared by Li intercalation and exfoliation is known to exit as 1T-MoS$_2$ polytype.

- MoS$_2$ prepared by Li intercalation and exfoliation is known to exit as 1T-MoS$_2$ polytype.
- 1T-MoS$_2$ is metallic.
HRTEM and ED showing 1T state

Mo + S → 2H S 1T
**H₂ evolution by chemically exfoliated MoS₂(1T)**

Time course of H₂ evolution by 1T-MoS₂ over a period of 30 hrs with purging after every 6 hrs.

Time course of H₂ evolution by 1T-MoS₂ - as prepared dispersion & dispersion stored for 30 days.
Mechanism of H₂ evolution by 1T-MoS₂

2H-MoS₂

1T-MoS₂

- Electron transfer directly from EY⁻ to empty 4d_{xy, xz, yz} MoS₂
- Presence of makes it metallic as well as highly active catalyst

2H- MoS₂ – filled 4d² and four empty doubly degenerate orbitals composed of (4d_{xy}, x² - y²) and (4d_{xz}, yz)

1T MoS₂ - three triply degenerate orbitals 4d_{xy, xz, yz} containing two unpaired electron and two empty doubly degenerate orbital 4d_{x² - y², z²}.
Comparison of H$_2$ evolution by 2H and 1T MoS$_2$

![Graph showing comparison of H$_2$ evolution by 2H and 1T MoS$_2$](image)

- **H$_2$ evolved (mmoles g$^{-1}$ h$^{-1}$)**
- **Yield (mmoles g$^{-1}$ h$^{-1}$)**
- **TOF (h$^{-1}$)**

- **MoS$_2$**
- **RGO-MoS$_2$**
- **NRGO-MoS$_2$**
- **1T-MoS$_2$**
Comparison of $\text{H}_2$ evolution by 2H and 1T MoSe$_2$

$\text{H}_2$ evolved (mmoles/g)

Time(h)

2H-MoSe$_2$

1T-MoSe$_2$

Rao et. al APL (Materials) (2014)
### Hydrogen evolution activity of MoSe$_2$, MoS$_2$ and TaS$_2$ based catalysts

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Light Source</th>
<th>Activity (mmol h$^{-1}$ g$^{-1}$)</th>
<th>TOF (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/CdS</td>
<td>300 W Xe lamp</td>
<td>5.3</td>
<td>ca. 0.7</td>
</tr>
<tr>
<td>TaS$_2$/CdS</td>
<td>400 W Xe lamp ($\lambda&gt;$399nm)</td>
<td>2.32</td>
<td>0.57</td>
</tr>
<tr>
<td>2H MoS$_2^[a]$</td>
<td>100 W Halogen lamp</td>
<td>0.05</td>
<td>0.008</td>
</tr>
<tr>
<td>NRGO-MoS$_2^[a]$</td>
<td>100 W Halogen lamp</td>
<td>10.8</td>
<td>2.9</td>
</tr>
<tr>
<td>1T MoS$_2^[a]$</td>
<td>100 W Halogen lamp</td>
<td>30</td>
<td>6.5</td>
</tr>
<tr>
<td>1T-MoSe$_2^[a]$</td>
<td>100 W Halogen lamp</td>
<td>70±5</td>
<td>19.2</td>
</tr>
<tr>
<td>Few layer 2H MoSe$_2^[a]$</td>
<td>100 W Halogen lamp</td>
<td>0.05</td>
<td>0.02</td>
</tr>
</tbody>
</table>

TOF calculated per mole of catalytically active material (Graphene is considered to be inactive compared to MoS$_2$). [a] Eosin Y dye sensitized
Conclusions

i. Obtained *highest photocatalytic H₂ evolution rate* in any MoS₂ based system reported thus far.

ii. Nanoflakes of MoS₂ with *high density of catalytically active edges*, grown on *heavily N-doped graphene* gives the best yield among all 2H-polytype of MoS₂.

iii. N-doping of graphene not only *improved the electron donating ability of graphene* but also created a *p-n junction* that suppresses charge recombination.

iv. Metallic 1T-polytype of MoS₂ shows *extraordinary HER activity* by virtue of its metallic nature and intrinsic high catalytic activity.

v. Catalytic activity of 1T-MoS₂ is about 600-1000 times that of 2H-MoS₂.

vi. 1T-MoSe₂ shows *extraordinarily high catalytic activity*, being the *best catalyst* by far.


