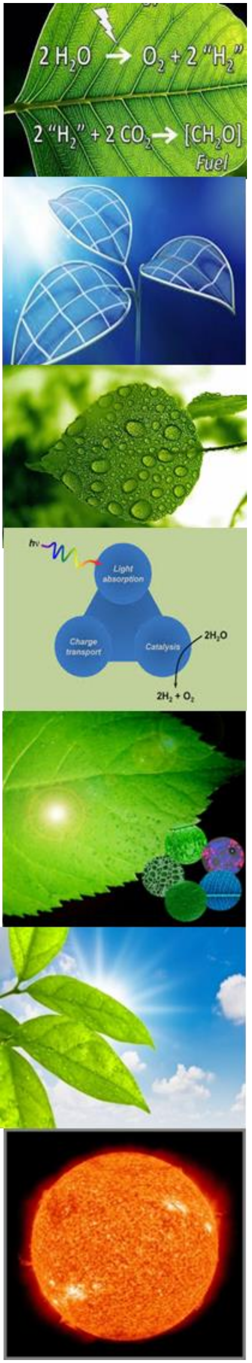


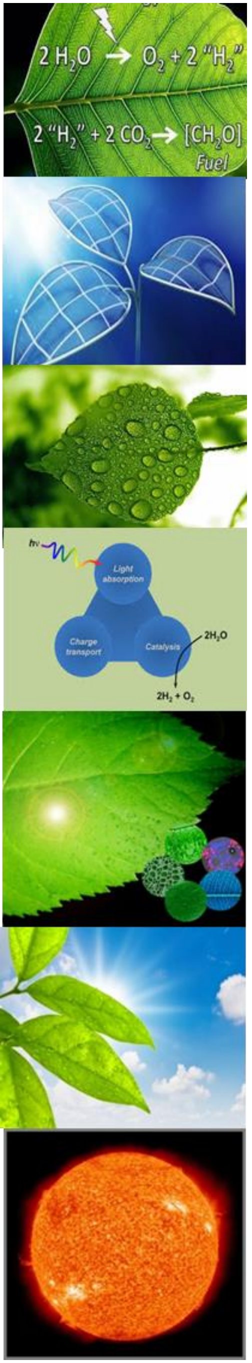
Synchrotron Radiation-based X-Ray studies

Mmantsae Moche Diale

African Light Source

18 – 20 November 2020; Virtual

Sustainable development goals

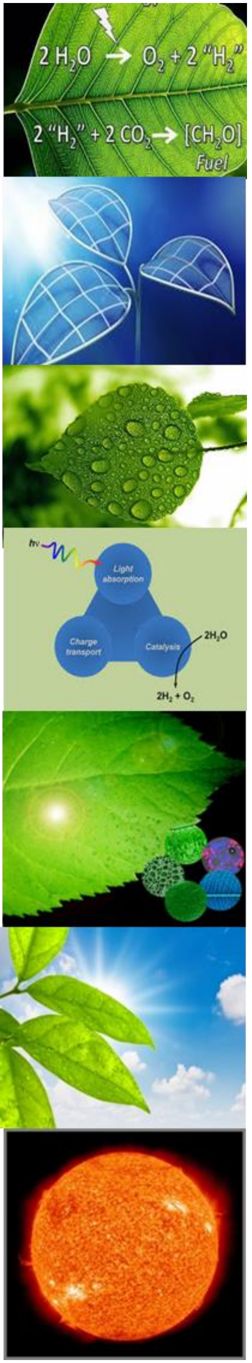


2. Zero hunger

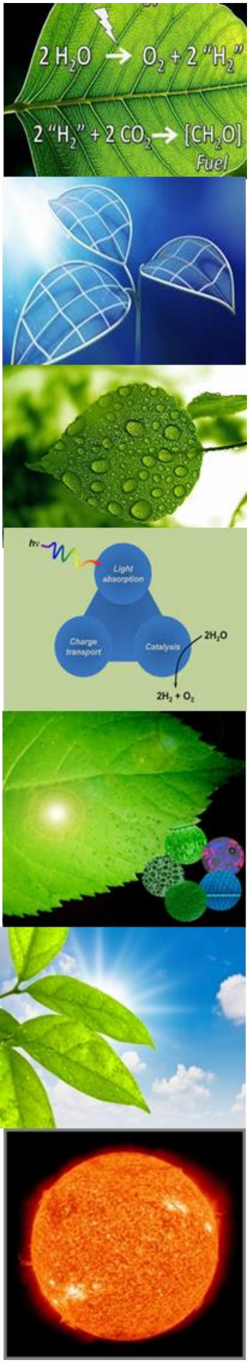
6. Clean water and sanitation

7. Affordable clean energy

World synchrotron radiation sites

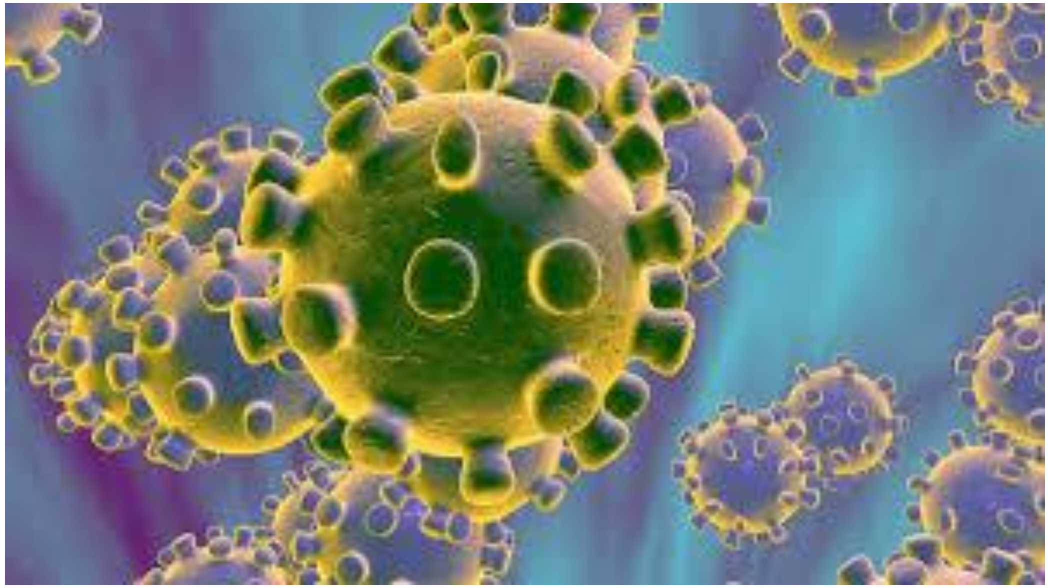


USA – 14
EU – 17
UK – 1
Japan – 5
Russia – 5
Italy – 4
China – 4
Singapore – 1
Thailand – 1
Sot Korea – 1
Brazil - 1

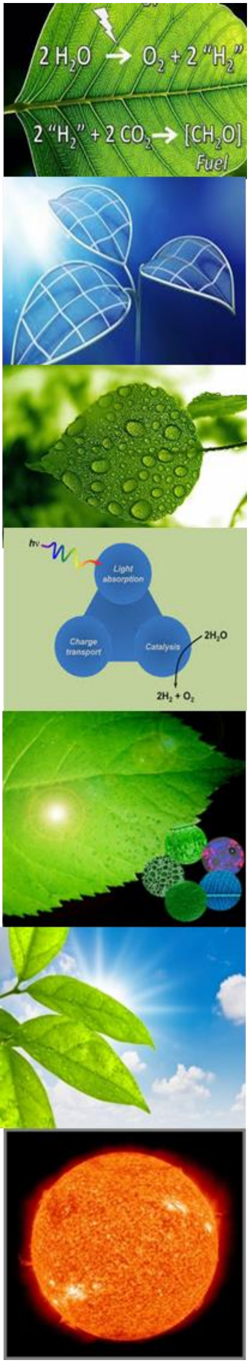


Berkeley Lab COVID-19 related research and additional information.

X-rays allow researchers to map out the 3D structure of proteins relevant to diseases at the scale of molecules and atoms, and Lawrence Berkeley National Laboratory's (Berkeley Lab's) Advanced Light Source (ALS) X-ray facility has been recalled to action to support research related to COVID-19, the coronavirus disease that has already infected about millions people around the world



Advanced light source for Africa

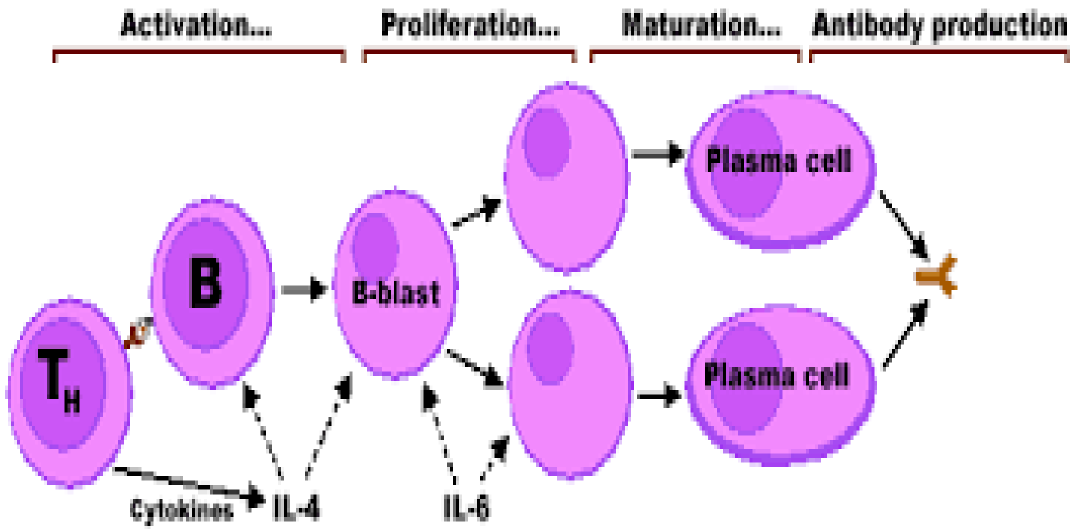


Advanced Photon Source at Argonne labs

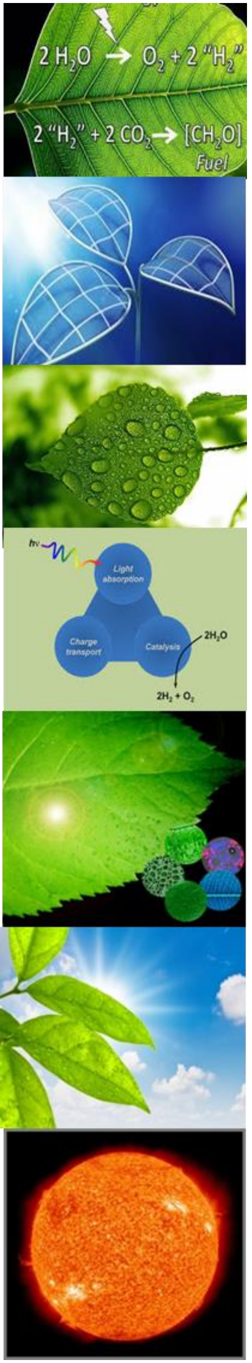
A bright light for drug delivery

Macromolecular X-Ray Crystallography

Closer to an Effective HIV Vaccine



European Synchrotron Radiation Facility Grenoble



UNLOCKING THE SECRETS OF MATTER

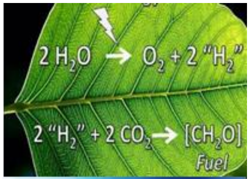
The ESRF, a state-of-the-art synchrotron, provides the international scientific community with unique opportunities for the study of materials and living matter.

ADDRESSING GLOBAL CHALLENGES

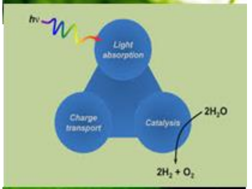
The ESRF is a centre of excellence for fundamental research, also committed to applied and industrial research. It contributes to overcoming the societal and environmental challenges facing the world.

BRINGING NATIONS TOGETHER

The ESRF owes its success to the international cooperation of 22 partner countries, all driven by the same quest for scientific excellence.



