HKIE YMC Webinar

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Hydrogen Power – A Sustainable Energy Supply

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Outline

1. Why Hydrogen?
2. Renewable Hydrogen Production
3. Fuel Cell
4. Hydrogen Storage
5. Conclusion

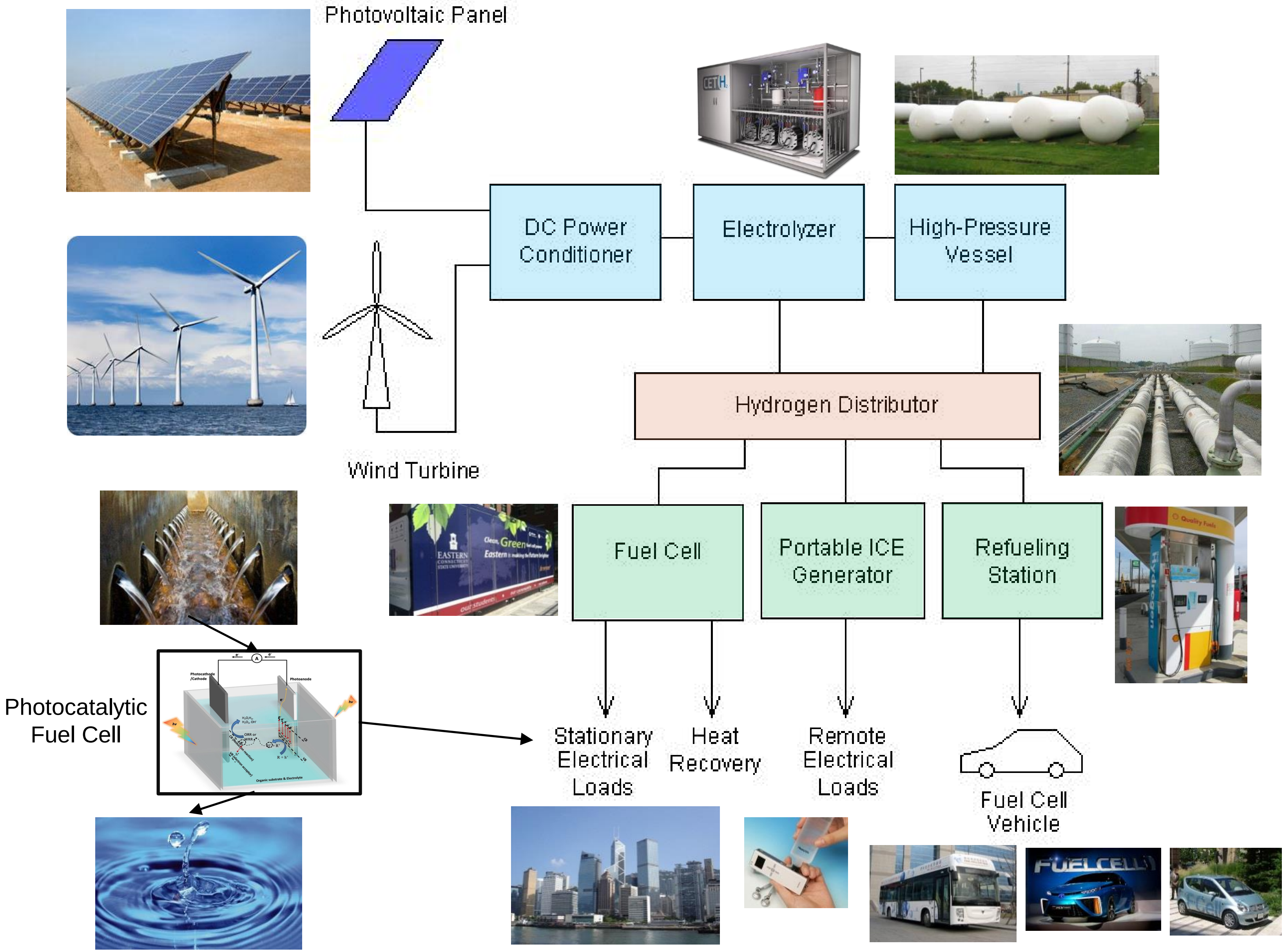
Hydrogen has highest energy content among different fuels