Are There Other Ways of Splitting Water?

1) by heat! (catalysis to bring down the temperature of decomposition)

2) Solar-Thermochemical route using oxides:

Basic two steps involved in high temp TCDS/TWS:

Endothermal Step: \( \text{MO}_n \rightarrow \text{MO}_{n-\delta} + \frac{\delta}{2} \text{O}_2 \)  

Exothermal step: \( \text{MO}_{n-\delta} + \delta \text{CO}_2 \rightarrow \text{MO}_n + \delta \text{CO} \)
State-of-art material

\[ \text{CeO}_2 \rightarrow \text{CeO}_2-\delta + \frac{\delta}{2} \text{O}_2 \]  \hspace{1cm} (1)

\[ \text{CeO}_2-\delta + \delta \text{H}_2\text{O(CO}_2) \rightarrow \text{CeO}_2 + \delta\text{H}_2(\text{CO}) \]  \hspace{1cm} (2)

Reaction set up of ETH’s High flux solar simulator. Solar cavity receiver containing a porous ceria cylinder that is directly exposed to high-flux solar irradiation entering through a windowed aperture. Reacting gases flow radially across the porous ceria, while product gases exit the cavity through an axial outlet port.
Perovskite oxides

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is recently came into the picture & reported to show good activity than $\text{CeO}_2$.

- Sr$^{2+}$ substitutes La$^{3+}$ and Mn$^{4+}$ concentration increases.
- Reduction at 1400$^\circ$C converts Mn$^{4+}$ to Mn$^{3+}$; evolves O$_2$.
- Mn$^{3+}$ converts back to Mn$^{4+}$: splits H$_2$O and CO$_2$

Noteworthy performance of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

LCM 50 evolves 1.5 times and 5 times greater amount of $\text{O}_2$ and/or $\text{CO}$ than LSM 50 and ceria respectively.


<table>
<thead>
<tr>
<th>Composites</th>
<th>$\text{O}_2$ released (µmol/g)</th>
<th>$\text{CO}$ produced (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}<em>{0.5}\text{Sr}</em>{0.5}\text{MnO}_3$</td>
<td>201.3</td>
<td>325</td>
</tr>
<tr>
<td>$\text{La}<em>{0.5}\text{Ca}</em>{0.5}\text{MnO}_3$</td>
<td>315.6</td>
<td>525</td>
</tr>
<tr>
<td>Ceria</td>
<td>62.5</td>
<td>112</td>
</tr>
</tbody>
</table>
The amount of $\text{H}_2$ produced by LCM 50 (407 $\mu$mol/g) is larger than the LSM 50 (308 $\mu$mol/g).
Thermochemical CO₂ Splitting of Ln₀.₅ₐ₀.₅MnO₃ (Ln=lanthanide; A=Sr, Ca)

Decrease in size of Ln
Decrease tolerance factor (τ)
O$_2$ evolution of Ln$_{1/2}$Sr$_{1/2}$MnO$_3$

O$_2$ evolution increases with decreasing the size of the rare earth ions.
O₂ evolution increases with decreasing the tolerance factor (τ)

Y₀.₅Sr₀.₅MnO₃ shows superior O₂ production activity.
Difference in Reduction temperature

$\text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ starts to reduce at lower temp.
Size variance ($\sigma^2$) also plays a major role ($\sigma^2_{(\text{La, Sr})} > > \sigma^2_{(\text{La, Ca})}$)
Remarkable performance of $Y_{1/2}Sr_{1/2}MnO_3$