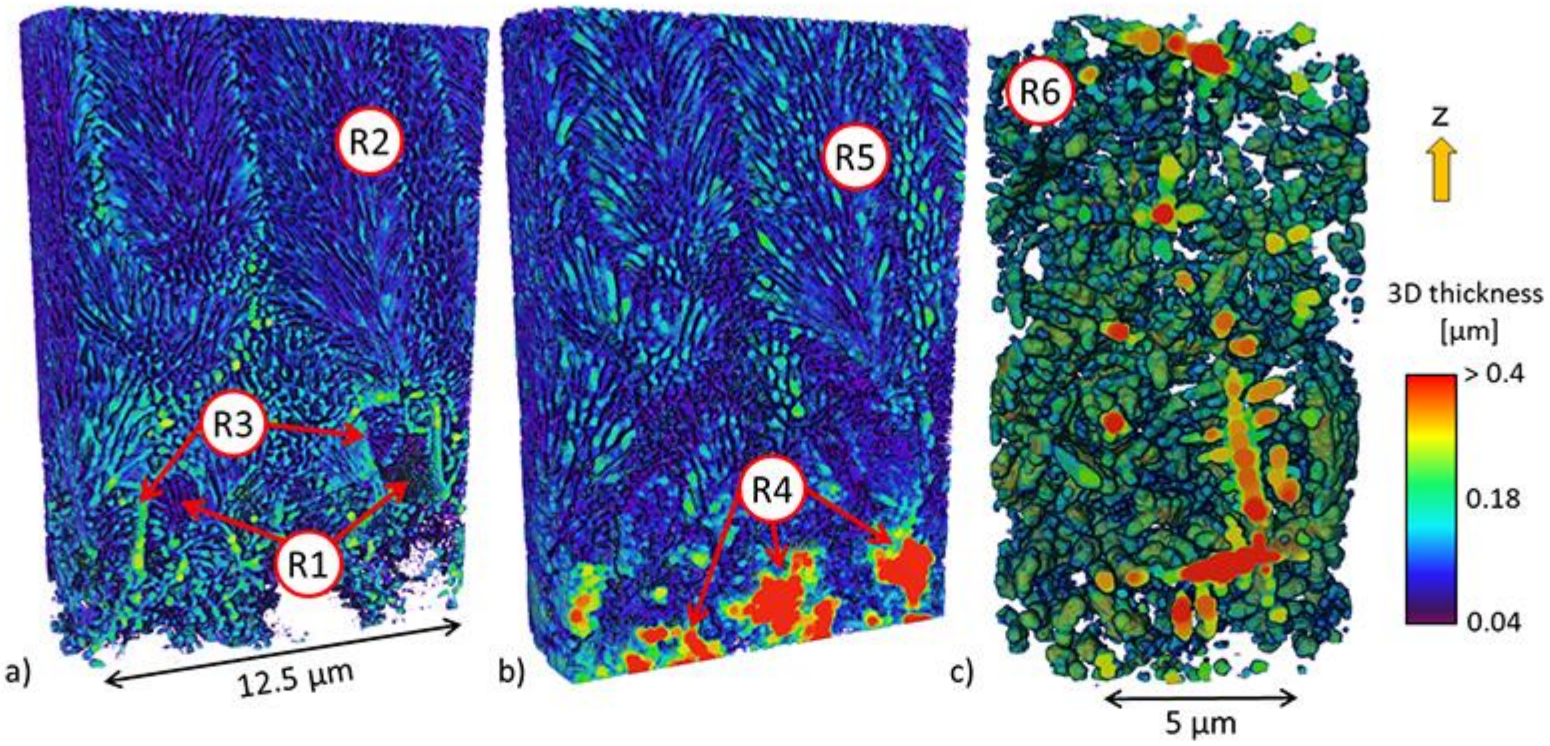


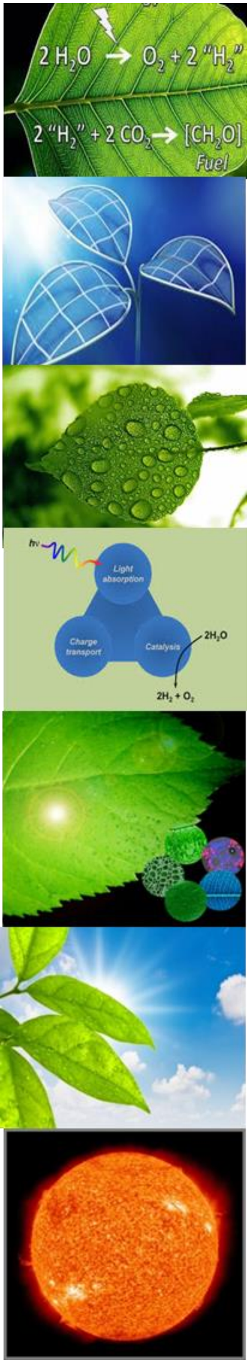




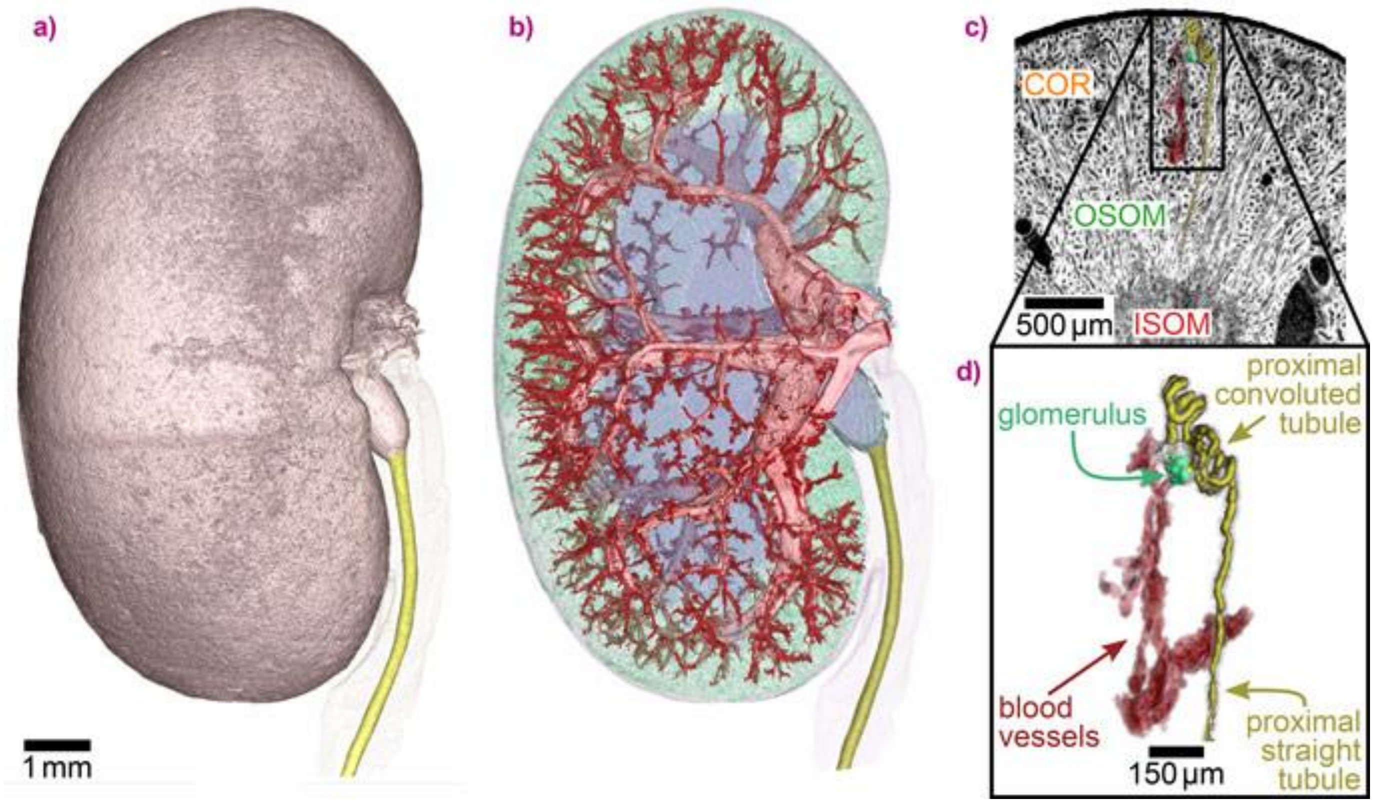
Ptychographic X-ray CT of ultrafine eutectic Ti-Fe-based alloy

High-resolution near-field synchrotron ptychographic X-ray computed tomography carried out at ID16A reveals the ultrafine eutectic microstructures of a titanium-iron-based alloy. The material was produced by additive manufacturing, exploiting the high solidification rates of laser-based 3D printing

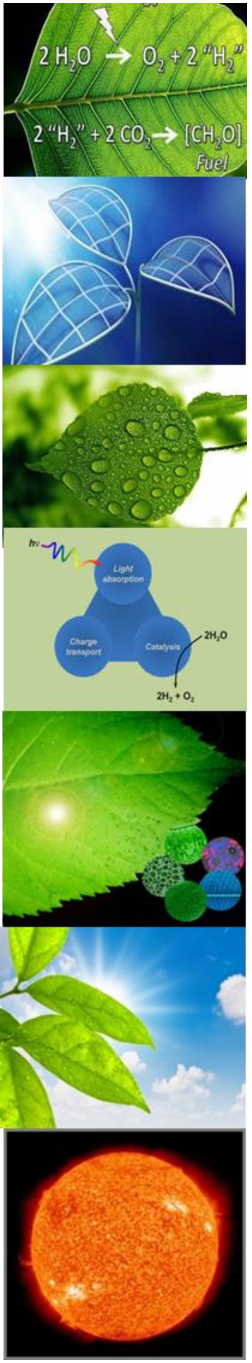




X-ray imaging with sandpaper enables advanced 3D virtual histology

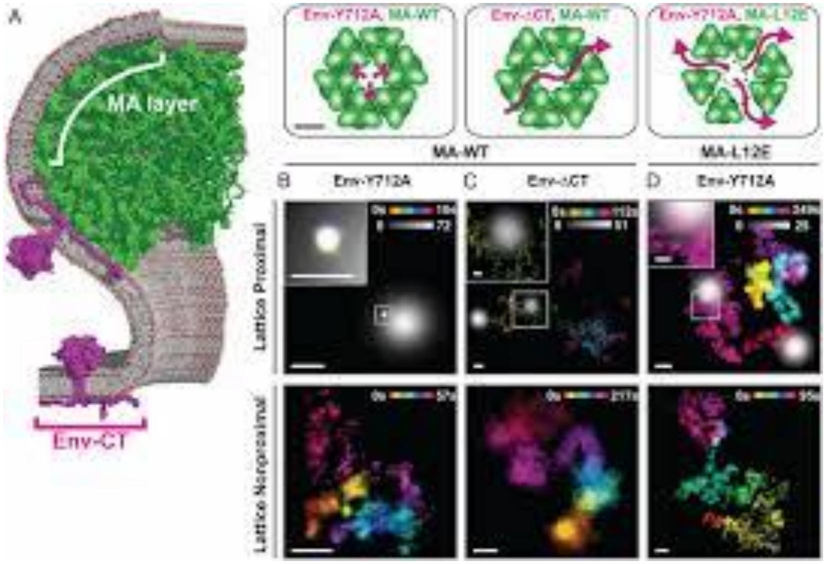


Three-dimensional images of a kidney with unprecedented quality have been obtained with the simple, cost-effective addition of sandpaper as an optical element to an X-ray imaging beamline. The results demonstrate the potential of X-ray speckle-based tomography for quantitative 3D virtual histology.

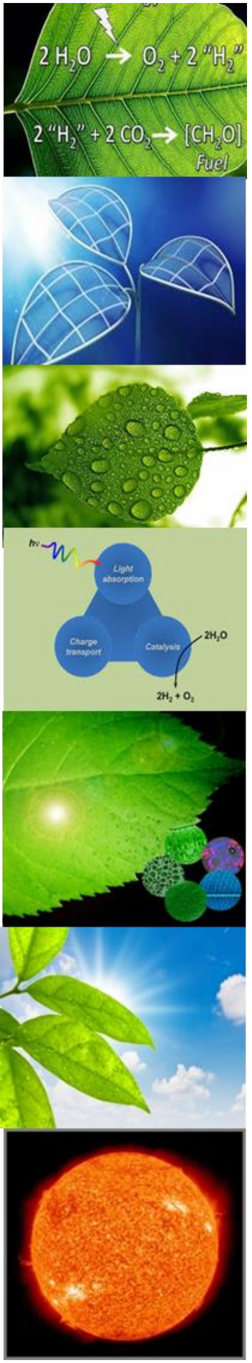


Advanced Light Source for Africa

Finding cures for diseases

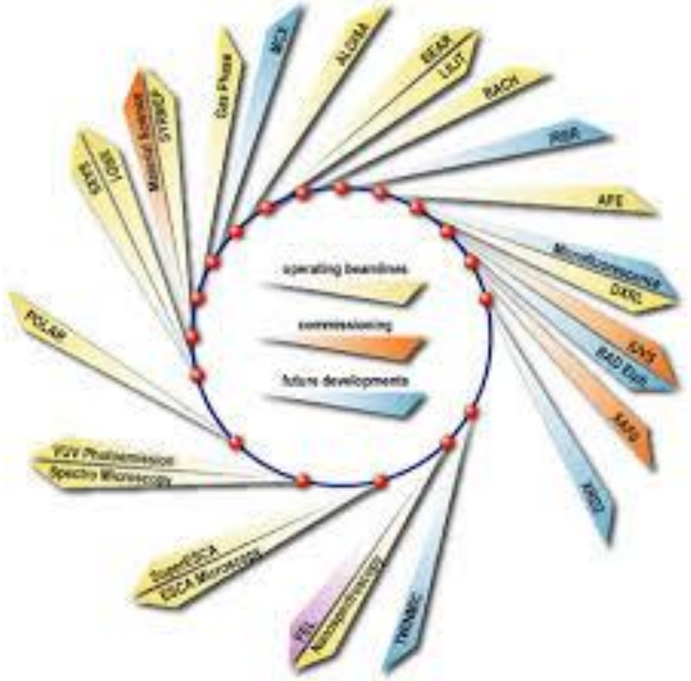


Bringing major breakthrough in Materials and Life Sciences

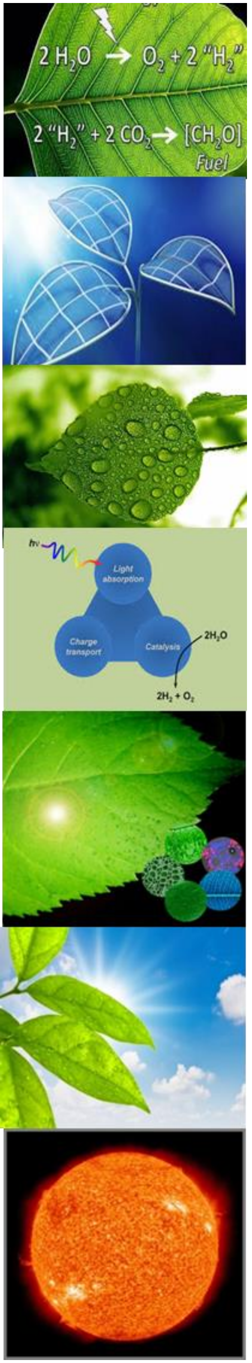


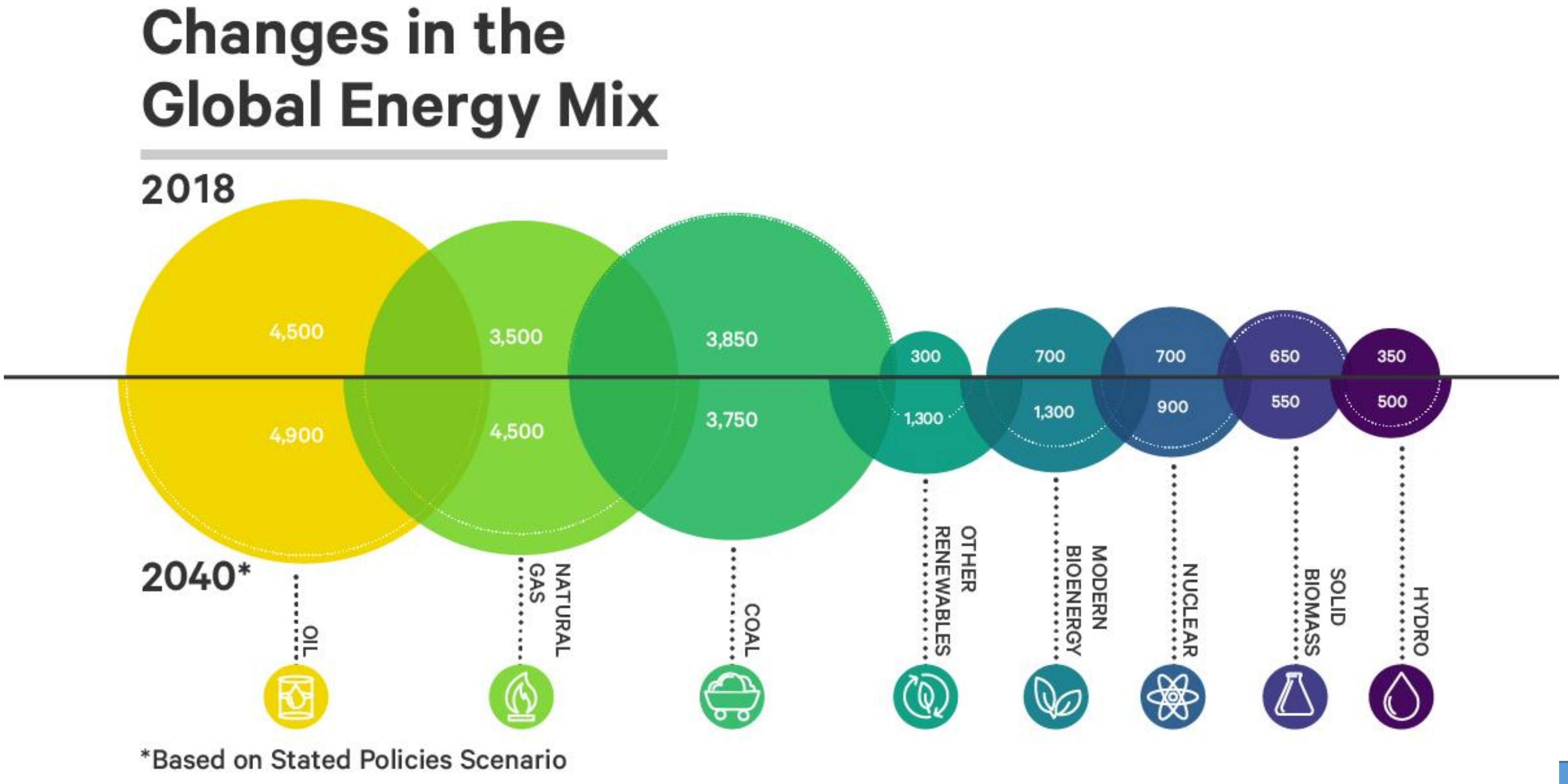
Ellatra

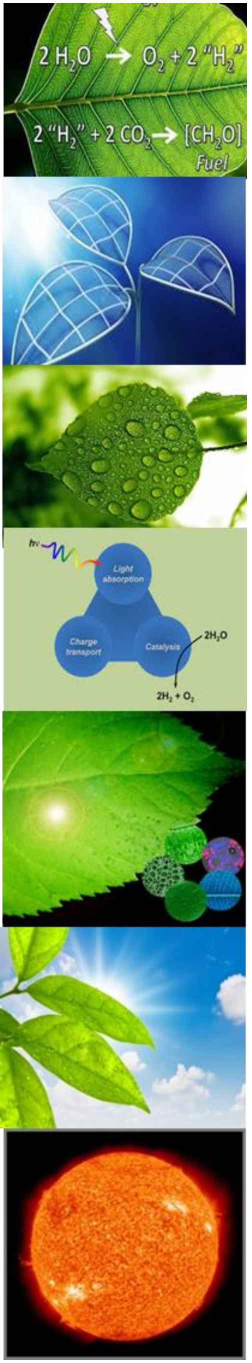
An international multi-disciplinary research centre; specialized in synchroton and free electron laser radiation and their applications to materials and life sciences.