Fuel type	Energy content (MJ/kg)
Hydrogen	120
Liquefied natural gas	54.4
Propane	49.6
Aviation gasoline	46.8
Automotive gasoline	46.4
Automotive diesel oil	45.6
LPG	34.4
Ethanol	29.6
Coke	27
Methanol	19.7
Wood (dry)	16.2
Bagasse	9.6

Transition from Fossil Fuels to Hydrogen

- Reduce greenhouse gas emissions
- Reduce depletion of finite fossil fuels
- Hydrogen is clean and, in practice, it can be produced from water, which is abundant.
- Promote diverse, domestic, and sustainable energy resources
- Increase reliability and efficiency of electricity generation
- Hydrogen technologies can be viable with a transition from conventional technologies

Sustainable Future



Hydrogen Energy Technologies

Hydrogen Production

Water electrolysis
- Alkaline electrolyzer
- Proton Exchange Membrane (PEM) electrolyzer
- Solid oxide electrolyzer

Biomass
- Biomass pyrolysis
- Biomass gasification
- Biological water-gas shift Reaction
- Photo fermentation
- Dark fermentation

Photocatalysis
- Solar activated photocatalyst

Hydrogen Storage

- High-pressure gas compression
- Metal hydrides
- Liquefaction
- Carbon nanotube adsorption

Hydrogen Energy Conversion

Fuel cells
- Proton exchange membrane fuel cell
- Solid oxide fuel cell
- Alkaline fuel cell
- Phosphoric acid fuel cell
- Molten carbonate fuel cell

Combustion Engines
- Gas turbine
- Internal combustion engine

1. Hydrogen Production

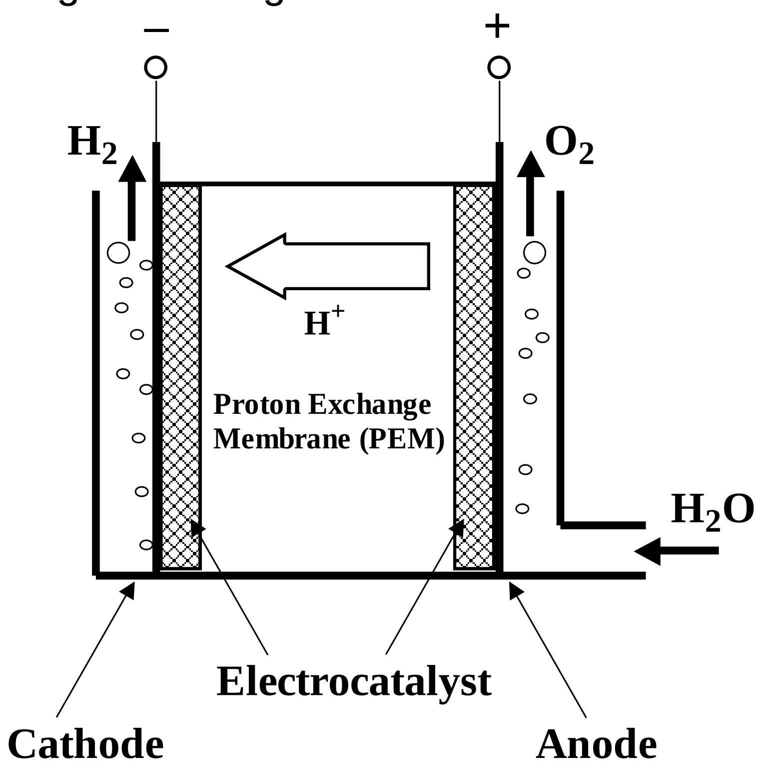
Currently, about 95% of all hydrogen produced is derived from natural gas through steam–methane reforming:

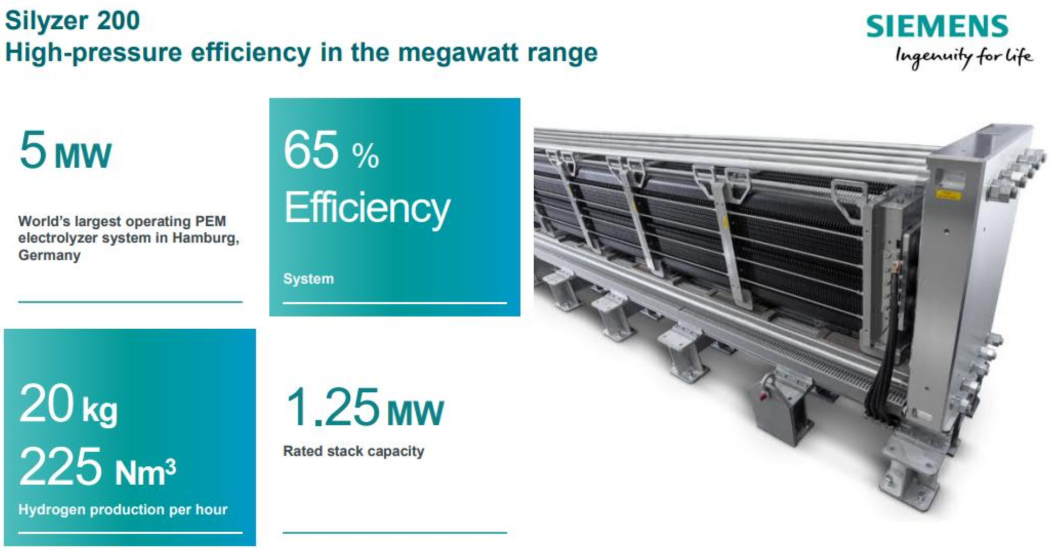
$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

Greenhouse Gases

PEM Electrolyzer

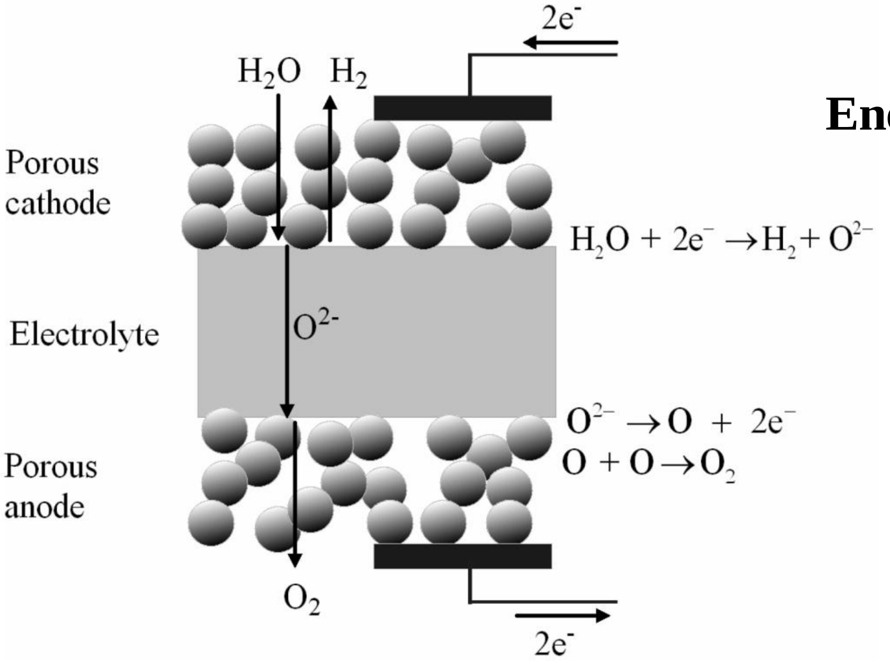
The membrane electrode assembly is the key component of a proton exchange membrane (PEM) electrolyzer. In this structure, the proton exchange membrane is sandwiched between the two catalyst-loaded electrodes. As a proton-conducting solid electrolyte, the membrane is usually made of perfluoroalkyl sulfonic acid polymers. Porous noble metal catalysts are metallized on the surface of PEM as electrodes. Water is fed to the anode where it decomposes into oxygen, electrons, and protons. The protons migrate through the PEM to the cathode where they are reduced to hydrogen molecules, while the electrons migrate through the external circuit to the cathode to combine with the protons.

