Enhance Solar Water Splitting Performance by Utilizing Near Infrared Radiation with Composite Films of Hematite and Rare Earth Doped Upconversion Materials

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ECI: Rare Earth Minerals/Metals –Sustainable Technologies for the Future

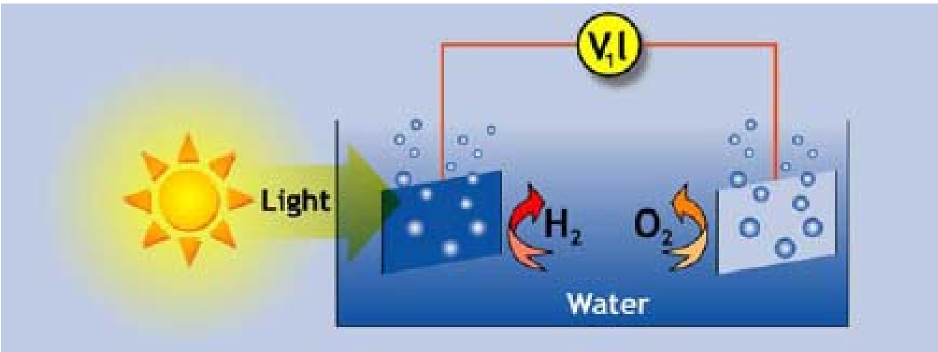
August 12-17, 2012, San Diego, California, USA

Section: Alternative Source of REE and Applications

Introduction

Water splitting is the general term for a chemical reaction in which water is separated into oxygen and hydrogen. Efficient and economical water splitting would be a key technology component of a hydrogen economy.

- Clean – no greenhouse gases
- Energy secure – can be produced from abundant sources
- Efficient – fuel cells ~75% efficiency
- Portable: Car tanks, micro fuel cells…

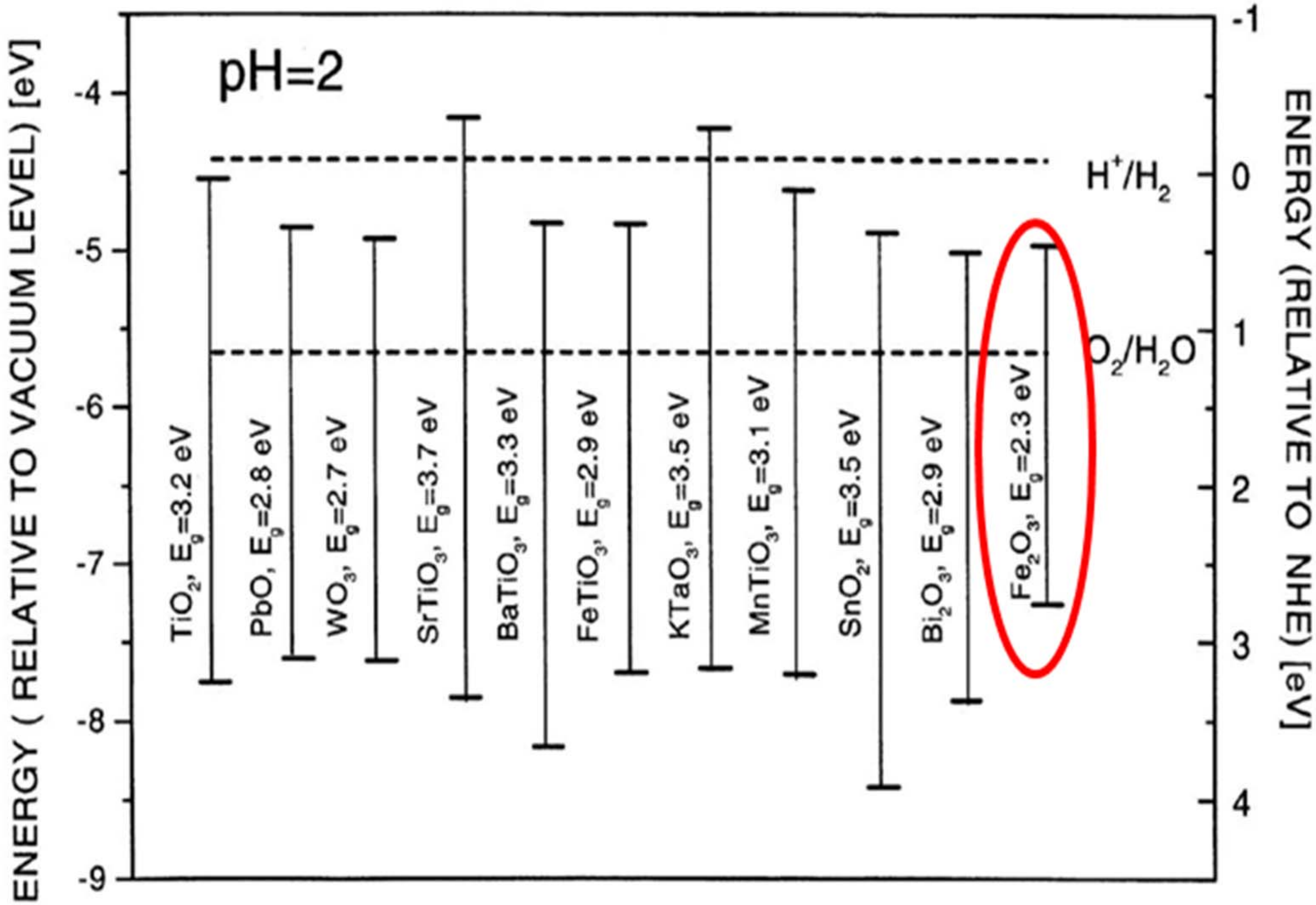


Solar Energy is an inexhaustible clean energy resource with minimal environmental impact.