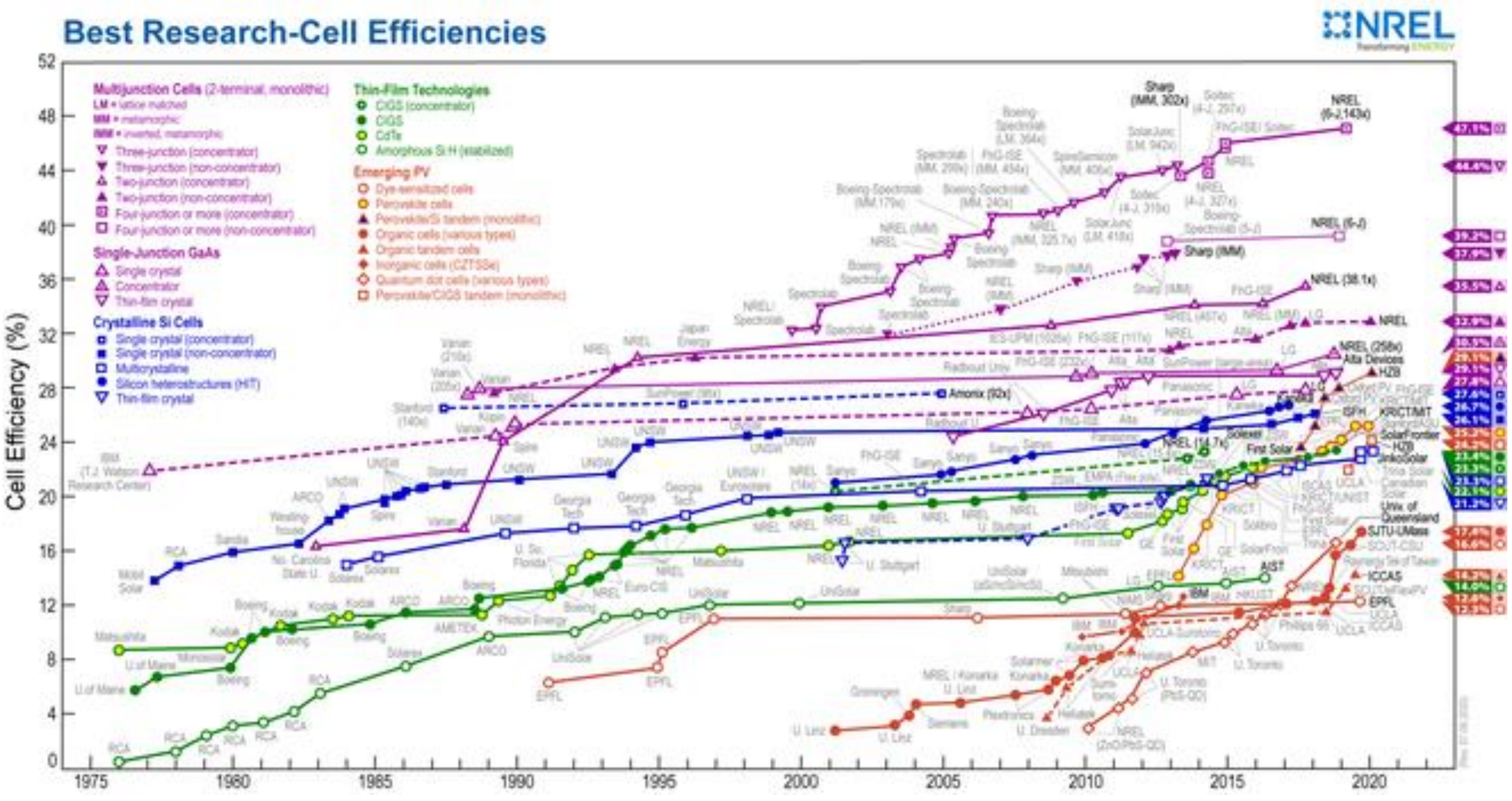
Energy MIX


2 H2O → O2 + 2 "H2"
2 "H2" + 2 CO2 → [CH2O]
Fuel
Light absorption
Charge transport
Catalysis
2H2O
2H2 + O2


Changes in the Global Energy Mix
2018
2040*
4,500
4,900
3,500
4,500
3,850
3,750
300
1,300
700
1,300
700
900
650
550
350
500
OIL
NATURAL GAS
COAL
OTHER RENEWABLES
MODERN BIOENERGY
NUCLEAR
SOLID BIOMASS
HYDRO
*Based on Stated Policies Scenario

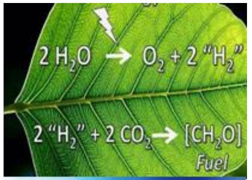


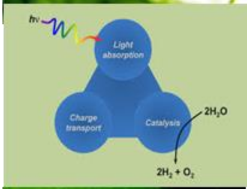
Materials and devices



New materials need to match Silicon material properties
Using advanced technologies such as synchrotrons may crack the Silicon code to make solar energy cheaper

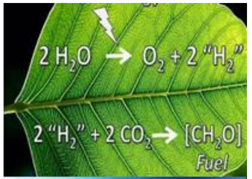
Advanced light source for Africa



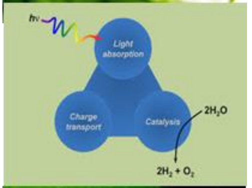


Research opportunities for the African continent.

World synchrotron radiation sites



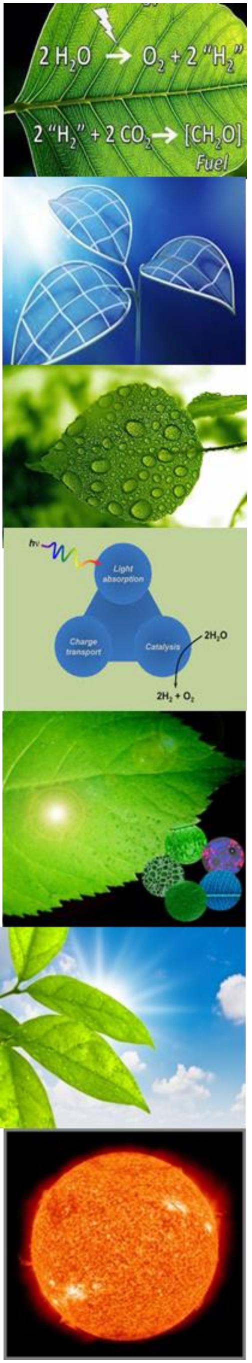






USA – 14
EU – 17
UK – 1
Japan – 5
Russia – 5
Italy – 4
China – 4
Singapore – 1
Thailand – 1
Sot Korea – 1
Brazil - 1

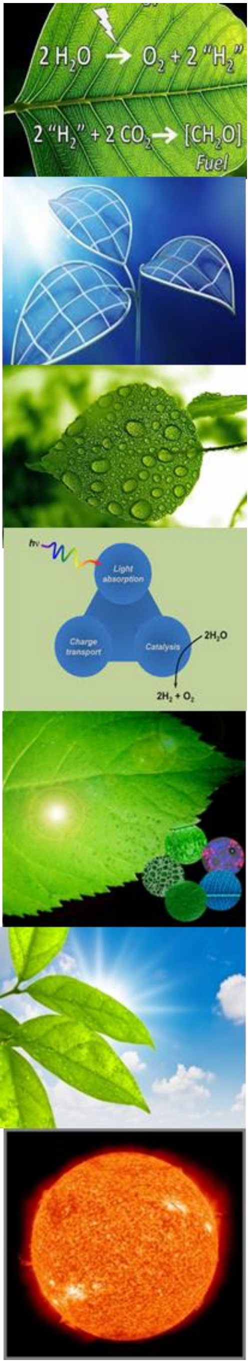
Experimental Techniques and usage



Synchrotron light is an ideal tool for many types of research in materials science, physics, and chemistry and is used by researchers from academic, industrial, and government laboratories.

Several methods take advantage of the high intensity, tunable wavelength, collimation, and polarization of synchrotron radiation at beamlines which are designed for specific kinds of experiments.

The high intensity and penetrating power of synchrotron X-rays enables experiments to be performed inside sample cells designed for specific environments.



Diffraction and scattering

X-ray diffraction (XRD) and scattering experiments are performed at synchrotrons for the structural analysis of crystalline and amorphous materials.

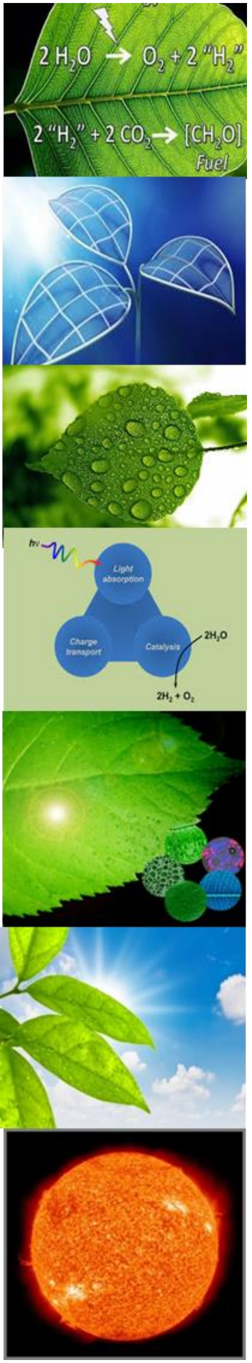
These measurements may be performed on powders, single crystals, or thin films.

The high resolution and intensity of the synchrotron beam enables the measurement of scattering from dilute phases or the analysis of residual stress.

X-ray crystallography of proteins and other macromolecules (PX or MX) are routinely performed.
Synchrotron-based crystallography experiments were integral to solving the structure of the ribosome; this work earned the Nobel Prize in Chemistry in 2009.

The size and shape of nanoparticles are characterized using small angle X-ray scattering (SAXS). Nano-sized features on surfaces are measured with a similar technique, grazing-incidence small angle X-ray scattering (GISAXS).

Diffraction and scattering

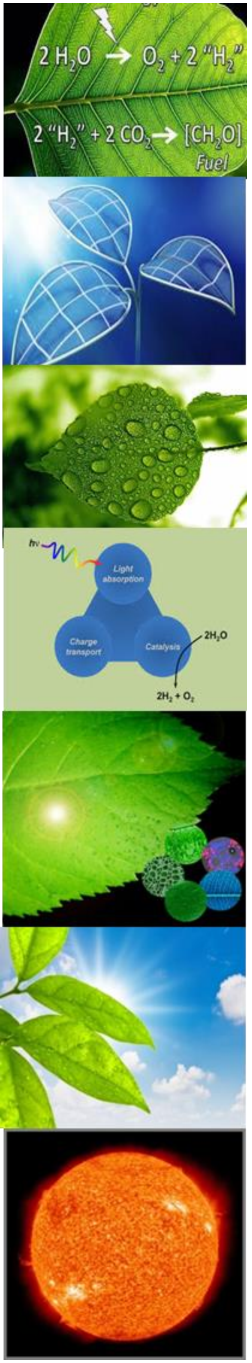


The atomic- to nano-scale details of surfaces, interfaces, and thin films can be characterized using techniques such as X-ray reflectivity (XRR) and crystal truncation rod (CTR) analysis.[10] X-ray standing wave (XSW) measurements can also be used to measure the position of atoms at or near surfaces; these measurements require high-resolution optics capable of resolving dynamical diffraction phenomena.

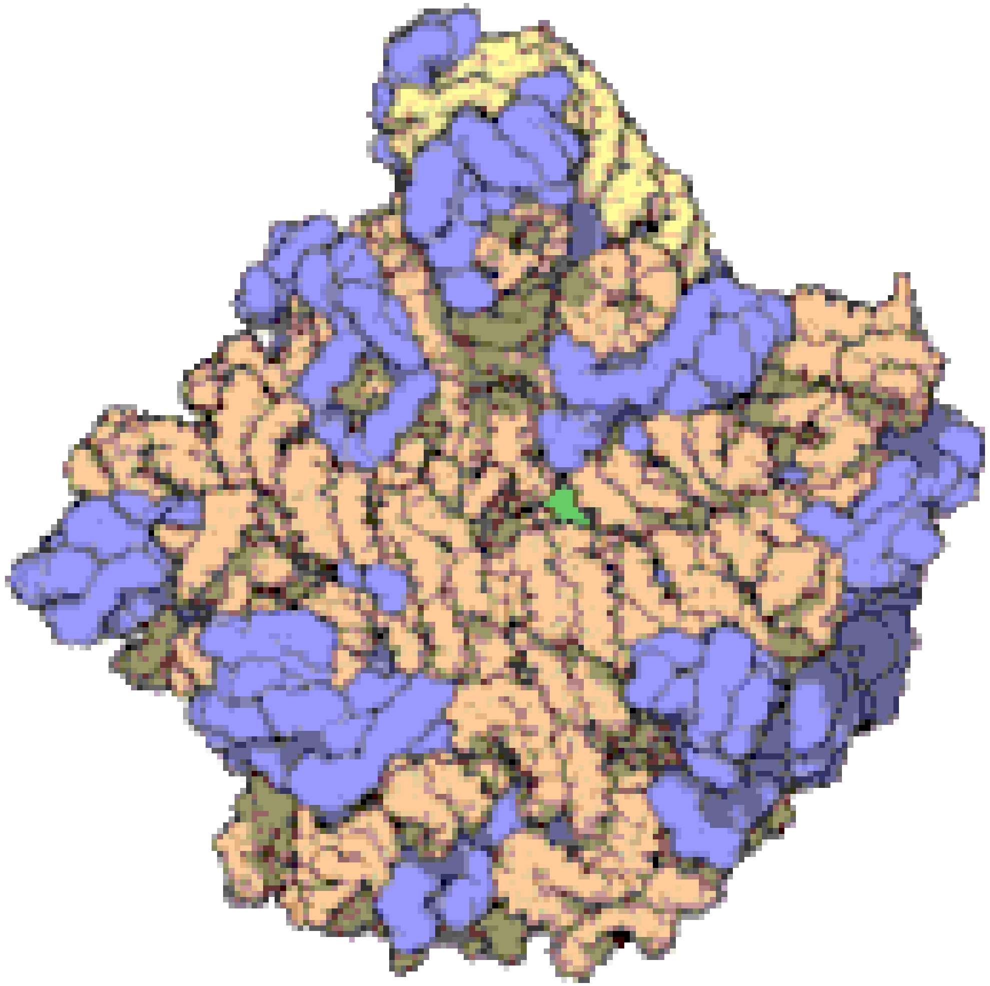
Amorphous materials, including liquids and melts, as well as crystalline materials with local disorder, can be examined using X-ray pair distribution function analysis, which requires high energy X-ray scattering data.

By tuning the beam energy through the absorption edge of a particular element of interest, the scattering from atoms of that element will be modified. These so-called resonant anomalous X-ray scattering methods can help to resolve scattering contributions from specific elements in the sample.

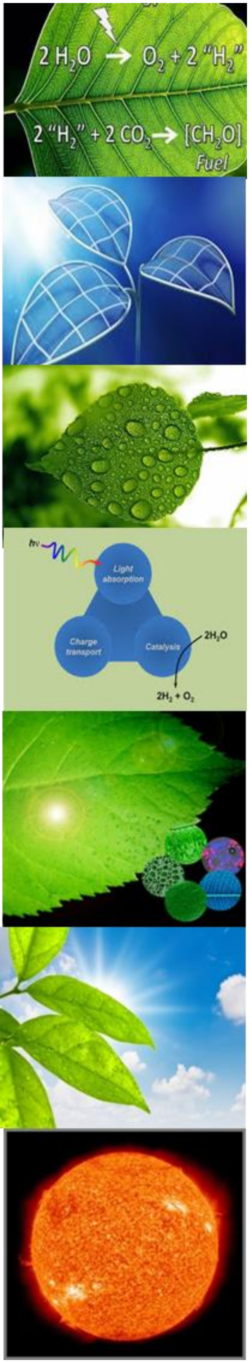
Other scattering techniques include energy dispersive X-ray diffraction, resonant inelastic X-ray scattering, and magnetic scattering.



Applications to proteins.



Structure of a ribosome subunit solved at high resolution using synchrotron X-ray crystallography.



Spectroscopy

X-ray absorption spectroscopy (XAS) is used to study the coordination structure of atoms in materials and molecules.

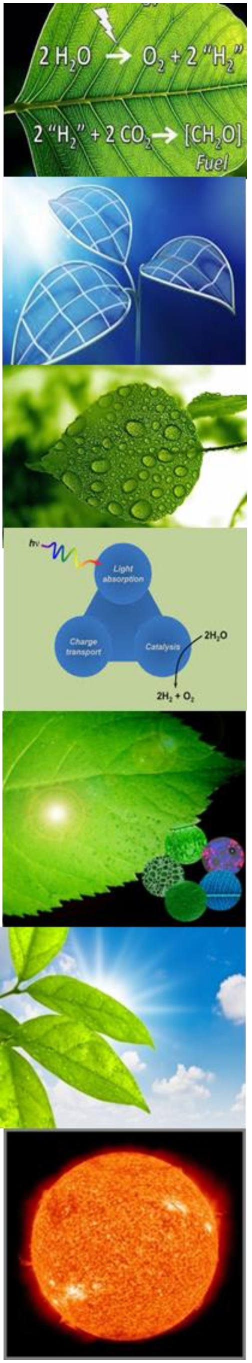
The synchrotron beam energy is tuned through the absorption edge of an element of interest, and modulations in the absorption are measured.

Photoelectron transitions cause modulations near the absorption edge, and analysis of these modulations (called the X-ray absorption near-edge structure (XANES) or near-edge X-ray absorption fine structure (NEXAFS)) reveals information about the chemical state and local symmetry of that element.

At incident beam energies which are much higher than the absorption edge, photoelectron scattering causes "ringing" modulations called the extended X-ray absorption fine structure (EXAFS).
Fourier transformation of the EXAFS regime yields the bond lengths and number of the surrounding the absorbing atom; it is therefore useful for studying liquids and amorphous materials[13] as well as sparse species such as impurities.

A related technique, X-ray magnetic circular dichroism (XMCD), uses circularly polarized X-rays to measure the magnetic properties of an element.

Imaging



Synchrotron X-rays can be used for traditional X-ray imaging, phase-contrast X-ray imaging, and tomography.