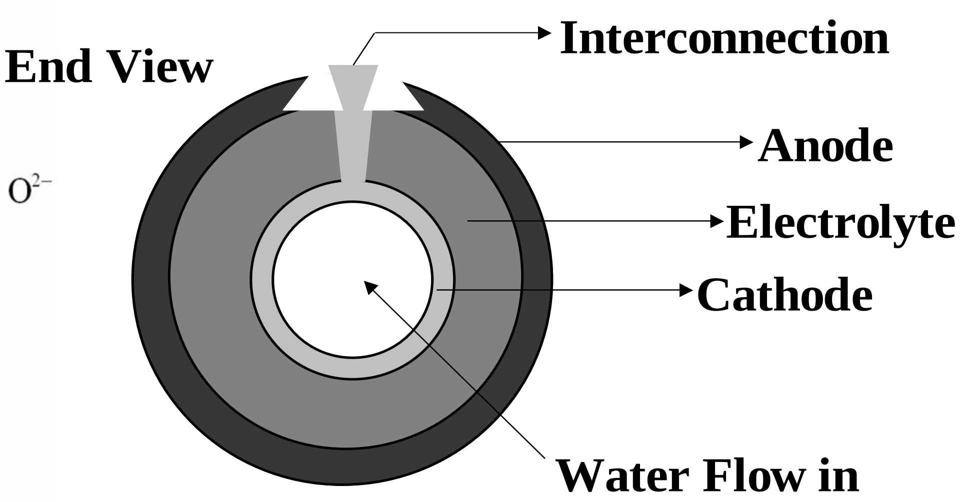




Solid Oxide Steam Electrolyzer

Solid oxide electrolyzer is another new and prospective technology for large-scale hydrogen production due to its high efficiency. At a high operating temperature (800-1000^oC), energy for water splitting is partly provided by heat, leading to a high electrical efficiency. However, such high temperature limits the materials suitable for solid oxide electrolyzer. Yttria-stabilized zirconia (YSZ) is the most commonly used ceramic material for solid oxide electrolyzer because of its high thermal resistance and pure ionic conduction (with no electronic conduction). During the operation, water vapor is fed into the tubes and is reduced at the inner nickel cathode to hydrogen and oxygen ions. The oxygen ions migrate through the YSZ electrolyte to the outer perowskite anode, where they are oxidized to form oxygen molecules. The waste heat can be recovered and used for cogeneration system, leading to an overall efficiency as much as 90%.





Hydrogen Production from Biomass

- Net zero carbon

Energy Crop

Wood

Sawdust

Biomass Pyrolysis

Pyrolysis is the heating of biomass at 650-800K and 0.1-0.5 MPa in the absence of air to convert biomass into liquid oils, solid charcoal and gaseous compounds. Pyrolysis can be further classified into slow pyrolysis and fast pyrolysis. As the products are mainly charcoal, slow pyrolysis is normally not considered for hydrogen production. Fast pyrolysis is a high-temperature process, in which the biomass feedstock is heated rapidly in the absence of air, to form vapor and subsequently condensed to a dark brown mobile bio-liquid.