Our goal is to utilize this solar energy for water splitting with high efficiency.

Energy harvested from the sun needs to be efficiently converted into chemical fuel that can be stored, transported, and used upon demand.

Hematite is a Promising Candidate for Solar Water Splitting

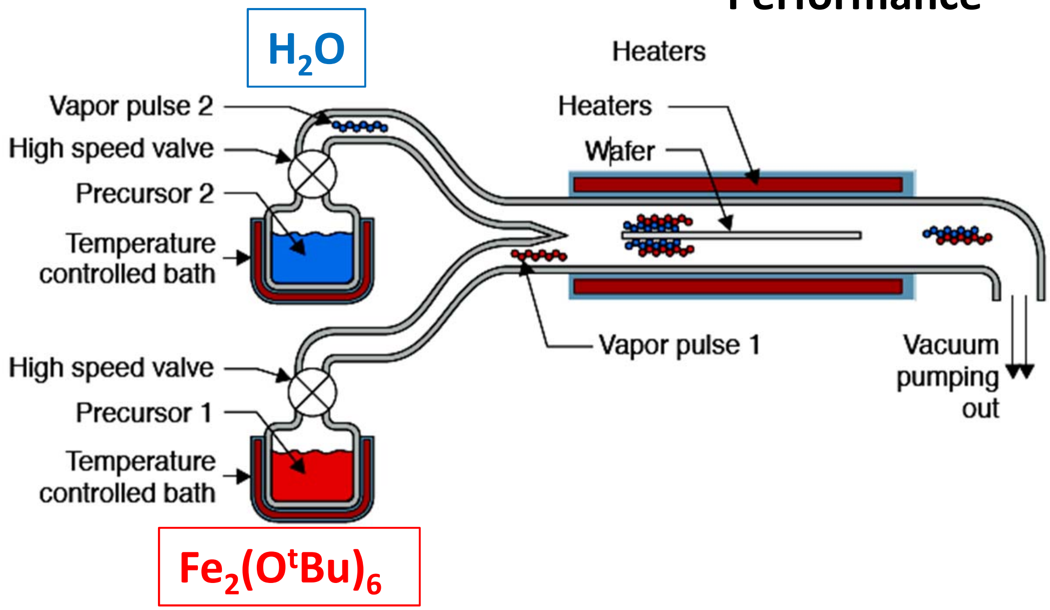


1.Low cost and abundant. Iron is the fourth most common element

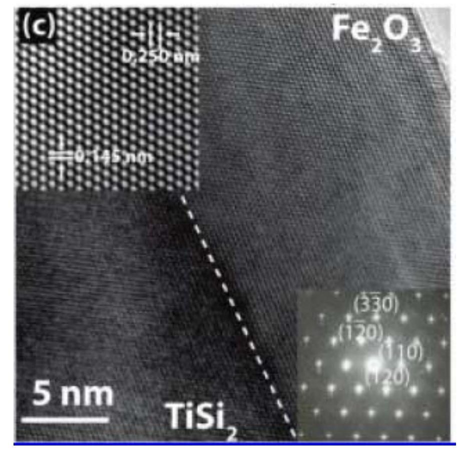
2. Non-toxicity and stable

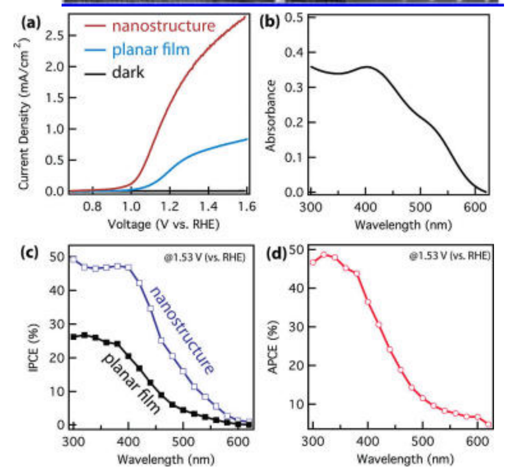
3. Suitable band-gap (Eg= 2.0-2.3 eV)

Atomic Layer Deposition (ALD) of Hematite Film on Surfaces and Their Water Splitting Performance



Schematic diagram for ALD process





ALD is a method of applying thin films to various substrates with atomic scale precision.