Oxidation yield of YSM 50 is less at 1100°C

Oxidation is carried out at 900°C

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_{\text{red}}$ ($^\circ$C)</th>
<th>$T_{\text{oxd}}$ ($^\circ$C)</th>
<th>Total CO ($O_2$) produced ($\mu$mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSM 50</td>
<td>1400</td>
<td>900</td>
<td>757 (483)</td>
</tr>
<tr>
<td>YSM 50</td>
<td>1300</td>
<td>900</td>
<td>624 (389)</td>
</tr>
<tr>
<td>YSM 50</td>
<td>1200</td>
<td>900</td>
<td>418 (258)</td>
</tr>
</tbody>
</table>

### Remarkable performance of $Y_{0.5}Sr_{0.5}MnO_3$

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{red}}$ temp (°C)</th>
<th>$O_2$ evolved (μmol/g)</th>
<th>Oxidation temp (°C)</th>
<th>CO evolved (μmol/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{0.5}Sr_{0.5}MnO_3$</td>
<td>1400</td>
<td>483</td>
<td>900</td>
<td>757</td>
<td>Present work</td>
</tr>
<tr>
<td>$Y_{0.5}Sr_{0.5}MnO_3$</td>
<td>1300</td>
<td>389</td>
<td>900</td>
<td>624</td>
<td>Present work</td>
</tr>
<tr>
<td>$Y_{0.5}Sr_{0.5}MnO_3$</td>
<td>1200</td>
<td>258</td>
<td>900</td>
<td>418</td>
<td>Present work</td>
</tr>
<tr>
<td>$Y_{0.5}Ca_{0.5}MnO_3$</td>
<td>1400</td>
<td>575</td>
<td>1100</td>
<td>671</td>
<td>Present work</td>
</tr>
<tr>
<td>$La_{0.5}Ca_{0.5}MnO_3$</td>
<td>1400</td>
<td>315</td>
<td>1100</td>
<td>525</td>
<td>PCCP, 2015</td>
</tr>
<tr>
<td>$La_{0.5}Sr_{0.5}MnO_3$</td>
<td>1400</td>
<td>298</td>
<td>1000</td>
<td>298</td>
<td>J.Phys. Chem. C, 2014</td>
</tr>
<tr>
<td>$La_{0.6}Sr_{0.4}MnO_3$</td>
<td>1400</td>
<td>205$^{a)}$</td>
<td>800</td>
<td>397</td>
<td>J.Mater. Chem. A, 2014</td>
</tr>
<tr>
<td>$La_{0.6}Sr_{0.4}Al_{0.6}Mn_{0.4}O_3$</td>
<td>1350</td>
<td>120</td>
<td>1000</td>
<td>247</td>
<td>Energy. Environ. Sci, 2013</td>
</tr>
</tbody>
</table>

Remarkable performance of $Y_{0.5}Sr_{0.5}MnO_3$.

The amount of H₂ produced by YSM 50 (320 μmol/g) is large than the YCM 50 (300 μmol/g) in 140 mins span of time.
Our aim:

1. Lowering of reaction temperature below 850°C (steps 1 & 2)
2. Increasing the H₂ evolution rate (step 2)

2Mn₃O₄ + 3Na₂CO₃ → 4NaMnO₂(s) + 2MnO + Na₂CO₃ + 2CO₂(g) — (1)
2MnO + Na₂CO₃ + H₂O(g) → 2NaMnO₂(s) + CO₂(g) + H₂(g) ——— (2)
6NaMnO₂(s) + ayH₂O(l) + (3 + b)CO₂(g)
→ 3Na₂CO₃(aq) + aHₓMnO₂·yH₂O(s) + bMnCO₃ + cMn₃O₄ ——— (3)
aHₓMnO₂·yH₂O(s) + bMnCO₃ → (2 – c)Mn₃O₄(s) + ayH₂O(g) + bCO₂(g) + 0.5O₂(g) ——— (4)

where a+b+3c=6 and (4-x)a+2b+8c=18

Davis and Coworkers, *PNAS, 2012, 109, 9260*
Thermochemical H$_2$O splitting

Step 1:

1. $\text{Mn}_3\text{O}_4$ (s) + $\text{Na}_2\text{CO}_3$ (s) $\xrightarrow{850^\circ\text{C}}$ MnO (s) + NaMnO$_2$ (s)

$\text{CO}_2$ (g)