Hydrogen can be produced directly through pyrolysis if high temperature and sufficient volatile phase residence time are allowed,

$$\text{Biomass} + \text{heat} \rightarrow H_2 + CO + CH_4 + \text{other products}$$

Methane and other hydrocarbon vapors produced can be steam reformed for more hydrogen production,

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

In order to increase the hydrogen production, water-gas shift reactions can be applied,

$$CO + H_2O \rightarrow CO_2 + H_2$$

Pyrolysis reactor types, heat transfer modes and typical features

Reactor type	Mode of heat transfer	Features
Ablative	•95% conduction •4% convection •1% radiation	•Large size feedstocks •Very high mechanical char abrasion from biomass Compact design •Heat supply problematical •Heat transfer gas not required •Particulate transport gas not always required.
Fluidized Bed	•90% conduction •9% convection •1% radiation	•High heat transfer rates •Heat supply to fluidising gas or to bed directly Limited char abrasion •Very good solids mixing •Particle size limit <2 mm in smallest dimension •Simple reactor configuration
Circulating Fluidized Bed	•80% Conduction •19% convection •1% radiation	•High heat transfer rates •High char abrasion from biomass and char erosion Leading to high char in product •Char/solid heat carrier separation required •Solids recycle required •Increased complexity of system •Maximum particle sizes up to 6 mm •Possible liquids cracking by hot solids •Possible catalytic activity from hot char •Greater reactor wear possible
Entrained Flow	•4% conduction •95% convection •1% radiation	•Low heat transfer rates •Particle size limit < 2 mm •Limited gas/solid mixing

Reference: Bridgwater 1999

Biomass Gasification

Biomass can be gasified at high temperature around 1000 K. The biomass particles undergo partial oxidation resulting in gas and charcoal production. The charcoal is finally reduced to form H_2, CO, CO_2, and CH_4,

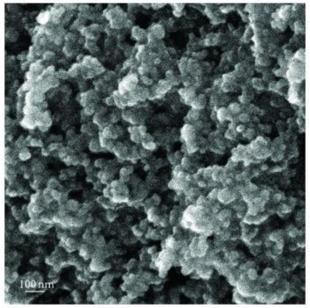
$$\text{Biomass + heat + steam} \rightarrow H_2\text{, CO, } CO_2\text{, } CH_4\text{, light and heavy hydrocarbons + char}$$

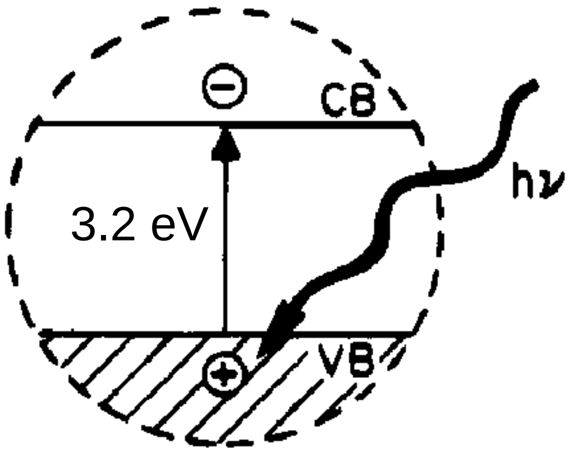
Unlike pyrolysis, gasification of solid biomass is carried out in the presence of O_2. Besides, gasification aims to produce gaseous products while pyrolysis aims to produce bio-oils and charcoal. The gases produced can be steam reformed to produce hydrogen and this process can be further improved by water-gas shift reactions. The gasification process is applicable to biomass having moisture content less than 35%.