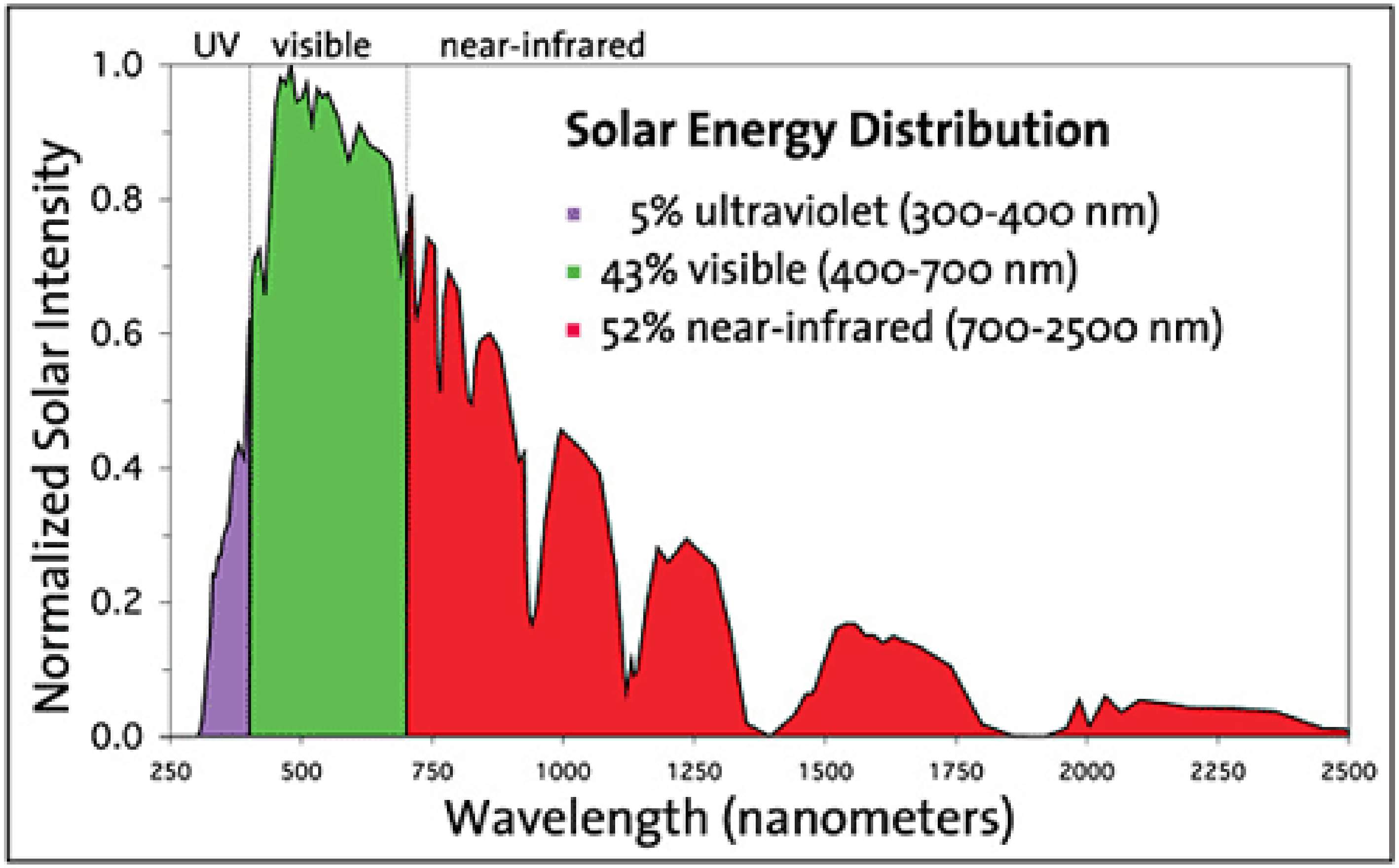
Hematite prepared by ALD uniformly and homogeneously cover substrates.

Photoelectrochemical measurement indicate hematite film could be used as semiconductor photocatalyst to split water for solar energy harvesting and storage.

J. Am. Chem. Soc., **2011**, *133*, 2398–2401

J. Am. Chem. Soc., **2012**, *134*, 5508–5511

Solar Energy Spectrum Distribution and Harvest by Semiconductor Photocatalyst



Solar energy distribution graph illustrating that infrared radiation makes up a large portion of the solar spectrum.

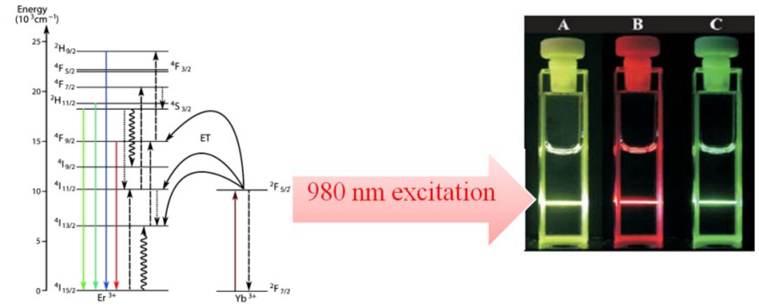
In current solar water splitting device using semiconductor as a photocatalyst, only UV and a small portion of visible light can be utilized to split water.

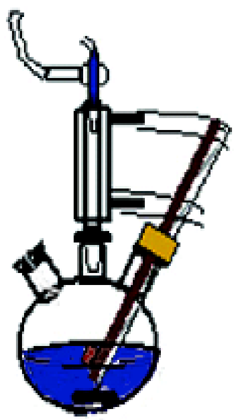
How to improve the efficiency of solar water splitting device?