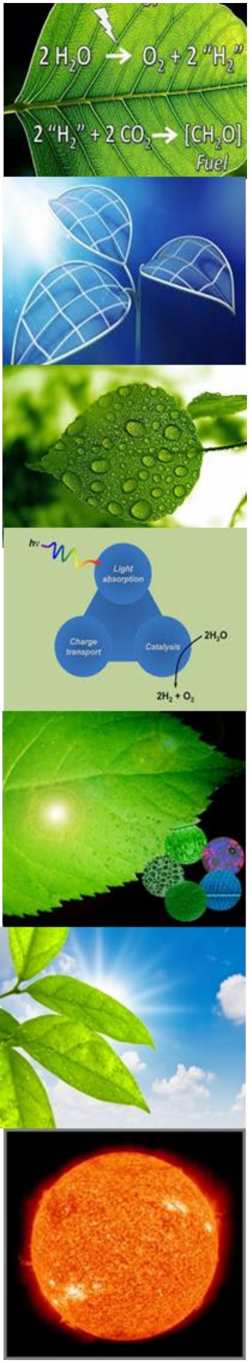
The Ångström-scale wavelength of X-rays enables imaging well below the diffraction limit of visible light, but practically the smallest resolution so far achieved is about 30 nm

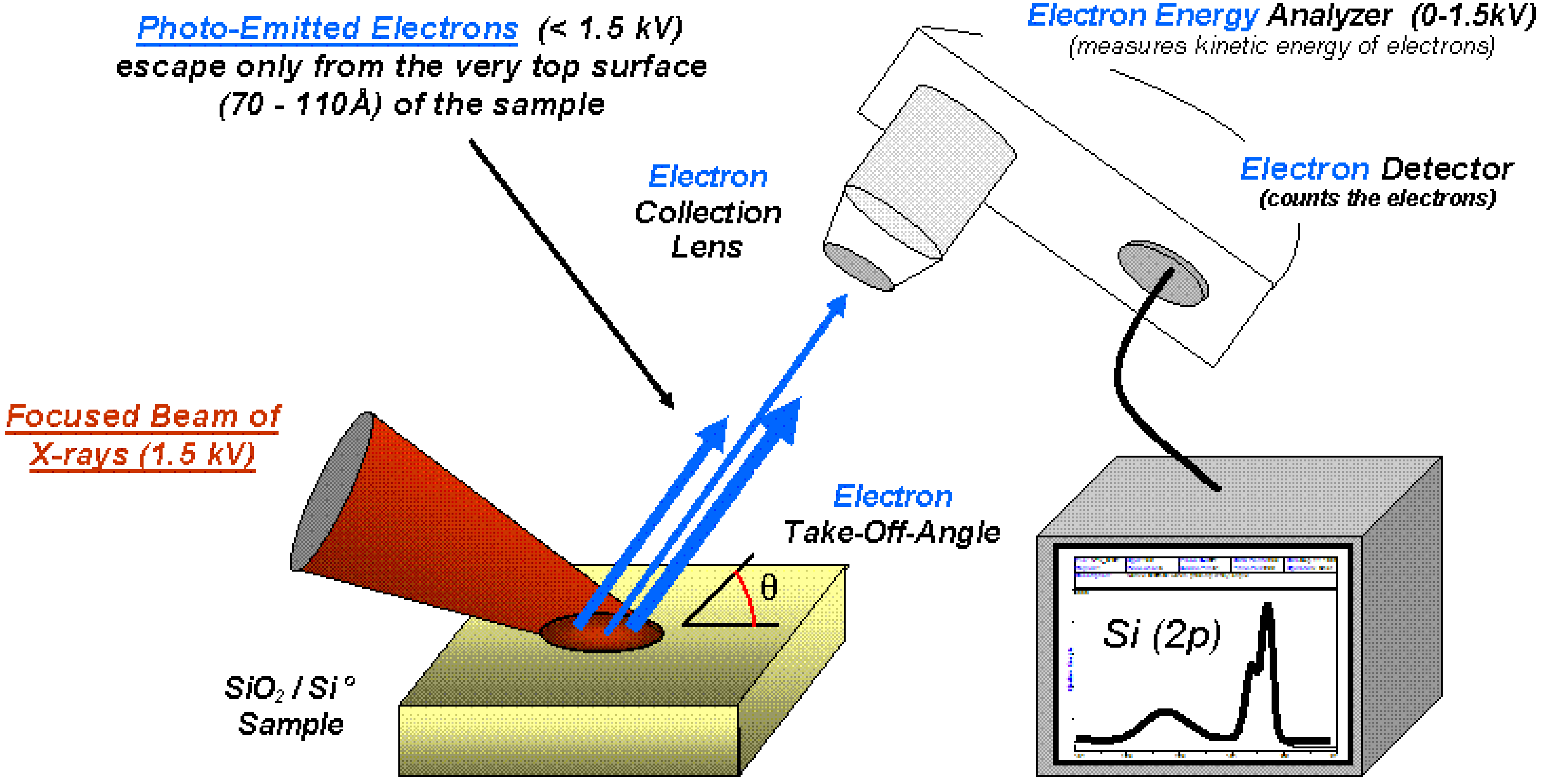
Such nanoprobe sources are used for scanning transmission X-ray microscopy (STXM). Imaging can be combined with spectroscopy such as X-ray fluorescence or X-ray absorption spectroscopy in order to map a sample's chemical composition or oxidation state with sub-micron resolution.

Other imaging techniques include coherent diffraction imaging.

Similar optics can be employed for photolithography for MEMS structures can use a synchrotron beam as part of the LIGA process.

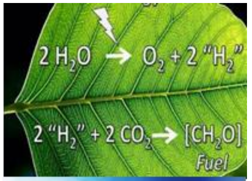
Conventional Laboratory techniques



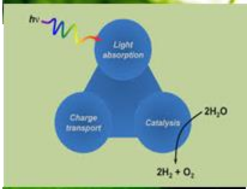


Samples are usually solid because XPS requires ultra-high vacuum ($<10^{-8}$ torr)

Si (2p) XPS signals from a Silicon Wafer









Synchrotron Radiation

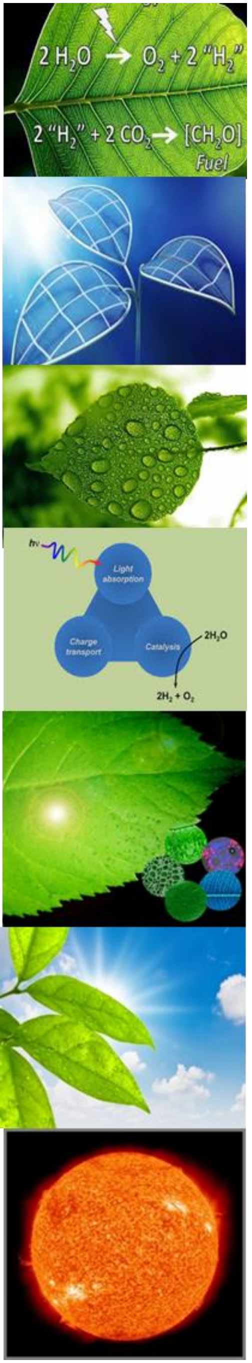
Synchrotron radiation is emitted by charged particles, traveling at speeds relative to the speed of light when accelerated by magnetic fields.

The major advantages of synchrotron radiation include very high intensity, tunable energy range, and inherently linear polarization.

However, one major drawback is the limited availability of the national and international synchrotron radiation facilities.

The availability of synchrotron radiation, with its characteristics of high brilliance, particular collimation, and multi-wavelength accessibility, continues to drive technical and theoretical advances in scattering and spectroscopy techniques.

An exciting area being developed is the exploitation of these advances in synchrotron radiation surface and bulk-specific probe techniques to study the underpinning issues of energy storage materials.



Synchrotron Radiation

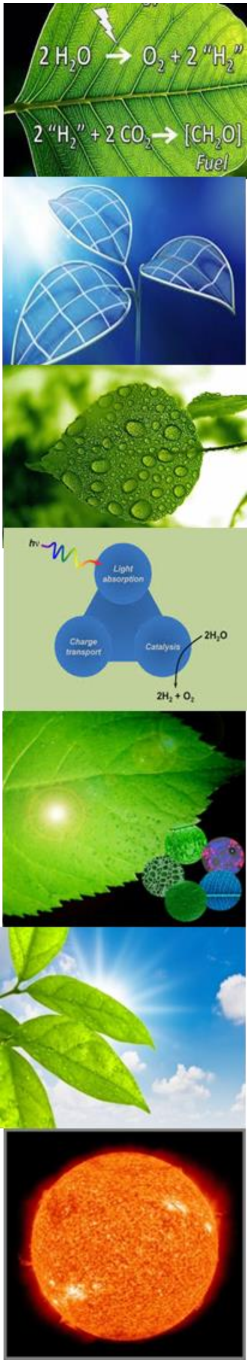
The long-term endurance of electrochemical devices, used in highly demanding applications like electric vehicles, is closely related to the ability of the cathode and anode materials to accommodate and release guest ions without any structural damage.

A challenge in developing the understanding of energy storage process in batteries is in the direct study of the electrochemical reactions involved during battery operation.

The characterization tool required needs to provide element-specific as well as overall structural information with high resolution.

Synchrotron radiation-based measurements under operating conditions of batteries are critical in order to map the mechanistic causality between the local and atomic structure of functional components of batteries and their electrochemical characteristics.

Synchrotron radiation-based X-ray methods provide inherent advantages and flexibility in obtaining detailed mechanistic information along with structural studies.



Electrochemical mechanisms

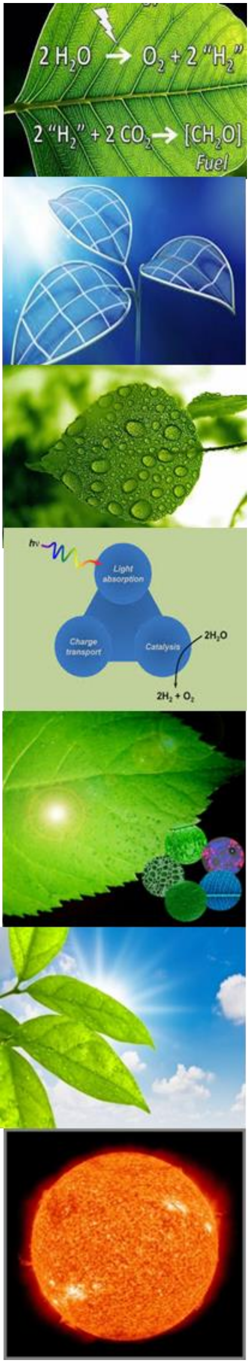
A "photoelectrochemical cell" is one of two distinct classes of devices.

The first produces electrical energy similarly to a dye-sensitized solar cell.

The second is a photo-lectrolytic cell, a device which uses light incident on a photosensitizer like semiconductor, or metal immersed in an electrolytic solution to directly cause a chemical reaction, for example to produce hydrogen via the electrolysis of water.

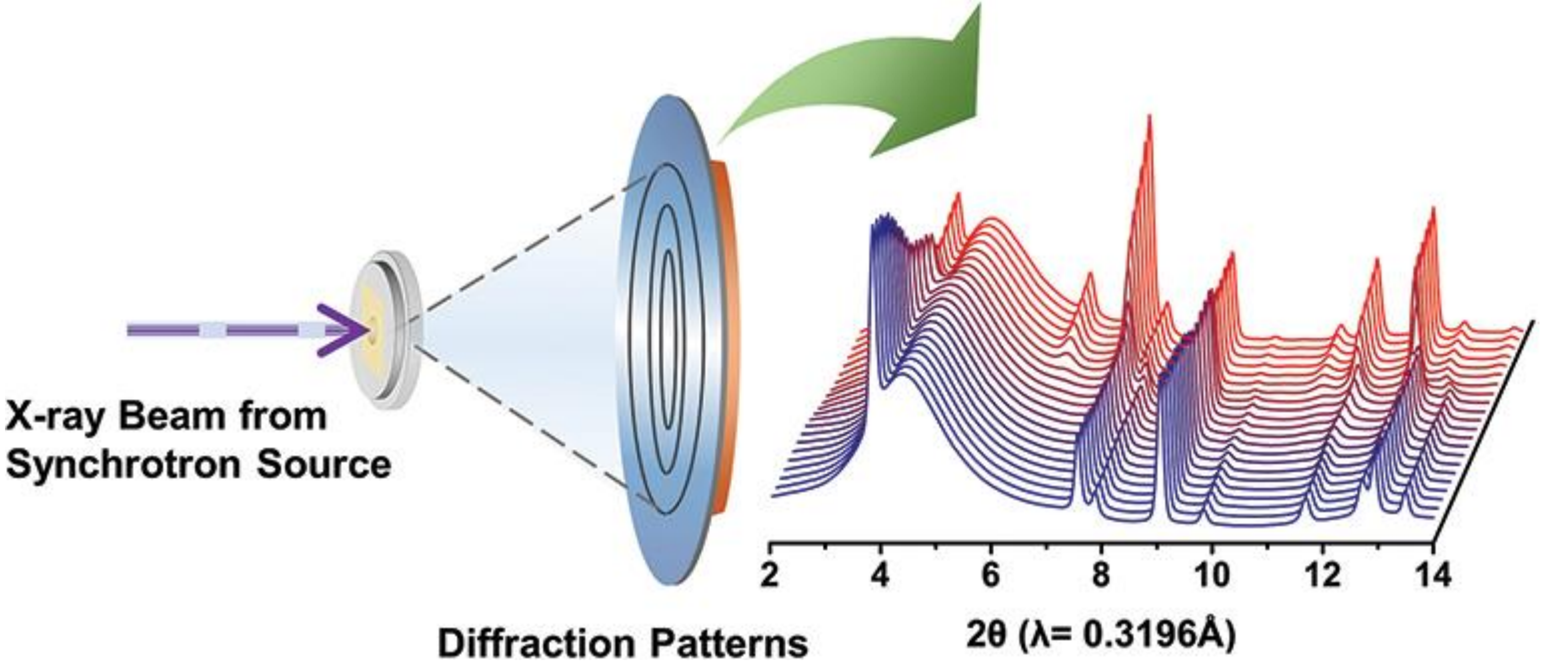
The function of a photoelectrochemical cell is to use the photoelectric effect and the photovoltaic effect to convert electromagnetic radiation (typically sunlight) either directly into electrical power, or into something which can itself be easily used to produce electrical power like hydrogen

Hydrogen, for example, can be burned to create electrical power.

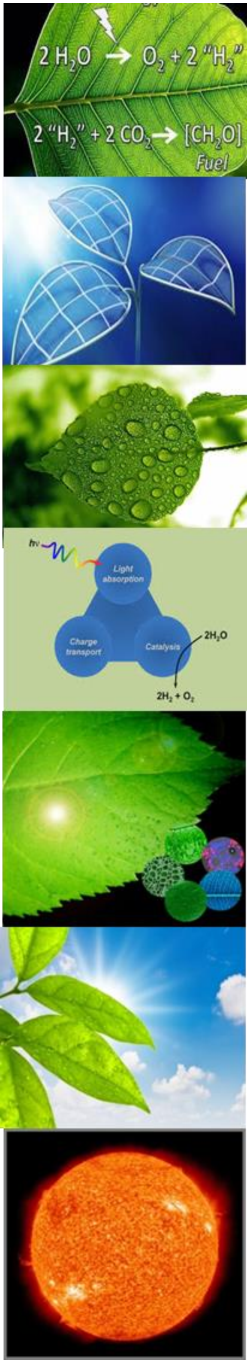


Synchrotron-based radiation techniques

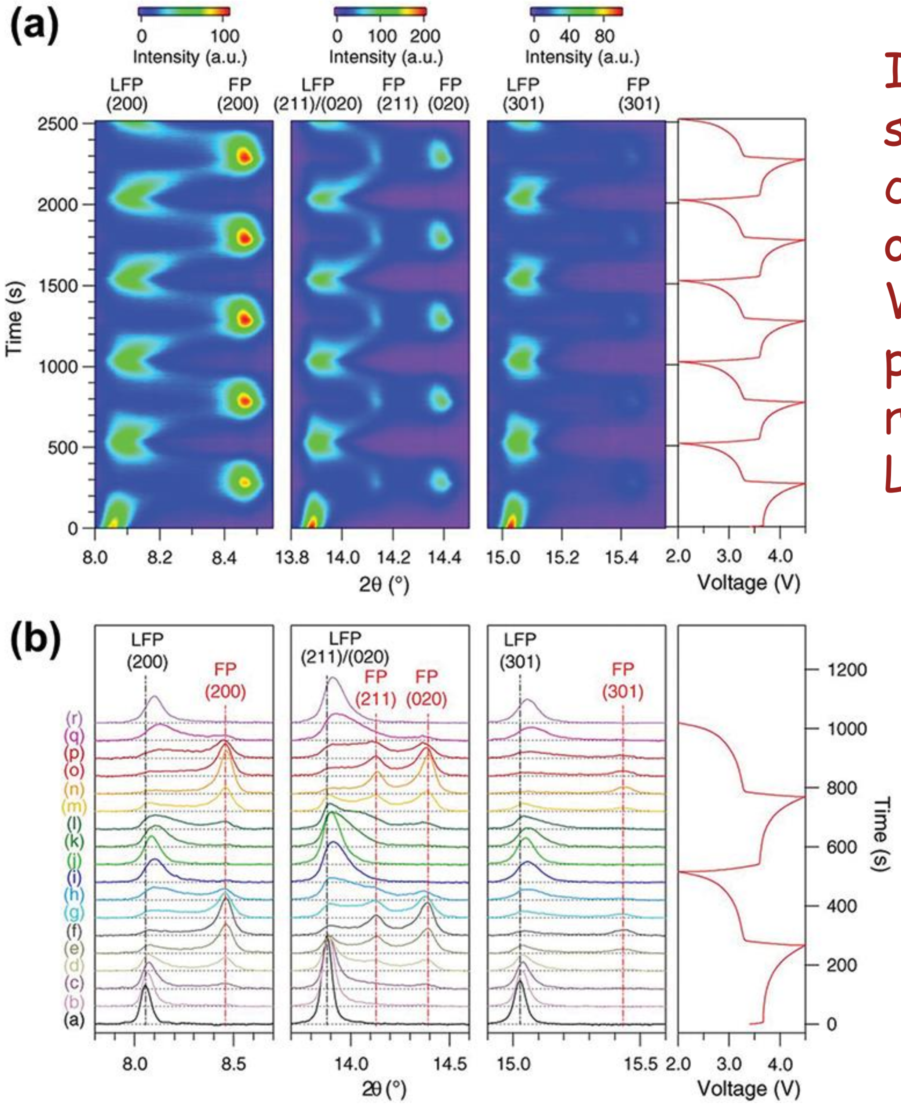
Wide-angle X-ray scattering (WAXS) has the ability to probe many different crystallographic planes simultaneously, resulting in fast and rich data acquisition.