Investigations on biomass gasification for hydrogen production

Feedstock	Reactor type	Catalyst used	Hydrogen production (vol%)	References
Sawdust	Not known	Na_2CO_3	48.31 at 700 ^oC 55.4 at 800 ^oC 59.8 at 900 ^oC	Yongjie, 1996
Sawdust	Circulating fluidized bed	Not used	10.5 at 810 ^oC	Chuangzhi et al. 1997
Wood	Fixed bed	Not used	7.7 at 550 ^oC	Xia & Dun, 2000
Sawdust	Fluidized bed	Not known	57.4 at 800^oC	Turn et al. 1998
Not known	Fluidized bed	Ni	62.1 at 830 ^oC	Rapagna et al. 1998
Sawdust	Fluidized bed	K_2CO_3 CaO Na_2CO_3	11.27 at 964 ^oC 13.32 at 1008 ^oC 14.77 at 1012 ^oC	Jian et al. 2001
Pine sawdust Bagasse Cotton stem Eucalyptus Gobulus Pinus Radiata	Fluidized bed	Not known	26-42 at 700-800 ^oC 29-38 at 700-800 ^oC 27-38 at 700-800 ^oC 35-37 at 700-800 ^oC 27-35 at 700-800 ^oC	Zhi et al. 2002
Sewage sludge	Downdraft	Not known	10-11	Midilli et al. 2002
Almond shell	Fluidized bed	La-Ni-Fe Perovskite	62.8 at 800 ^oC 63.7 at 900 ^oC	Rapagna et al. 2002
Switchgrass	Moving bed	Cu-Zn-Al	27.1	Brown, 2003

Photocatalysis





Titanium dioxide (TiO_2)

+

UV light

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$

$$h^+_{vb} + H_2O \rightarrow OH^{\cdot} + H^+$$

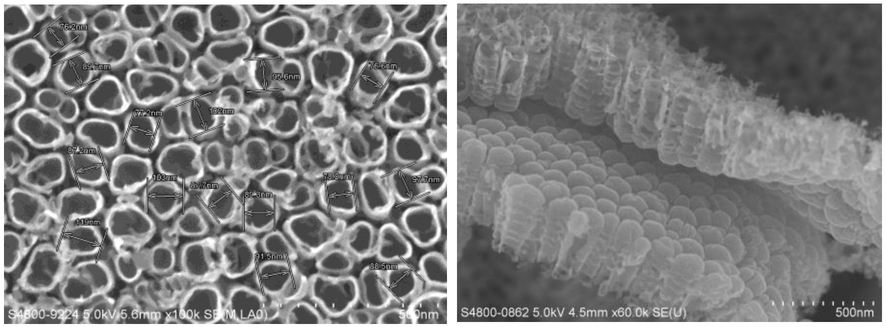
$$h^+_{vb} + OH^- \rightarrow OH^{\cdot}$$

$$e^-_{cb} + O_2 \rightarrow {}^{\cdot}O_2^-$$

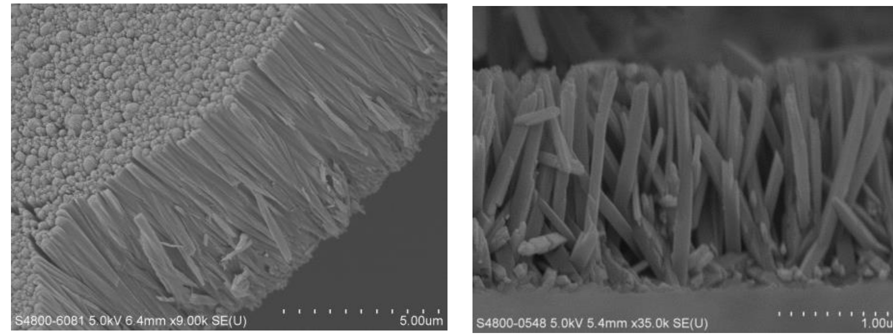
vb - valence band
cb - conduction band
h^+_{vb} - hole
$OH^{\cdot}$ - hydroxyl radical