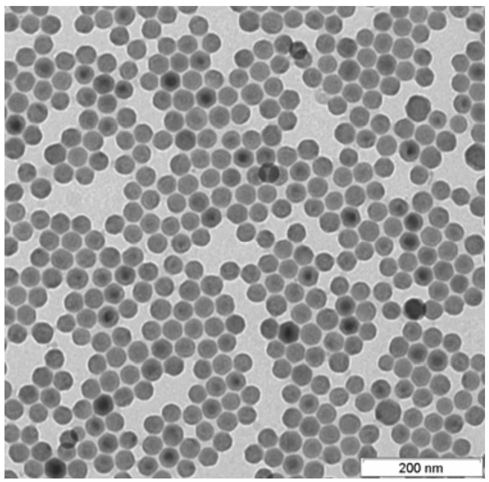
Utilizing the large amount of low energy photons in IR range.

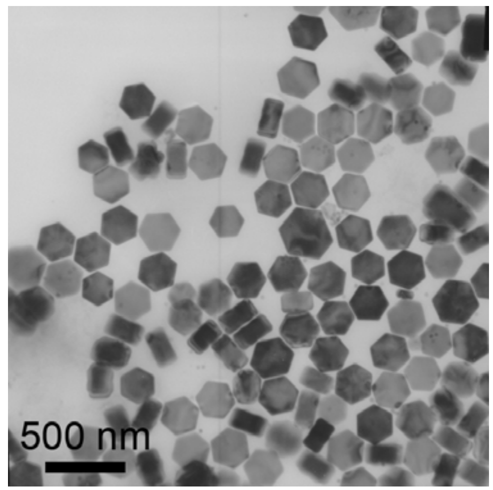
Synthesis and Characterization of Rare Earth Doped Upconversion Nanocrystals

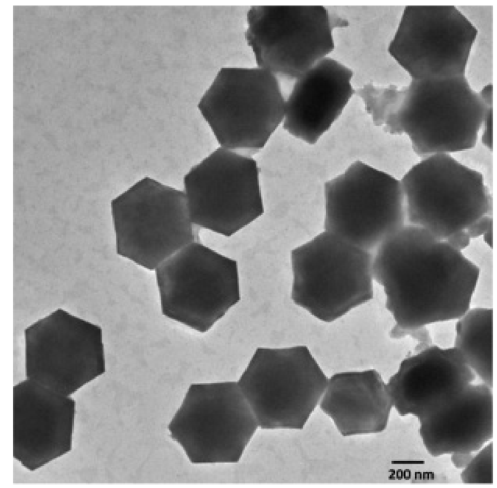
Upconversion is an optical process in which the sequential absorption of two or more long wavelength photons leads to emission of shorter wavelength photons.
The most efficient UC mechanisms are present in solid state materials doped with rare earth ions