The use of high energy, sometimes referred to as hard X-rays, is advantageous because these X-rays are not absorbed well in a solid material and therefore allow for deep penetration.



Case of Li-ion batteries

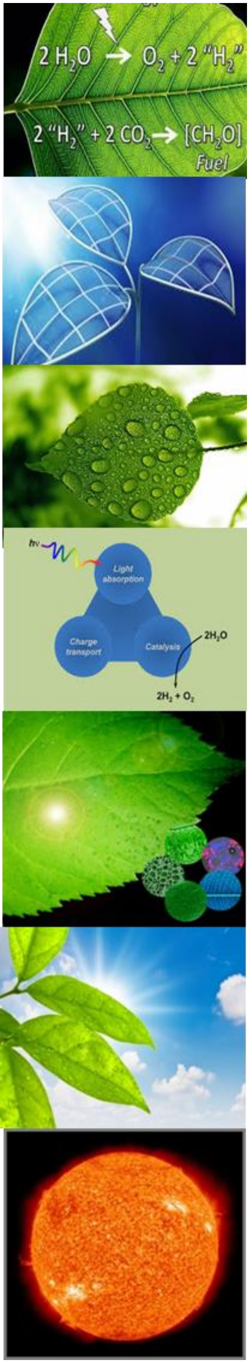


In situ XRD investigations performed on micrometer-sized $LiFePO_4$ show the emergence of a metastable crystalline phase with an intermediate Li composition of $Li_{0.6\text{-}0.75}FePO_4$ when cycled at high rates. Whereas, studies on nanometer-sized $LiFePO_4$ particles are limited to low and moderate current rates, and only small deviations in stoichiometry from $LiFePO_4$ and $FePO_4$ were observed during cycling

The variations of XRD pattern during the galvanostatic charge and discharge at a rate of 10 C.

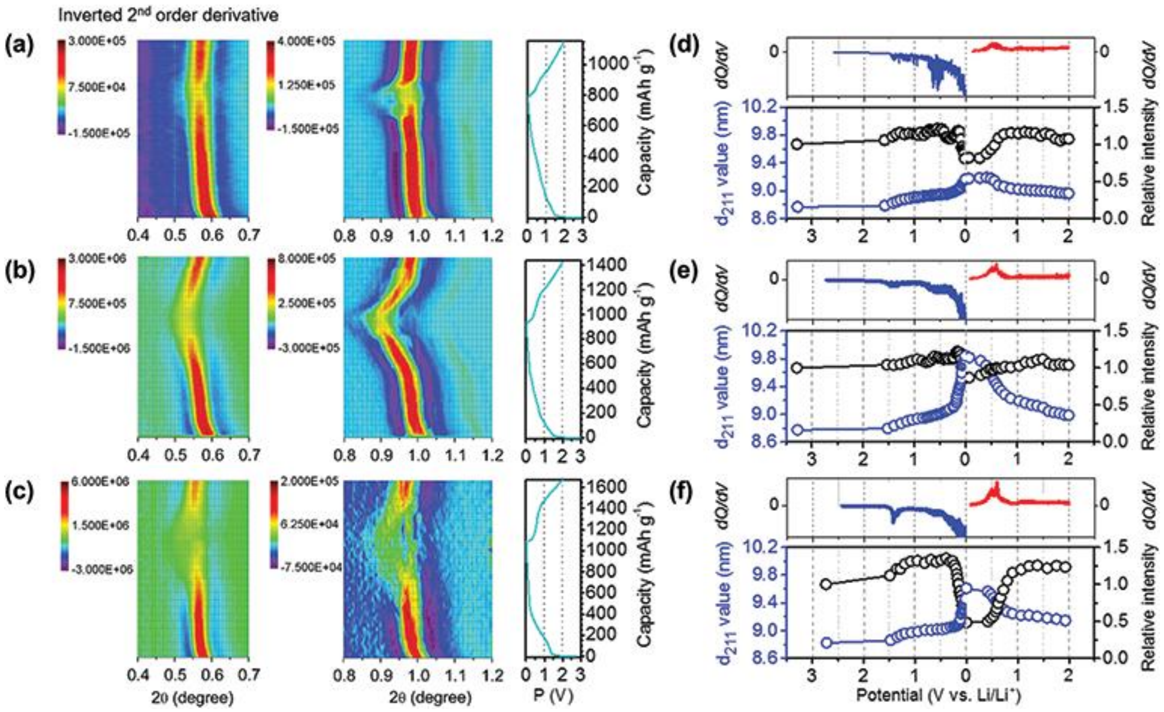
(a) The image plot of diffraction patterns for selected reflections during the first five electrochemical cycles. The corresponding voltage curve is plotted to the right.

(b) Selected individual diffraction patterns during the first two electrochemical cycles stacked against the voltage profile.

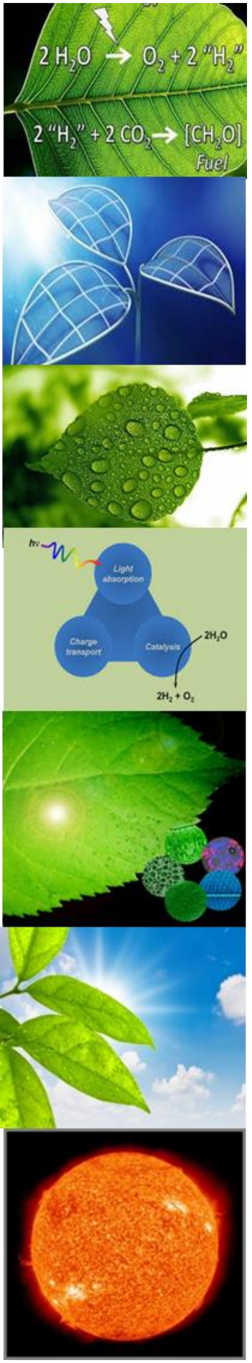


Case of li-ion batteries

Small-angle X-ray scattering (SAXS). SAXS is a technique to study material structures at small angles or large distances. SAXS is a powerful technique to determine, not only the object's size, size distribution, shape, surface structure, relative positions of particles, but it can also be used for the structure factor analysis. The size distribution function is a key piece of information that can be obtained from SAXS.



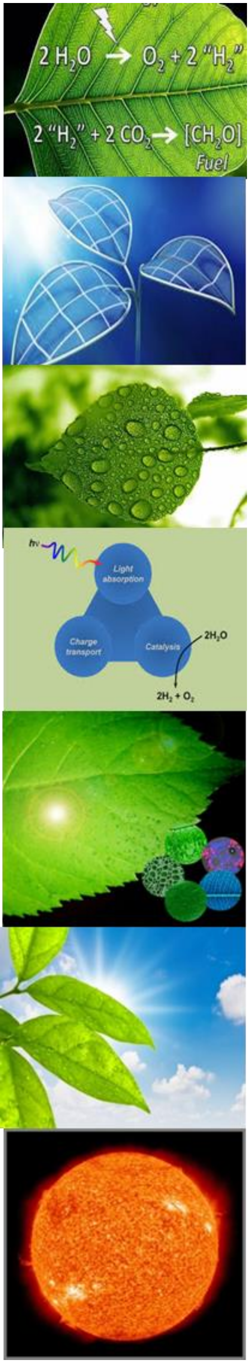
a–c) Color-coded contour projection maps during in situ experiment with corresponding voltage profile and (d–f) the changes in lattice parameters and resolved peak-relative intensities with the corresponding dQ/dV plot for meso-Co0.5Sn0.5, meso-Co0.3Sn0.7, and meso-Co0.1Sn0.9, respectively.



Synchrotron radiation-based X-ray absorption techniques

X-ray absorption spectroscopy (XAS): is a powerful technique that can characterize all forms of matter, irrespective of their degree of crystallinity. XAS spectrum can be divided in two parts, namely, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). In XANES phenomenon, an element-specific signal is generated, typically using a synchrotron radiation source. A core electron absorbs the energy of incident X-rays and gets excited beyond the Fermi level, leaving behind a core hole. The synchrotron radiation sources can provide energy that is right for desired electron transitions. When a sample is exposed to X-rays, it will absorb part of the incoming photon beams. Other phenomena occurring are heat, X-ray fluorescence, production of unbound electrons, and of course the scattering of X-rays

Hydrogen fuel

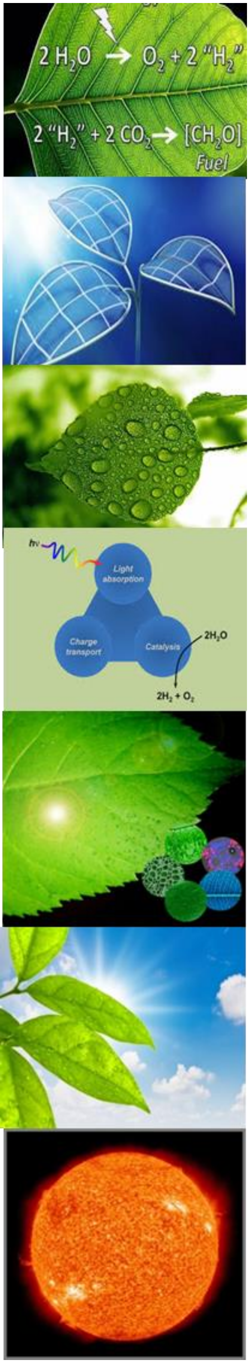


A case for hematite

"In rust we trust". Hematite – the prospective inorganic backbone for artificial photosynthesis.

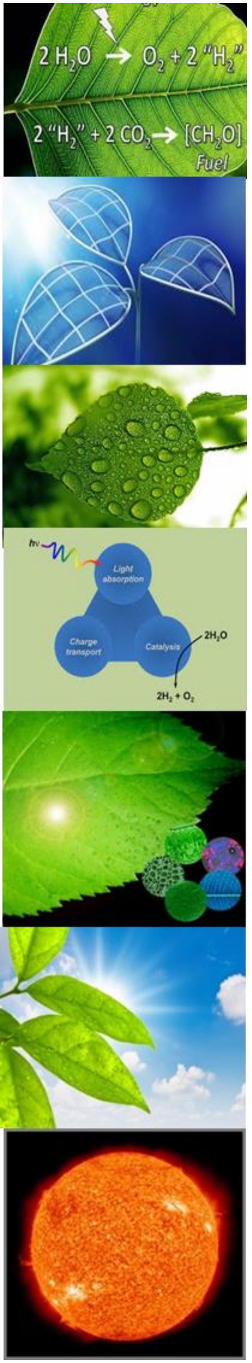
Several methods take advantage of the high intensity, tunable wavelength, collimation, and polarization of synchrotron radiation at beamlines which are designed for specific kinds of experiments.

The high intensity and penetrating power of synchrotron X-rays enables experiments to be performed inside sample cells designed for specific environments.



Semiconductor requirements

- ***Suitable band gap***
- ***Suitable band positions***
- ***Low overpotentials***
- ***Efficient charge transport***
- ***Stability***

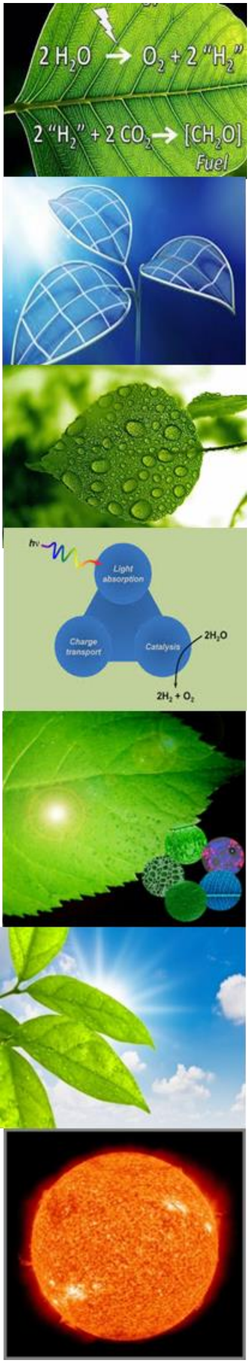


Low overpotential

The total potential (E_T) required to drive PEC water splitting is defined as follows:

$$E_T = 1.23\ eV + \eta_{anode} + \eta_{cathode} + \eta_{other}$$

where 1.23 eV is the thermodynamic potential value for water splitting, η_{anode} and $\eta_{cathode}$ represent the overpotentials at the anode and cathode side, respectively, and η_{other} is the voltage drop from other resistances in the electrochemical cell such as the solution resistance, contact resistance and the resistance in the external wires



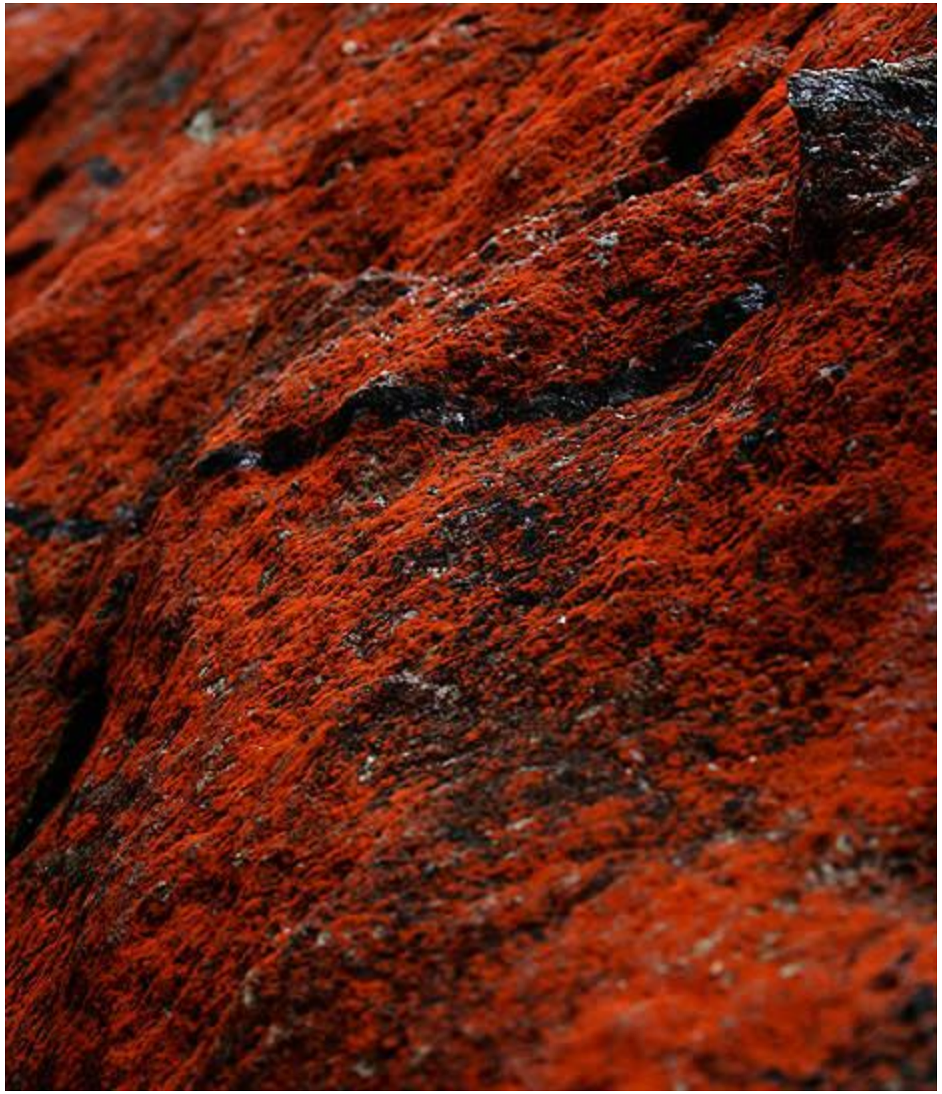
Stability

- Semiconductor materials such as CdS, ZnO, MoS_2 can easily undergo anodic photocorrosion in a PEC environment depending on the pH of the electrolyte (since decomposition potential is influenced by pH).