(1) $\text{Mn}_3\text{O}_4$-annealed + $\text{Na}_2\text{CO}_3$ bulk
(2) $\text{Mn}_3\text{O}_4$-commercial + $\text{Na}_2\text{CO}_3$ bulk
(3) $\text{Mn}_3\text{O}_4$-30 mins ball milled + $\text{Na}_2\text{CO}_3$ bulk
(4) $\text{Mn}_3\text{O}_4$-60 mins ball milled + $\text{Na}_2\text{CO}_3$ bulk
(5) ($\text{Mn}_3\text{O}_4$ + $\text{Na}_2\text{CO}_3$)-30 mins ball milled
(6) ($\text{Mn}_3\text{O}_4$ + $\text{Na}_2\text{CO}_3$)-60 mins ball milled

$\text{CO}_2$ evolution temperature decreases upto 600°$^\circ$C with the use of nanoparticles of both $\text{Mn}_3\text{O}_4$ + $\text{Na}_2\text{CO}_3$.

Thermochemical H$_2$O splitting

1. H$_2$O$_2$O splitting

Steps 1 and 2:

1. H$_2$ evolution rate increases
2. H$_2$ evolution temperature decreases up to 750°C and 700°C

Why not electrolysis of water using solar PV?

- Problem of over potential
- Need of a catalyst other than Pt
- BC$_X$N$_Y$?
Electrochemical Hydrogen Evolution

Selection of catalyst

\( i_0 \) as a function of the \( \Delta G_{H^*} \) for various catalysts

Limitations

- Innate overpotential.
- Durability in harsh acidic and basic medium.
- High cost and scarcity of precious metals.

Low cost metal free electrocatalysts

- Heteroatom doping – Active surface sites for \( H^+ \) adsorption
- Enhanced conductivity – low charge transfer resistance
- Examples- modified MoS\(_2\) based, \( C_3N_4@NG \), etc.

\[
B_X C_Y N_Z : ???
\]

Electrochemical Hydrogen Evolution

Linear Sweep Voltametry

Stability after 1000 cycles

Stability @ 20 mA/cm²

Electrochemical Impedance Spectroscopy

Tafel slope

Comparative study and literature

Summary of electrocatalytic activity

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET (m²/g)</th>
<th>Onset (a) (mV) vs Ag/AgCl</th>
<th>η@10 mA/cm² (a)</th>
<th>η@20 mA/cm² (a)</th>
<th>Tafel Slope</th>
<th>I₀ (A/cm²)</th>
<th>Rᶜₑ</th>
<th>Cᵈˡ (mF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC₇N₂</td>
<td>1950</td>
<td>-284</td>
<td>-298 mV</td>
<td>-330 mV</td>
<td>100 mV/dec</td>
<td>5.1 x 10⁻⁵</td>
<td>13.6 Ω</td>
<td>0.108</td>
</tr>
<tr>
<td>BC₄N₁.₂</td>
<td>1635</td>
<td>-314</td>
<td>-357 mV</td>
<td>-401 mV</td>
<td>127 mV/dec</td>
<td>3.2 x 10⁻⁵</td>
<td>60.1 Ω</td>
<td>0.103</td>
</tr>
<tr>
<td>BC₁₇N₀.₇</td>
<td>1470</td>
<td>-451</td>
<td>-487 mV</td>
<td>-642 mV</td>
<td>195 mV/dec</td>
<td>1.09 x 10⁻⁵</td>
<td>64.3 Ω</td>
<td>0.033</td>
</tr>
<tr>
<td>BC₁₇N₀.₈</td>
<td>1241</td>
<td>-444</td>
<td>-487 mV</td>
<td>-533 mV</td>
<td>145 mV/dec</td>
<td>9.1 x 10⁻⁶</td>
<td>268.9 Ω</td>
<td>0.022</td>
</tr>
<tr>
<td>BC₁₁N</td>
<td>1580</td>
<td>-428</td>
<td>-586 mV</td>
<td>-542 mV</td>
<td>178 mV/dec</td>
<td>4.4 x 10⁻⁶</td>
<td>384.6 Ω</td>
<td>0.020</td>
</tr>
<tr>
<td>Pt/C</td>
<td>--</td>
<td>-230</td>
<td>-250 mV</td>
<td>-266 mV</td>
<td>34 mV/dec</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