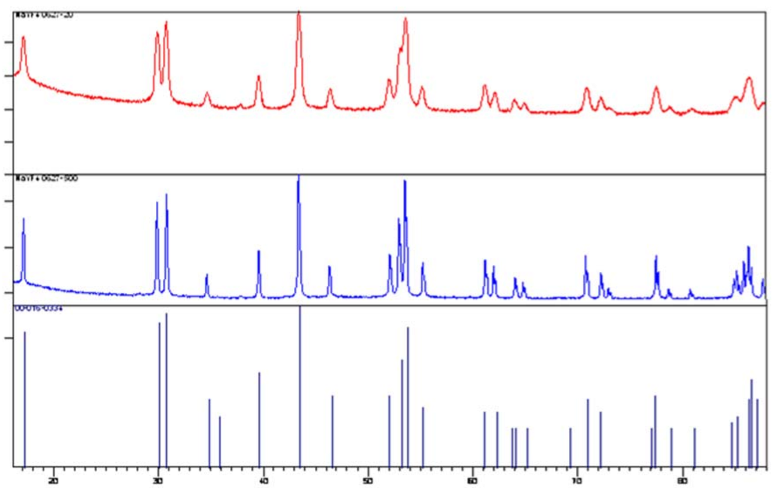


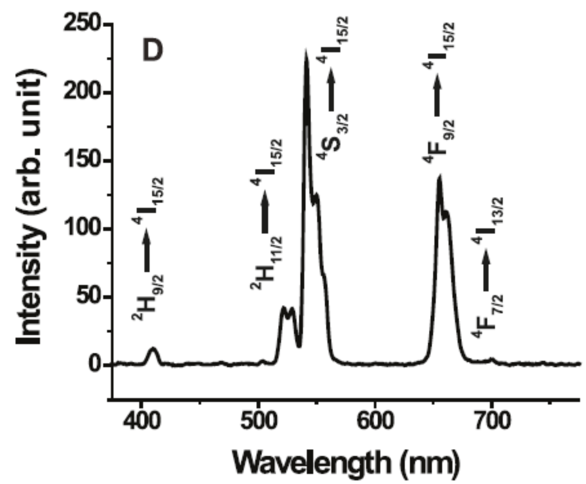


30 nm UCNP

500 nm UCNP

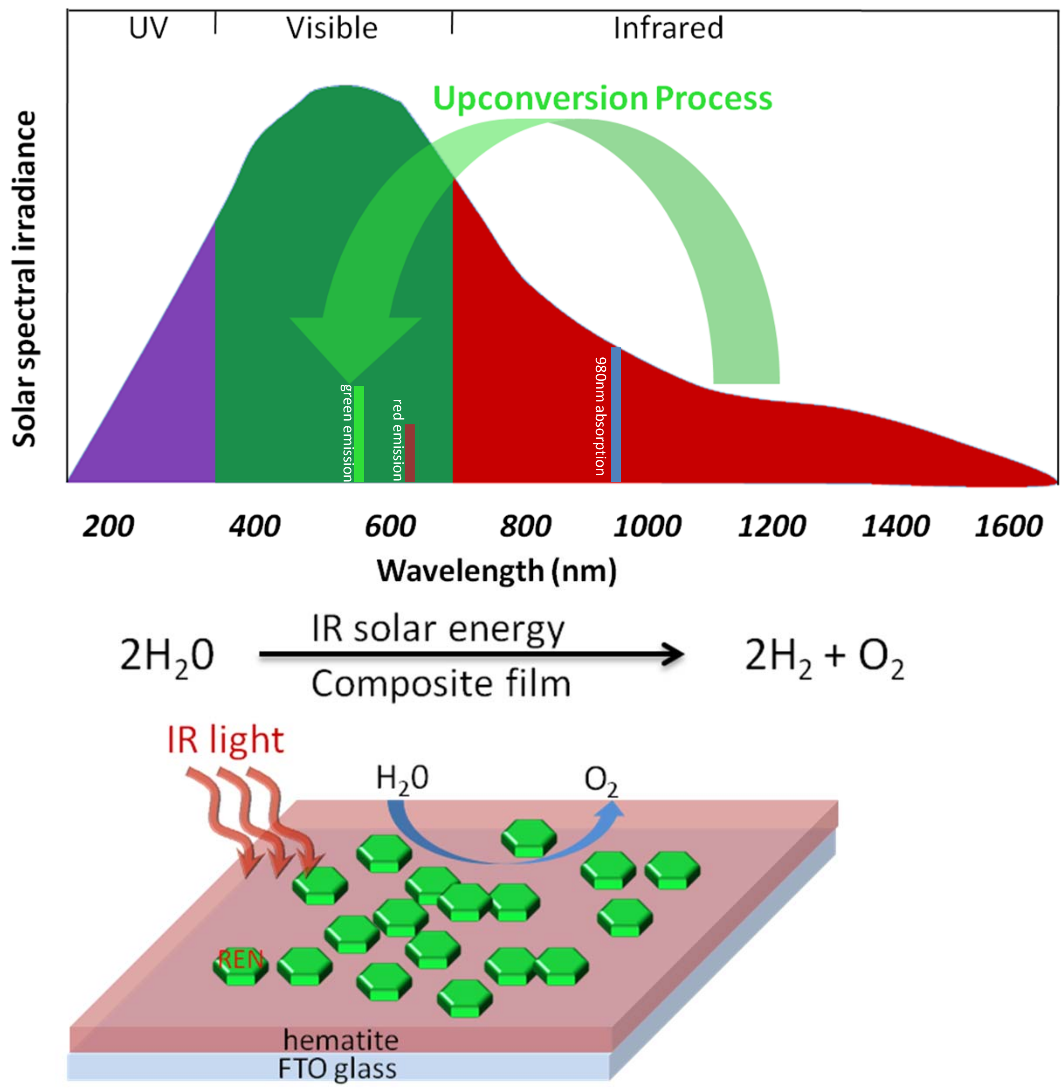
Standard $NaYF_4$ (PDF 016-034)