- On the contrary, photoanodes such as TiO_2, $BiVO_4$, α-Fe_2O_3 have shown great thermodynamic stability in a PEC device due to their slow decomposition reaction kinetics

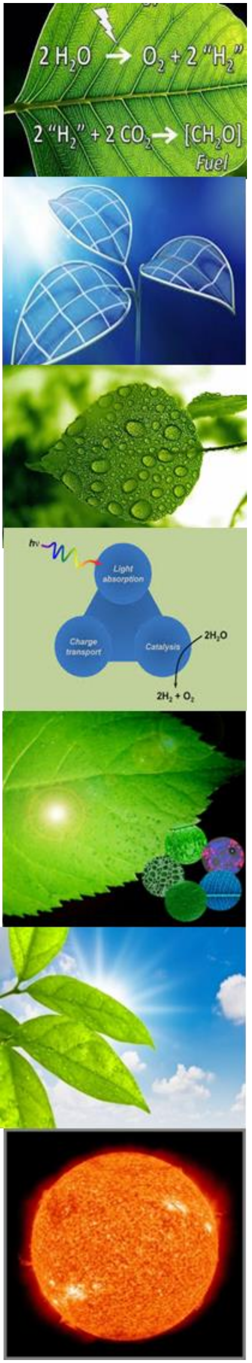
Hematite

Advantages
Small band gap of 2.0-2.2 eV
Relative abundance
Chemical stability in aqueous environments
Suitable band position for oxygen evolution reaction



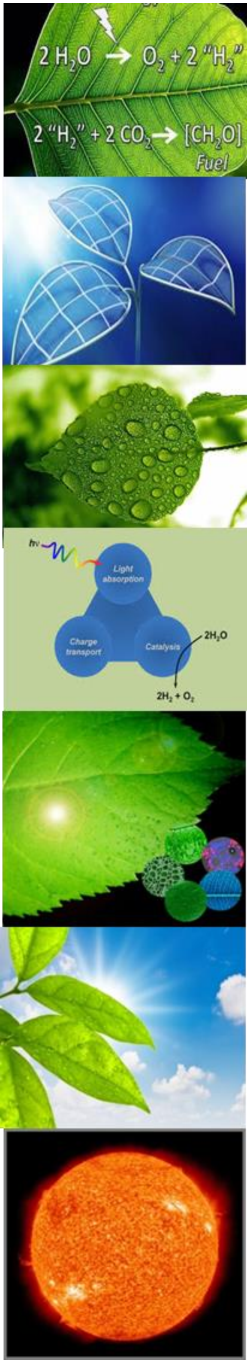
Disadvantages
poor conductivity
Short lifetime of excited state carrier (10^{-12} s)
Poor oxygen evolution reaction kinetics
Short hole diffusion length (2-4 nm).

Image sources: hhttps://www.mining-technology.com/projects/yukonolympicmine/attachment/yukonolympicmine1/



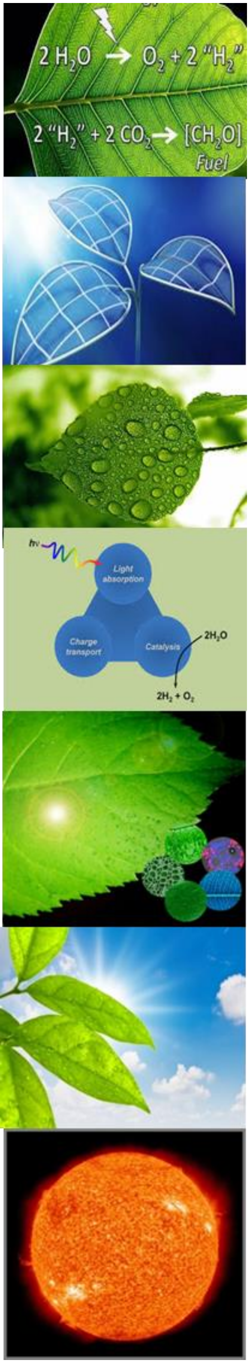
Methods of preparing hematite

- ***Solution based***
- ***Hydrothermal***
- ***Spray pyrolysis***
- ***Chemical vapour deposition***
- ***Electrodeposition***
- ***etc***

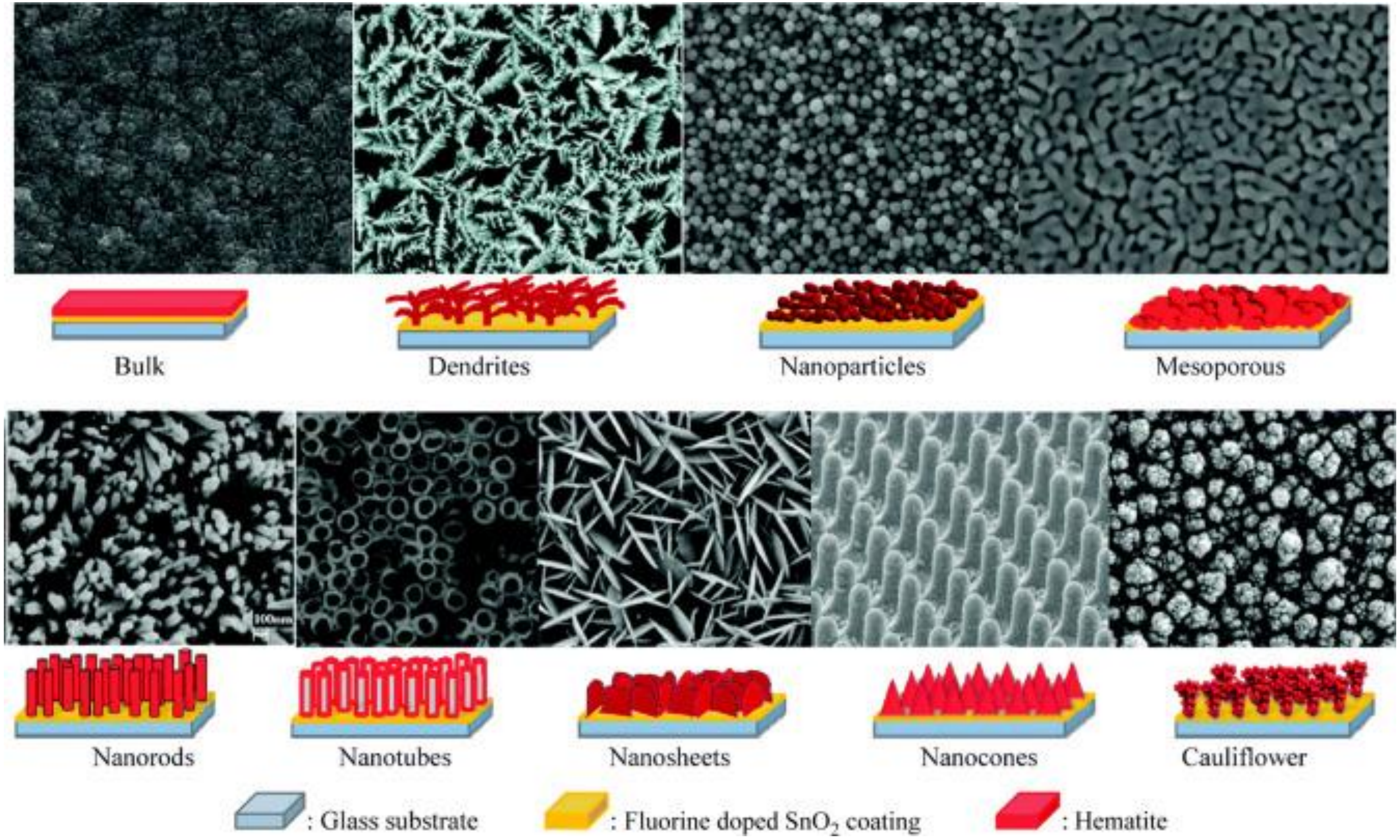


Strategies of improving PEC properties

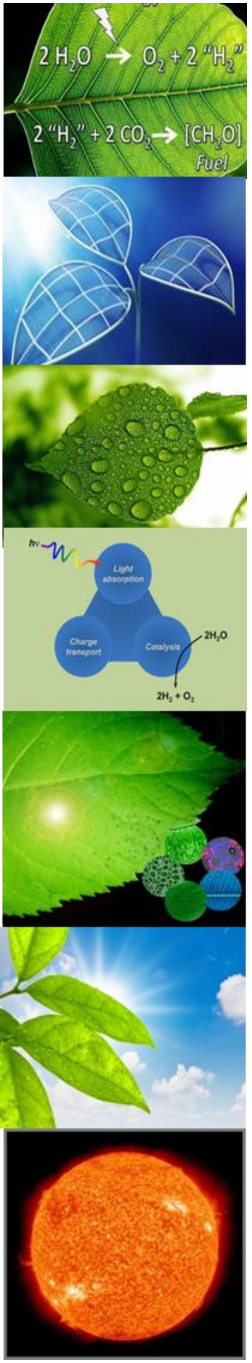
- ***Nanostructuring***
- ***Doping***
- ***Heterojunction structures***
- ***Modification with Co-catalyst***
- ***Plasmonic enhancement***



Nanostructuring



Impedance measurements



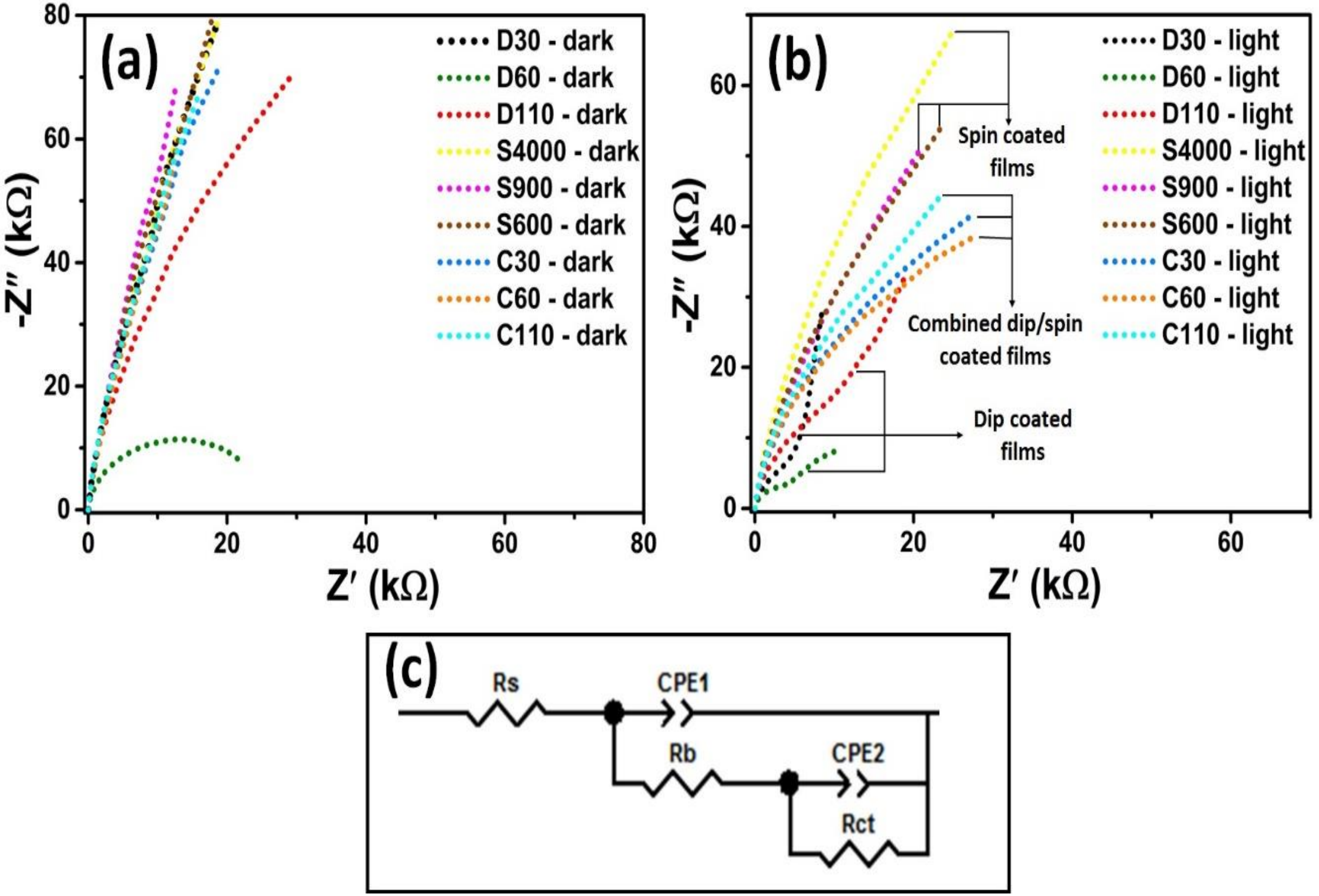
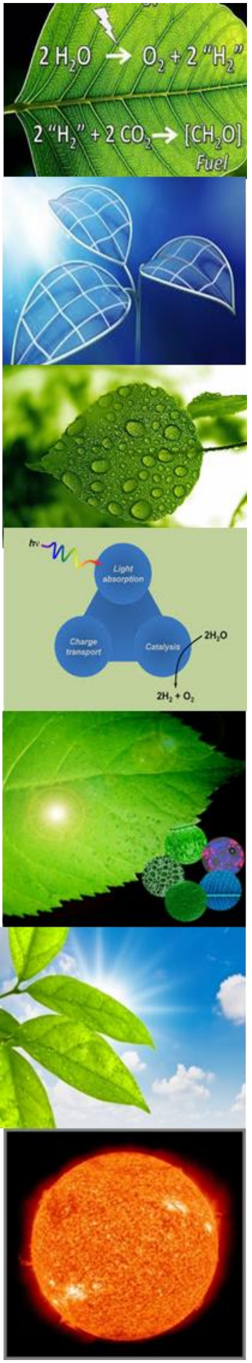


Figure 4.8. FE-SEM cross-sectional views of samples (a) D30, (b) D60 and (c) D110 prepared using dip coating and (d) S4000, (e) S900 and (f) S600 for spin coated films and (g) C30, (h) C60 and (i) C110 fabricated via the combined dip/spin coating techniques respectively.



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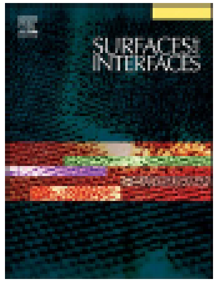

Influence of coating techniques on the optical and structural properties of hematite thin films

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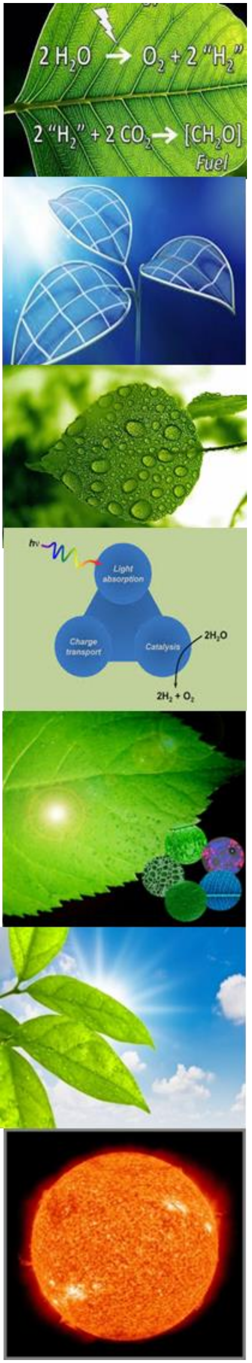
A R T I C L E I N F O