(a) Against RHE the values can be converted by adding 227.7 mV, following the equation for calibration against, $E_{(RHE)} = E_{(Ag/AgCl, 3 M NaCl)} + 0.059pH$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset (mV) Vs RHE</th>
<th>η@10mA/cm² vs RHE</th>
<th>Tafel slope (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D-MoS₂/N-GAs</td>
<td>-236</td>
<td>-261</td>
<td>230</td>
</tr>
<tr>
<td>N-MPG</td>
<td>-220</td>
<td>-239</td>
<td>109</td>
</tr>
<tr>
<td>C₃N₄@NG</td>
<td>-180</td>
<td>-240</td>
<td>51</td>
</tr>
<tr>
<td>g-C₃N₄ nanoribbons</td>
<td>-80</td>
<td>-200</td>
<td>54</td>
</tr>
<tr>
<td>N-graphene on Si</td>
<td>-200</td>
<td>-260</td>
<td>74</td>
</tr>
<tr>
<td>MoS₂/RGO hybrid</td>
<td>-100</td>
<td>-150</td>
<td>41</td>
</tr>
<tr>
<td>Mo₃C/C nanocomposite</td>
<td>-100</td>
<td>-</td>
<td>110</td>
</tr>
<tr>
<td>BC₇N₂</td>
<td>-56</td>
<td>-70</td>
<td>100</td>
</tr>
</tbody>
</table>

Faradaic Efficiency

$\sim 100\%$
First Principles calculations

**Presence of two Nitrogen**

**Presence of Boron**

**Composition dependant HER activity**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Relative Energy E(config)-E(lowest) (eV/supercell)</th>
<th>VBM (eV)</th>
<th>CBM (eV)</th>
<th>$E_F$ (eV)</th>
<th>DoS($E_F$) (arb. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>0</td>
<td>-4.888</td>
<td>-4.094</td>
<td>-2.934</td>
<td>1.747</td>
</tr>
<tr>
<td>Ib</td>
<td>1.076</td>
<td>-4.738</td>
<td>-4.341</td>
<td>-3.127</td>
<td>1.312</td>
</tr>
<tr>
<td>Ic</td>
<td>0.819</td>
<td>-4.976</td>
<td>-4.377</td>
<td>-3.086</td>
<td>1.143</td>
</tr>
<tr>
<td>Id</td>
<td>2.078</td>
<td>-4.830</td>
<td>-4.558</td>
<td>-3.171</td>
<td>1.193</td>
</tr>
<tr>
<td>II</td>
<td>-</td>
<td>-4.112</td>
<td>-3.595</td>
<td>-3.833</td>
<td>0</td>
</tr>
<tr>
<td>IIIa</td>
<td>0</td>
<td>-4.335</td>
<td>-3.832</td>
<td>-4.078</td>
<td>0</td>
</tr>
<tr>
<td>IIIb</td>
<td>0.132</td>
<td>-4.252</td>
<td>-3.966</td>
<td>-4.109</td>
<td>0</td>
</tr>
</tbody>
</table>
1. First report on the Efficacy of borocarbonitride sheets as an excellent low-cost, metal-free catalyst for hydrogen generation.

2. Carbon-rich BC$_7$N$_2$ shows the best activity with a performance superior to that of other non-precious metal electrocatalyst.

2. Faradaic Efficiency is $\sim$100%, showing almost no deviation from the theoretically calculated value of the volume of hydrogen evolved.

3. Theoretical studies show that substitution of B and N in equal concentrations opens up a gap, with the valence band unfavorably located relative to the HER potential.

4. Substitution of excess N results in the population of the conduction bands with electrons and shifts the valence and conduction bands to lower energy and favors the alignment of bands to facilitate electrocatalysis.

5. The optimal composition should be (a) Carbon-rich (hence low in B and N), (b) excess in N (relative to B).

6. Interplay of the relative ratio betwee B & N can afford entropic stability and an adequate number of active sites for HER,

OUTLOOK