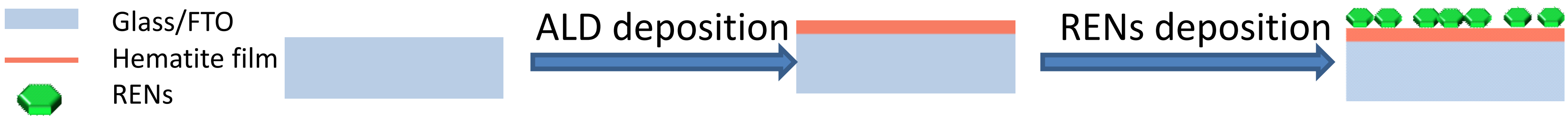


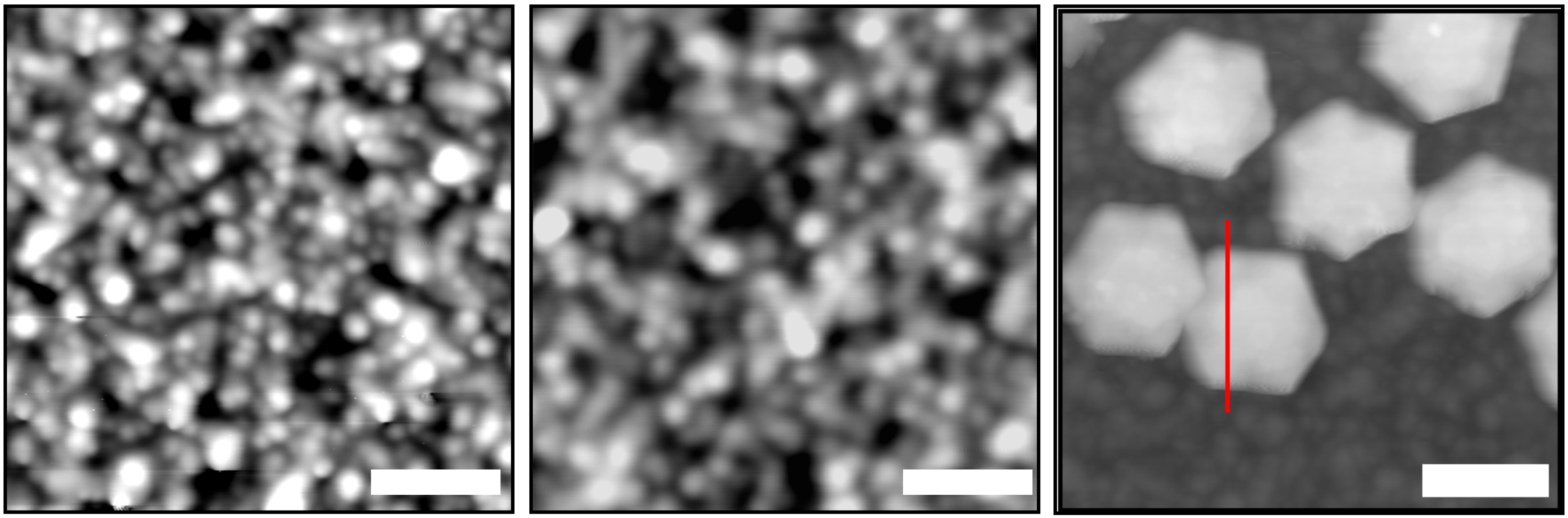
Heer, Kompe, Gudel, Haase, Adv. Mater. 16, 23 (2004)

Enhance Solar Water Splitting Performance by Utilizing Near Infrared Radiation With the Aid of Upconversion Materials



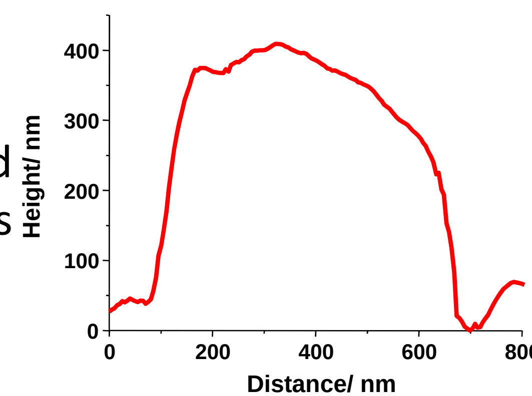
Integration of Hematite Semiconductors and Upconversion Material Into Composite Films