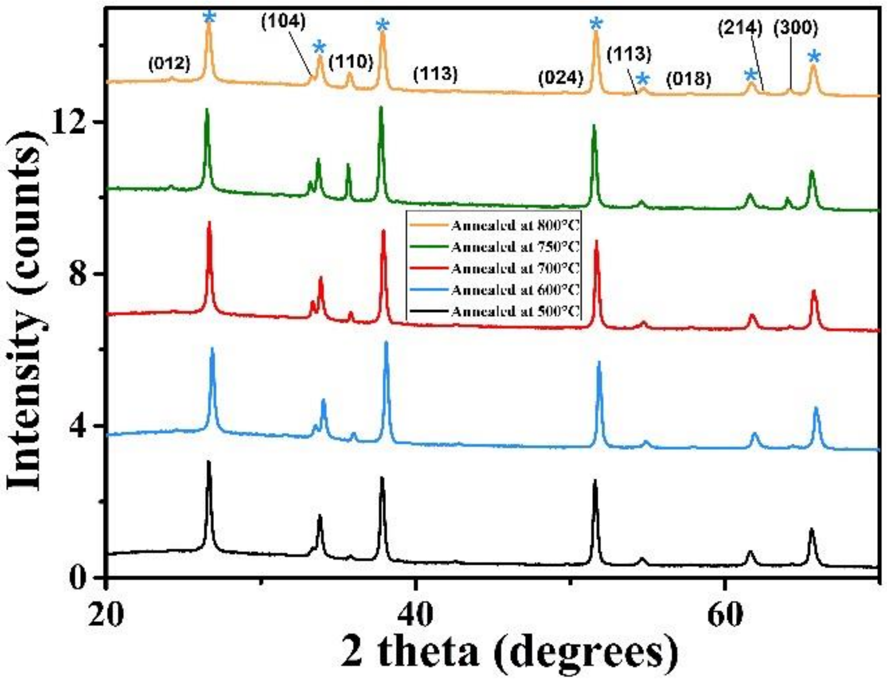
Keywords:
Hematite
Dip coating

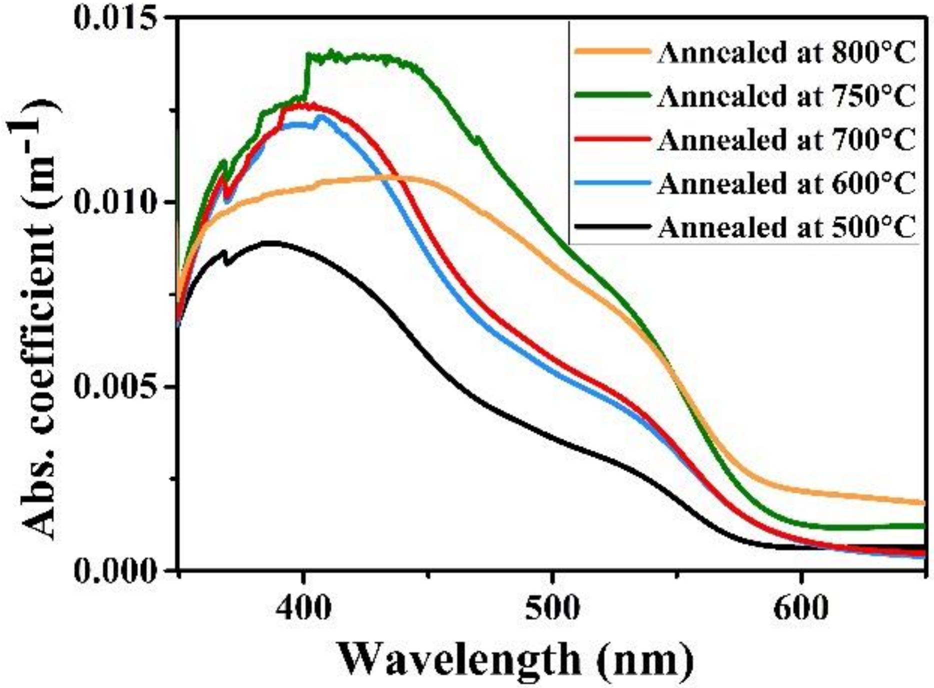
A B S T R A C T

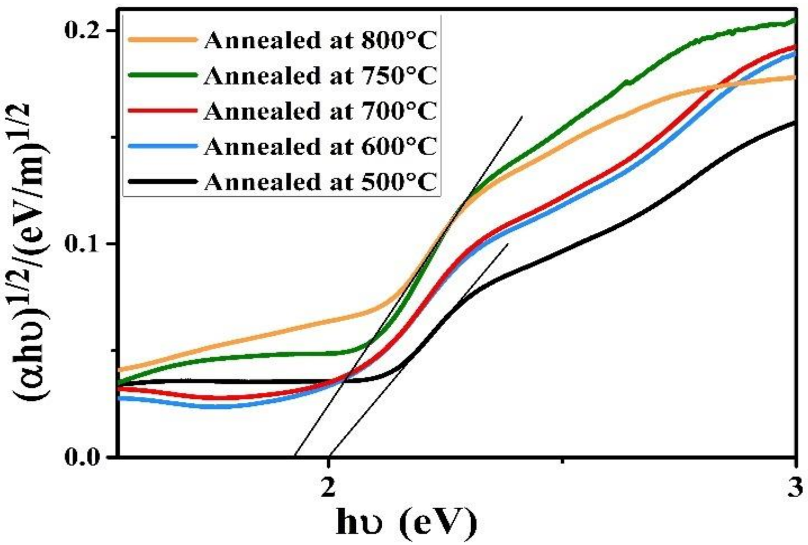
Hematite (α-Fe_2O_3) thin films were deposited by dip, spin and combined coating techniques on fluorine-doped tin oxide (FTO)/glass substrates. Structural properties observed from X-ray Diffraction (XRD) and Raman spectra analysis suggest better crystallinity for films prepared by dip and combined coating techniques as compared to

Structural and optical properties

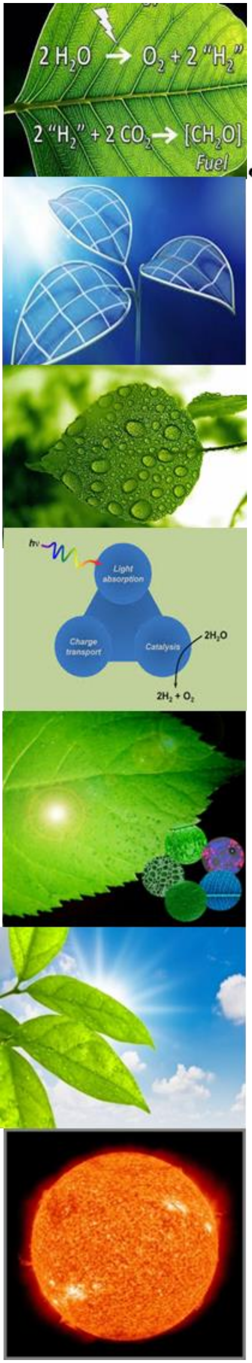


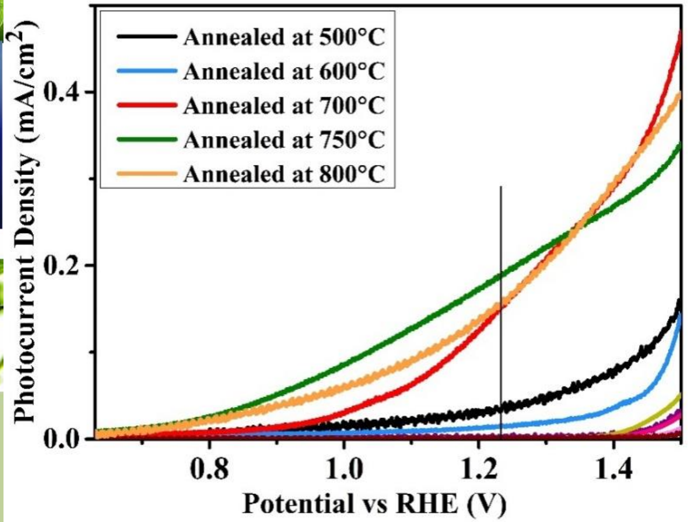


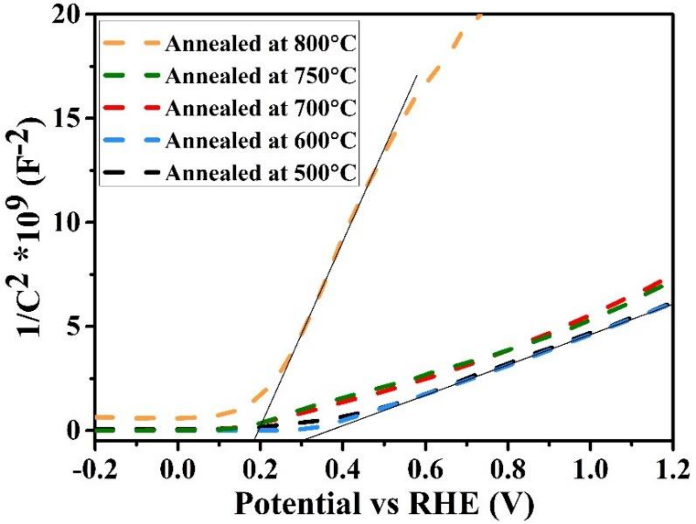




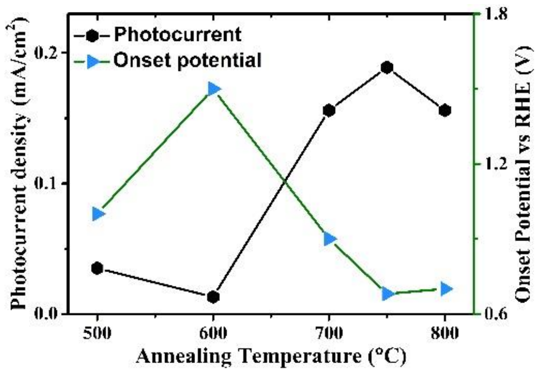
PEC performance

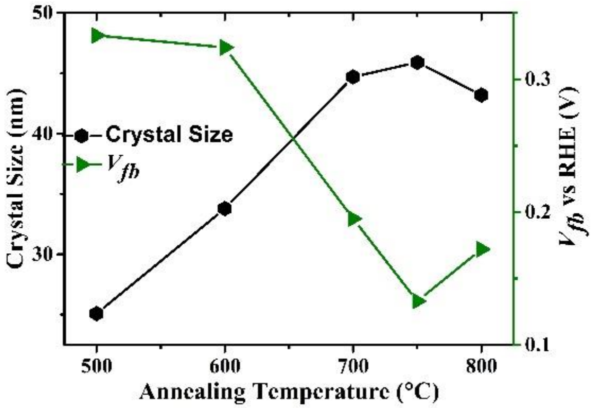


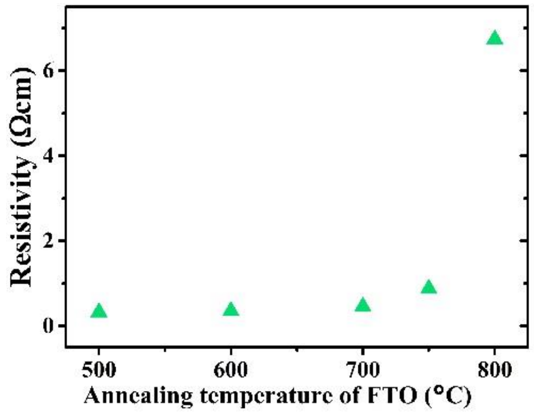




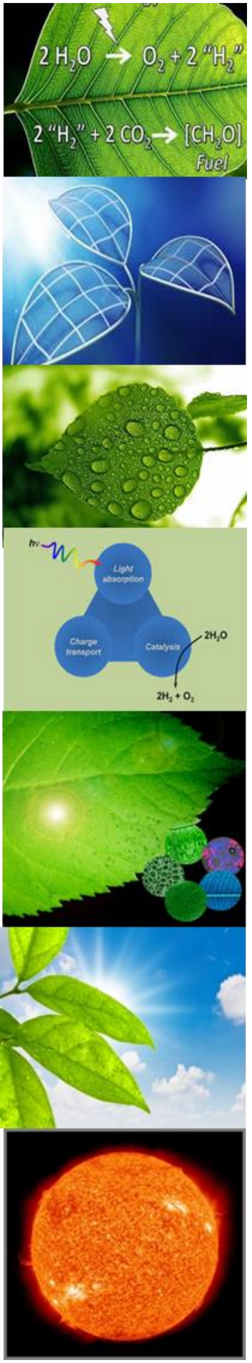
Sample	Flat band potential (V_{fb}) / V	$N_D \times 10^{19}$ /cm^{-3}
Annealed at 500°C	0.333	8.6
Annealed at 600°C	0.324	8.7
Annealed at 700°C	0.195	9.4
Annealed at 750°C	0.133	10.3
Annealed at 800°C	0.172	1.4



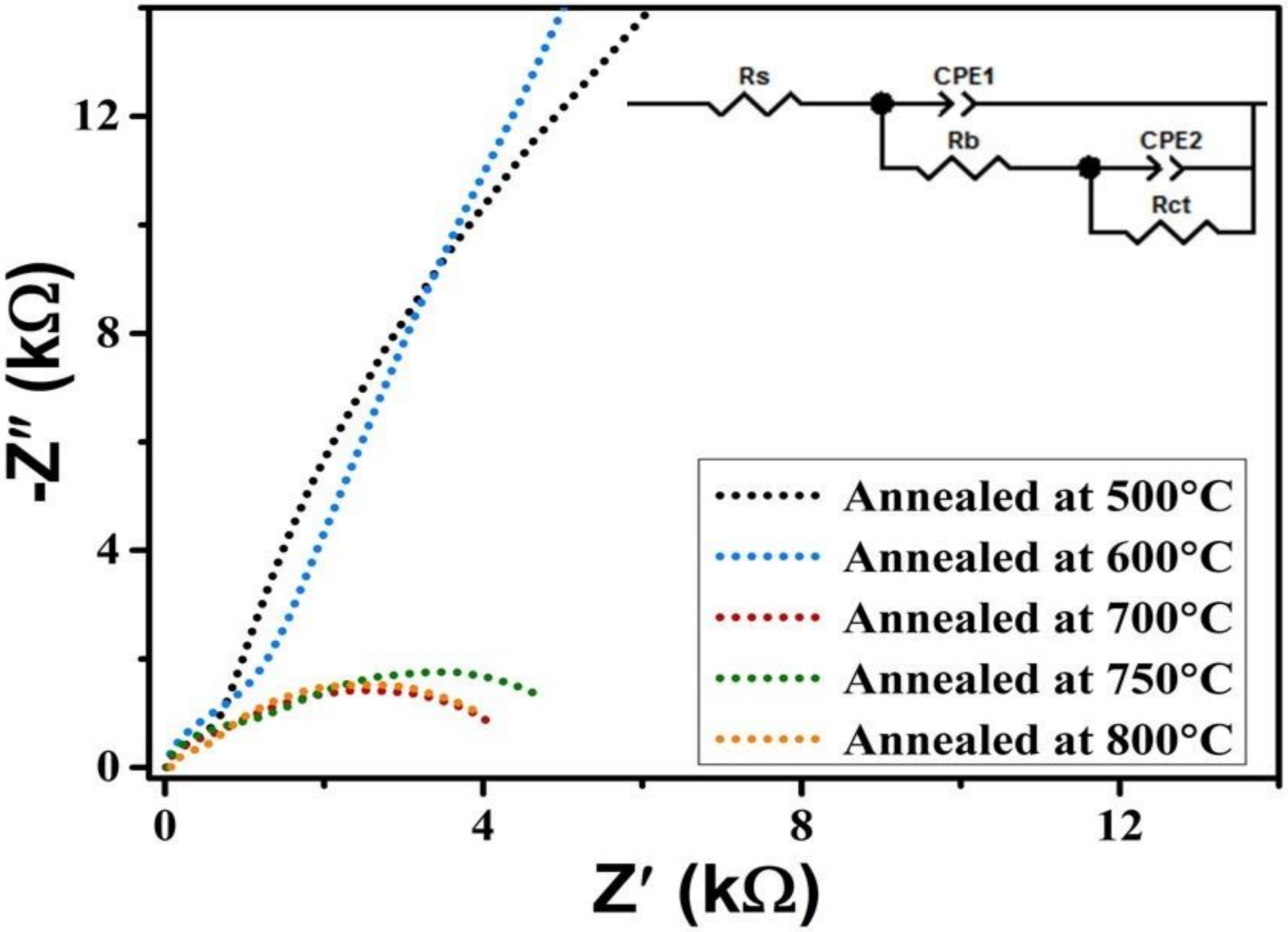




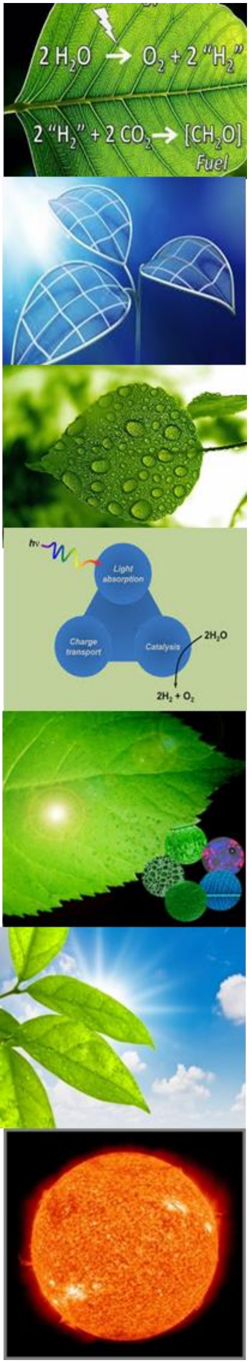
- Photocurrent was improved by a factor of 5.3 at 1.23 V vs RHE by annealing the last layers at 750°C. A cathodic shift of 300 mV of the onset potential was achieved.
- Mott-Schottky analysis revealed increase in donor density and lowering of flat band potential for films annealed at 750°C which contributed to the enhanced PEC performance observed.