Effective Nanostructures

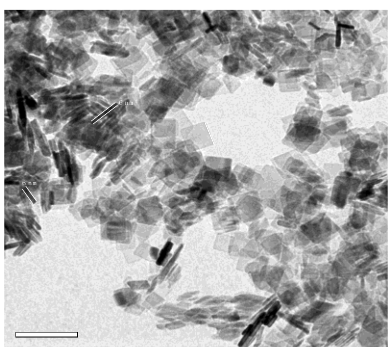
Nanotube Array



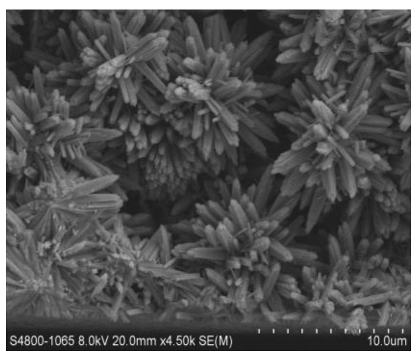
Nanorod Array



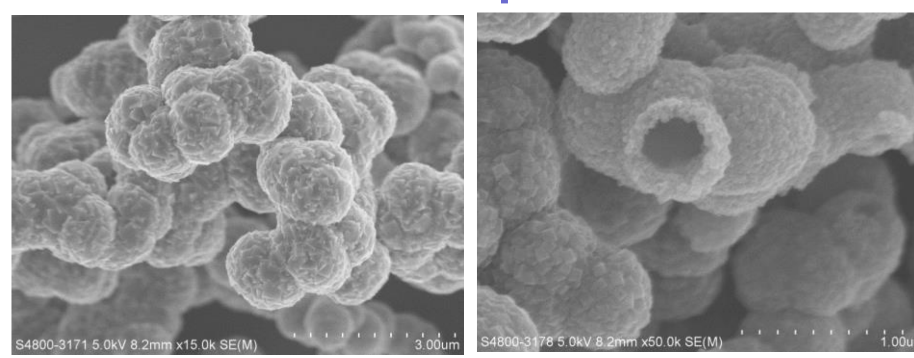
Nanosheet



Nano-flower



Hollow Sphere

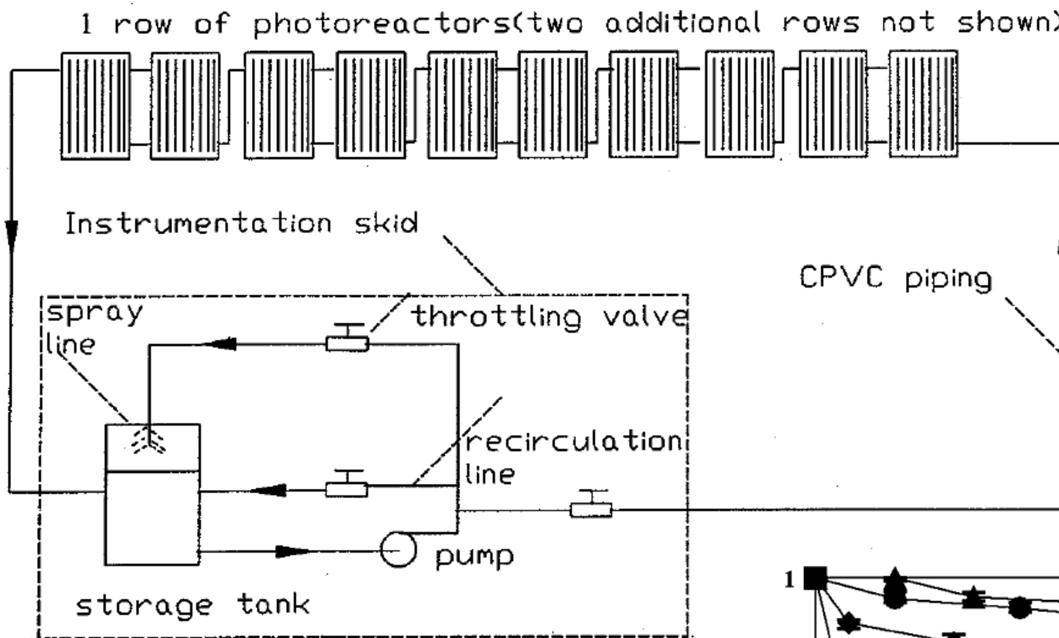