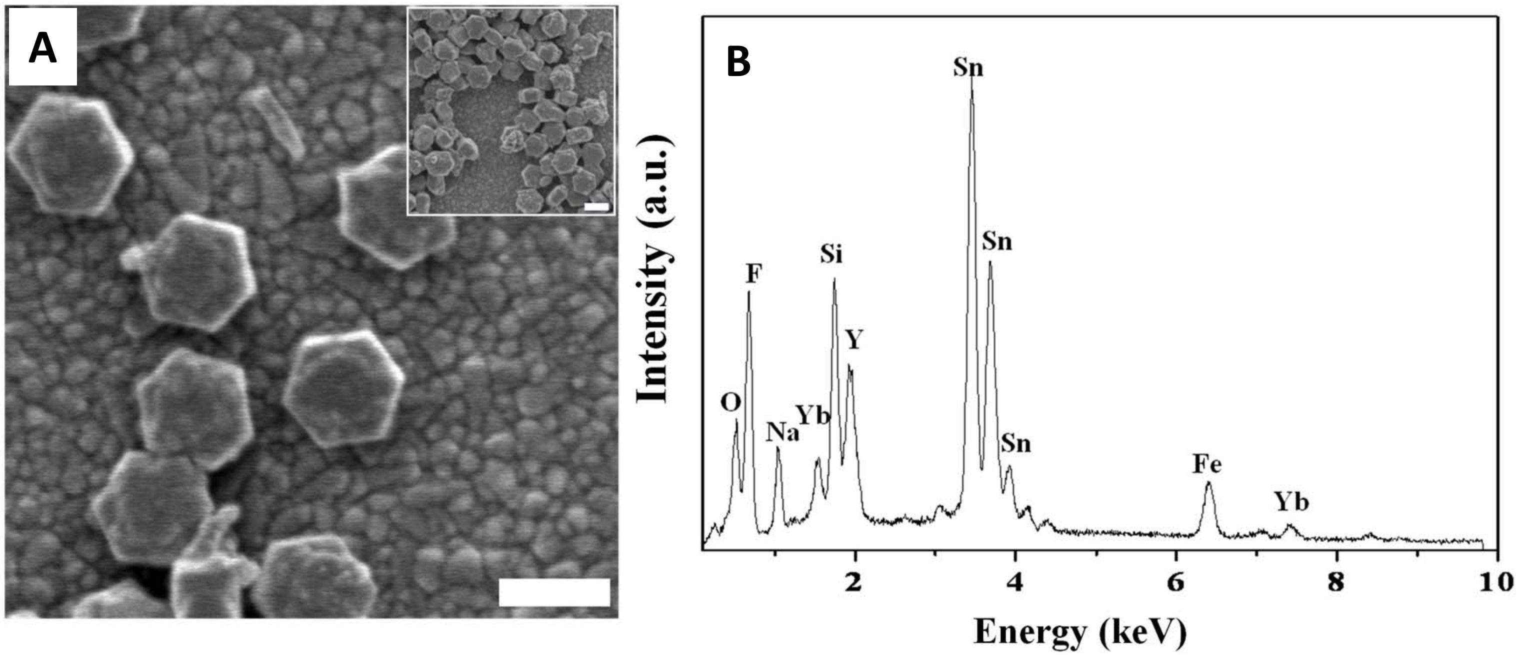
RMS 12.0 ± 0.7 nm

RMS 9.3 ± 0.5 nm



AFM topography image of FTO glass, hematite coated FTO glass and representative RENs on top of hematite coated FTO glass surfaces (2 µm x 2 µm). All scale bars are 500 nm.

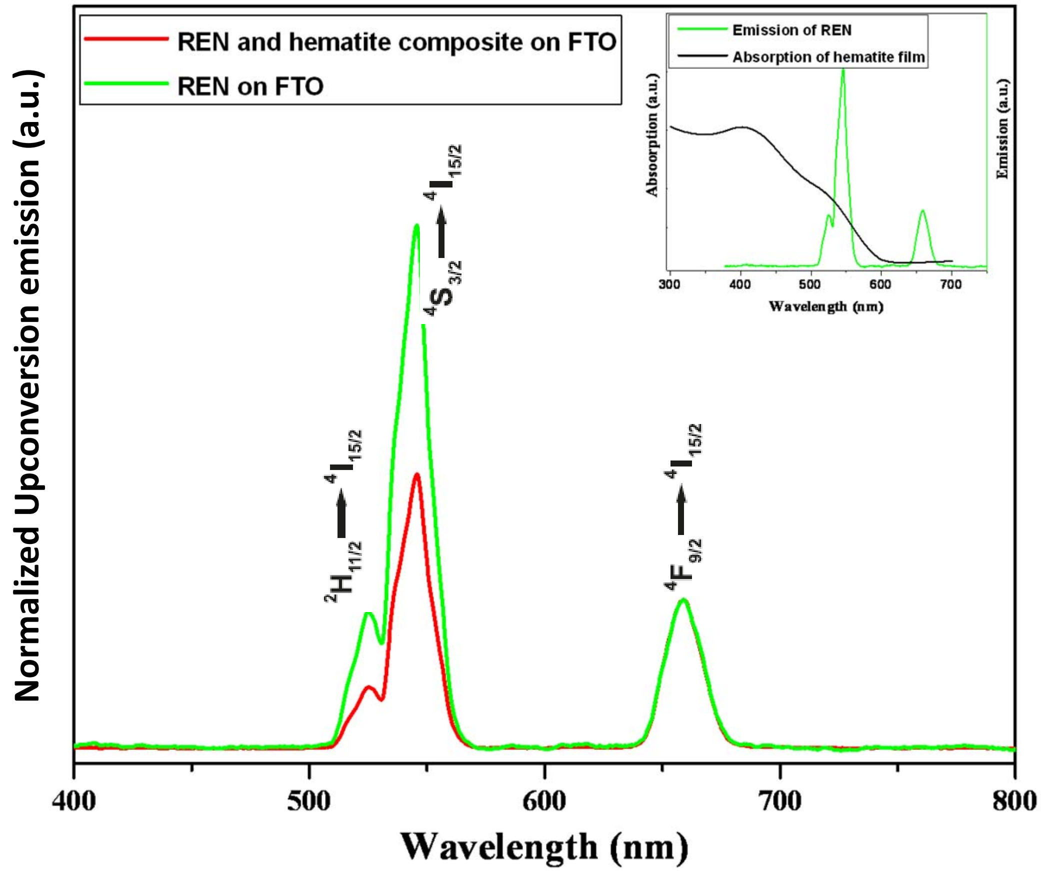
SEM/ EDS Characterization of RE UCNP / Hematite Composite Films on FTO Glass



(A). High resolution SEM images of composite material with rare earth upconversion nanoparticles on hematite film coated FTO glass; Inset is the SEM image of the same sample in large area. (B). EDS analysis of composite materials with rare earth upconversion nanoparticles on hematite film coated FTO glass.

The SEM image reveals that RENs were on top of hematite film with about 60% surface coverage and were mostly monolayer formation. The EDS analysis has confirmed the chemical composition of composite materials is consistent with hexagonal RENs $NaY_{0.78}Yb_{0.2}Er_{0.02}F_4$ and surrounding hematite film.