PEC performance - EIS



Sample	Rs (Ω)	R1 (kΩ)	CPE1 (µF)	R2 kΩ	CPE2 (µF)
Annealed at 500°C	11.07	1.24	27.91	70.99	49.54
Annealed at 600°C	11.27	2.17	21.11	183.28	58.312
Annealed at 700°C	16.22	1.1	16.81	3.5	105.3
Annealed at 750°C	32.78	1.66	22.81	3.88	170.51
Annealed at 800°C	68.57	1.55	70.19	3.15	45.24



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Modified annealing approach for preparing multi-layered hematite thin films for photoelectrochemical water splitting

Pannan I. Kyesmen[a,*], Nolwazi Nombona[b], Mmantsae Diale[a,*]

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A R T I C L E I N F O

Keywords:
Hematite

A B S T R A C T

Multi-layered hematite (α-Fe_2O_3) films were prepared on fluorine-doped tin oxide (FTO) using the dip coating method. The first three layers of the films were annealed at 500 °C and fourth layers at 500, 600, 700, 750 and

Structural and optical properties

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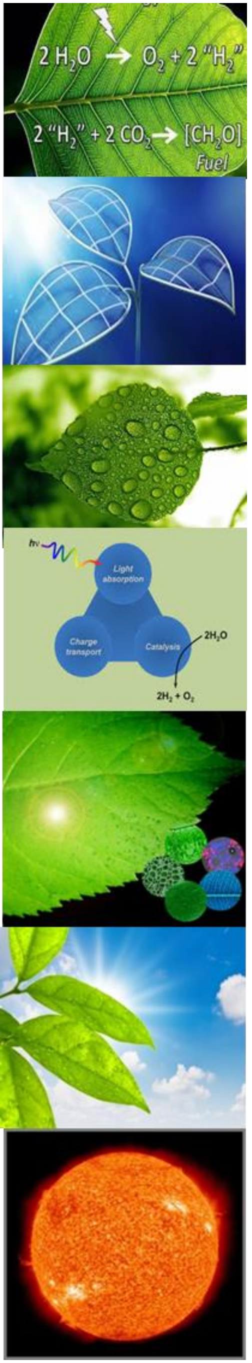
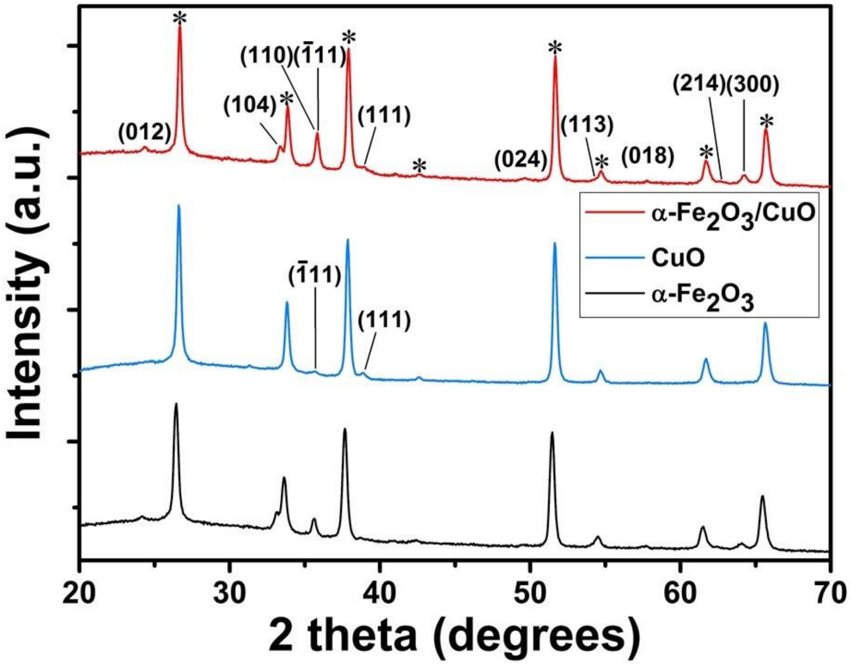
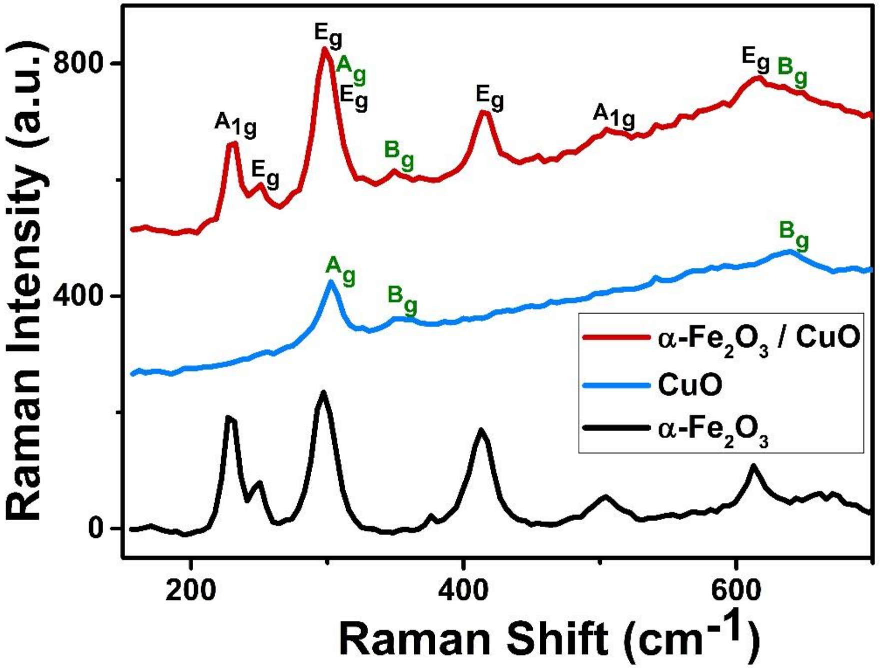
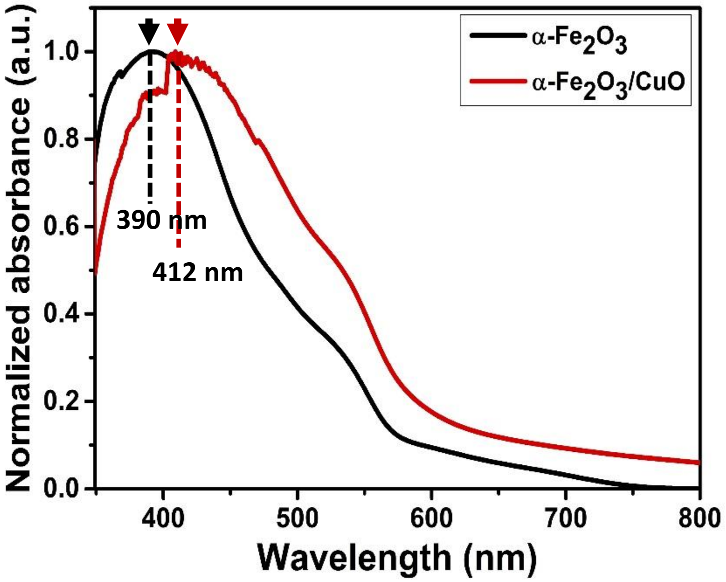
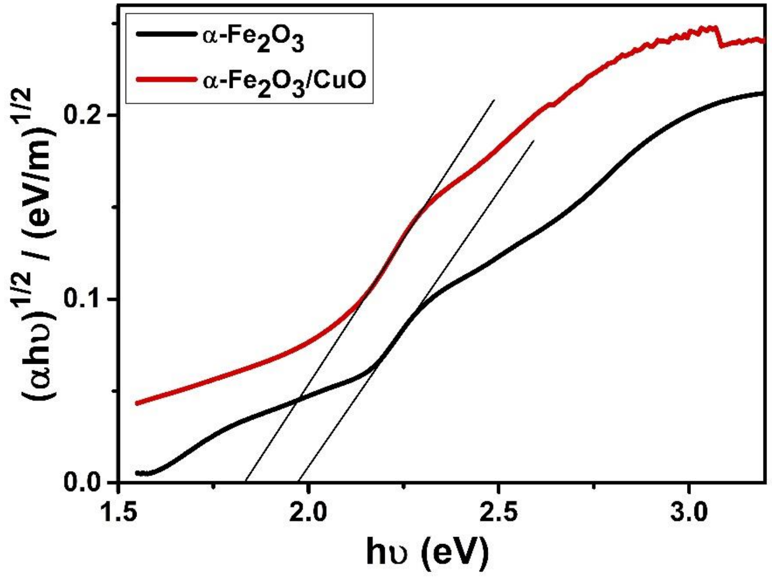


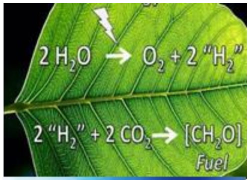


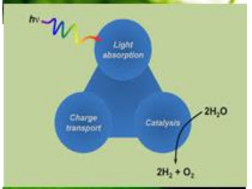


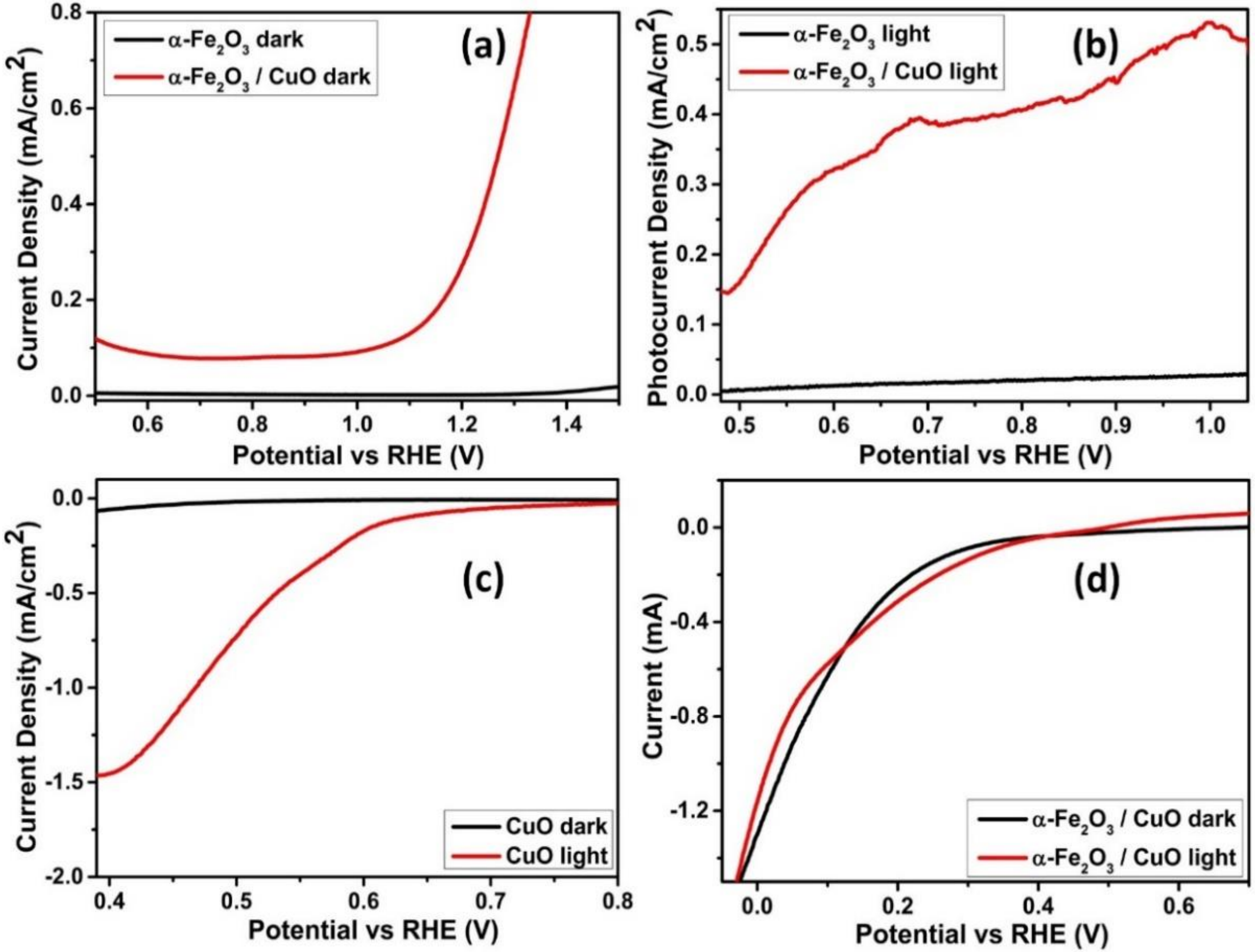




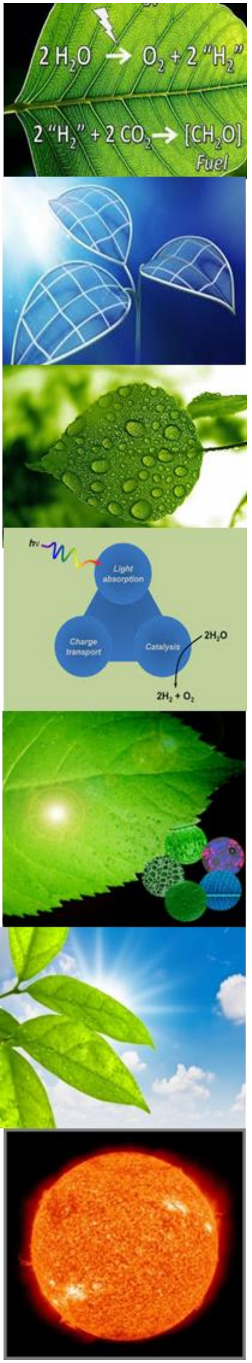
Photocurrent measurements

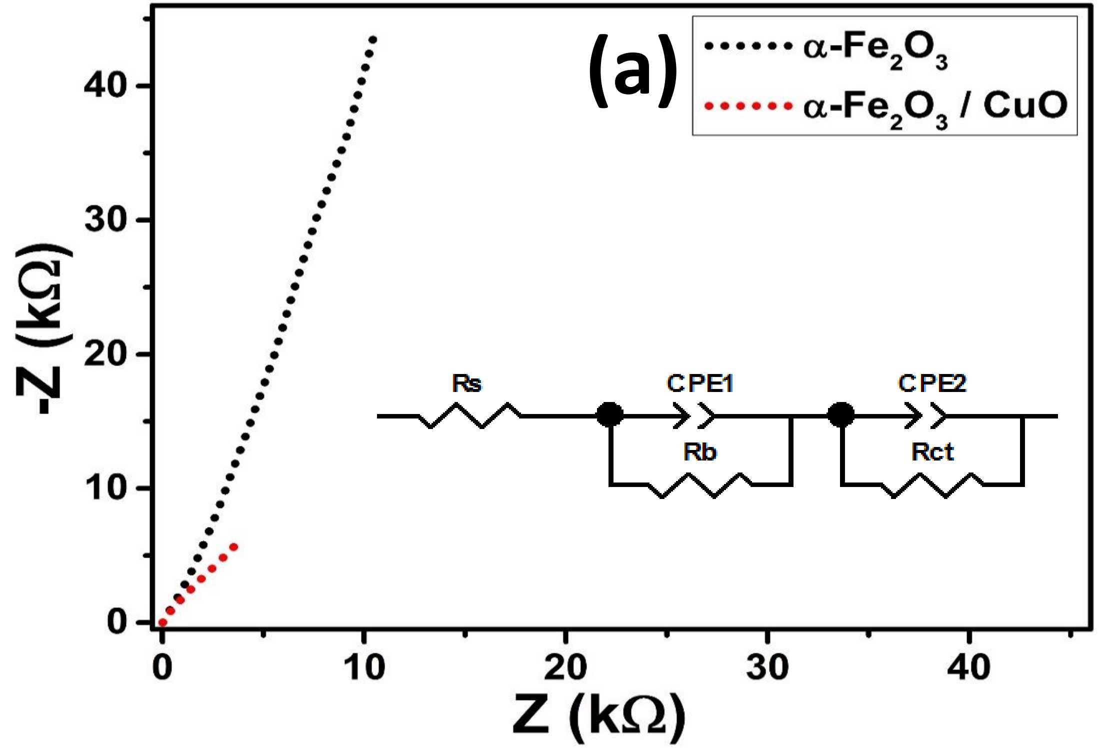






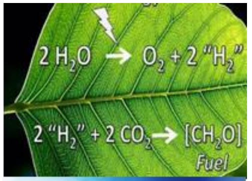
Impedance measurements



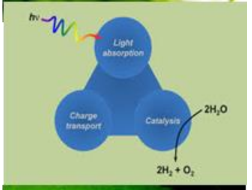


Sample	Rs (Ω)	Rb (kΩ)	CPE1 (μF)	Rct kΩ	CPE2 (μF)
α-Fe_2O_3	15.29	2.25	55.99	850	34.03
α-Fe_2O_3/CuO	15.19	1.68	240.62	29.6	226.05

List of selected publications









[1] P. I. Kyesmen, N. Nombona, and M. Diale, "Modified annealing approach for preparing multi-layered hematite thin films for photoelectrochemical water splitting," *Materials Research Bulletin,* vol. 131, p. 110964, 2020.

[2] P. I. Kyesmen, N. Nombona, and M. Diale, "Influence of coating techniques on the optical and structural properties of hematite thin films," *Surfaces and Interfaces,* vol. 17, p. 100384, 2019.

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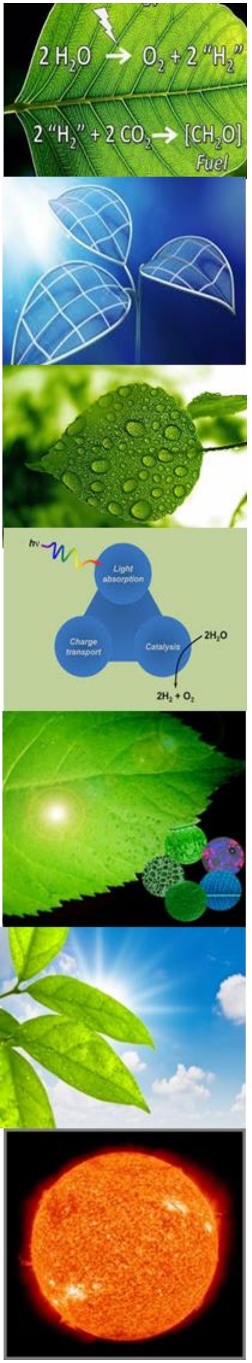

Summary

1. Strategies such as nanostructuring and the formation of heterojunction structures are efficient in enhancing the PEC properties of hematite.
2. Dip coated films produced the highest photocurrent densities while the films prepared using the spin coating method yielded the least values across samples of different thicknesses
3. Photocurrent was improved by a factor of 5.3 at 1.23 V vs RHE through modified annealing approach. It also resulted in cathodic shift of 300 mV of the onset potential.
4. The use of nanostructured heterojunction of hematite and porous CuO yielded 19-fold increase in photocurrent.

Acknowledgments

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Thank you
for listening