The Upconversion Emission of RENs Could Be Absorbed by Hematite For Water Splitting Process

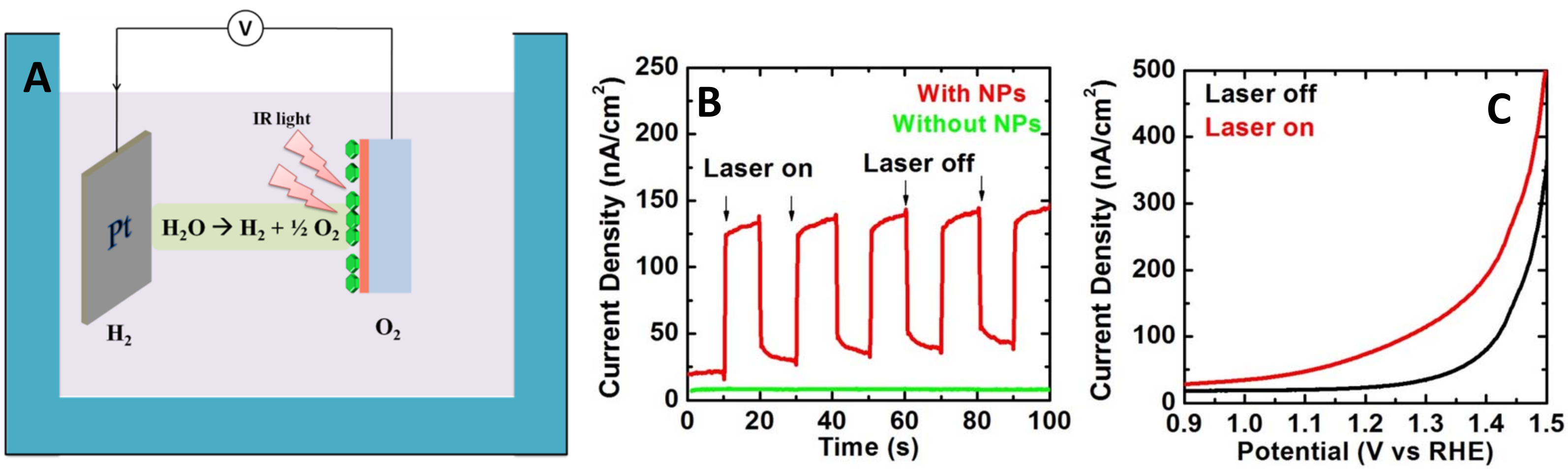


Upconversion emissions of rare earth nanoparticles on FTO glass with/without hematite film. The inset is the absorption spectra of hematite film on FTO glass and upconversion emission spectra of rare earth nanoparticles on FTO glass

The upconversion emission of rare earth doped particles has been absorbed by hematite

The ratio of peaks intensity at 550 nm and 670 nm has changed from 3.4 to 1.8 when hematite film was present. The green portion of upconversion emission has been absorbed by hematite.

PEC Measurement of UCNP and Hematite Composite Surface



A) Schematic of PEC measurement of UCNP and hematite composite surface. (B). current density vs time plot which will show water splitting enhancement with REN. (C) current vs potential plot shows clear separation of curve with and without IR light

The current density increased from 25 to 130 nA/cm^2 with RE NP on top of hematite surface and no obvious current increase was observed without UCNP. We have observed the clear photocurrent enhancement with the existence of rare earth doped upconversion material from current-potential plots which indicates that the barrier of absorbed photons for iron oxide water splitting device can be overcome with the aid of upconversion materials. The photocurrent enhancement factor in planar surface is around 105 nA/cm^2.

Conclusion

- ✓ A simple design of composite materials consisting of hematite thin films and rare earth nanoparticles were produced to investigate whether IR radiation can be harvested for solar water splitting.

- ✓ AFM and SEM characterization of these materials confirmed that rare earth nanoparticles are randomly deposited on thin hematite films.

- ✓ Molecular spectroscopy studies clearly revealed the absorption of 980 nm by rare earth materials, and the emission at 520， 550 and 670 nm via up conversion. The 520 and 550 nm emissions have been absorbed by hematite films.

- ✓ Photoelectrochemical measurements indicate that the water splitting by hematite is greatly enhanced upon 980 nm radiation.

- ✓ These observations collectively demonstrate the concept that semiconductor and rare earth composite films exhibit better efficiency and performance in solar water splitting. Our work opens new possibilities for utilizing IR radiation in solar spectrum towards harvesting solar energy.

Future Work

1. Optimize the device configuration to achieve better water splitting efficiency .
    - RE material can be put inside of hematite instead of on top of hematite film.
    - Increase the thickness of hematite film to improve the absorption of all upconverted light.
    - Find the best spectrum match composite of semiconductor and upconversion materials.

2. Test our composite film in the solar illumination instead of IR laser.

3. Improve the efficiency of the upconversion process by changing the host lattices, surface coating, doping percentage, etc.

4. Nanostructured film fabrication for improving the surface area, charge separation and transport of solar water splitting device.

5. Improve and expand the absorption to a much wider range than the narrow absorption at 980 nm by using various rare earth ions.

Acknowledgements

- **Profs. Gang-yu Liu, Chun-hua Yan and Dunwei Wang**

Dr. Virginia Altoe, LBNL
Dr. Tanghong Yi, LBNL
Liu Group Members

ICAM travel award