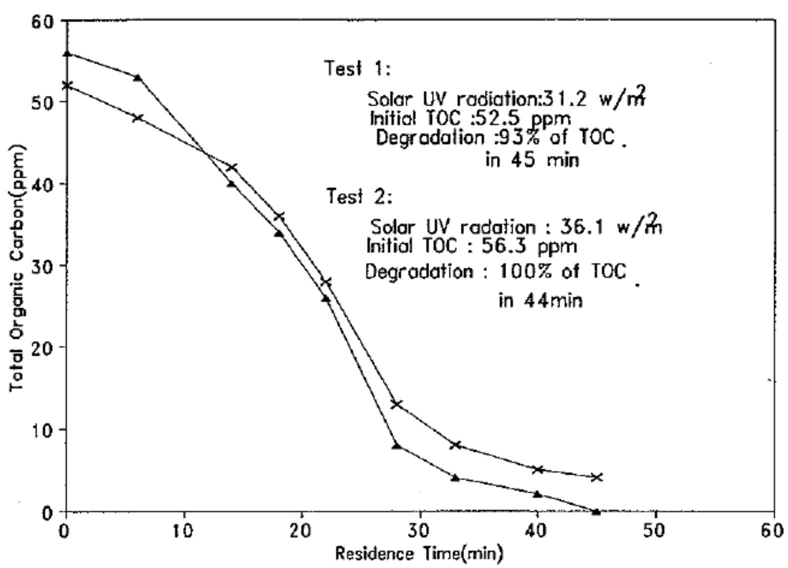
Solar Photocatalytic Water Purification

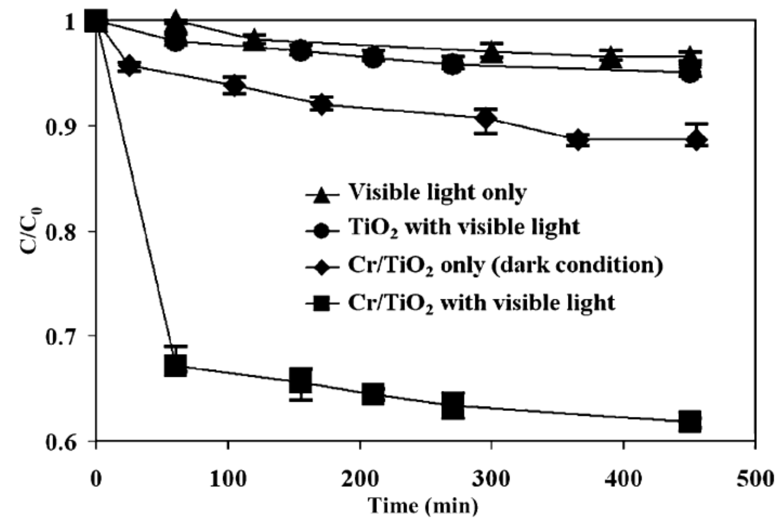
Photocatalyst: P25 TiO_2 powder

Recovery method: Sedimentation

Light source: Solar light





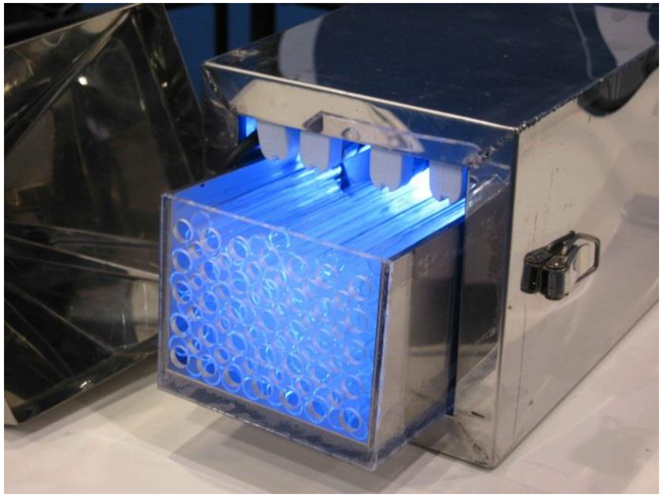


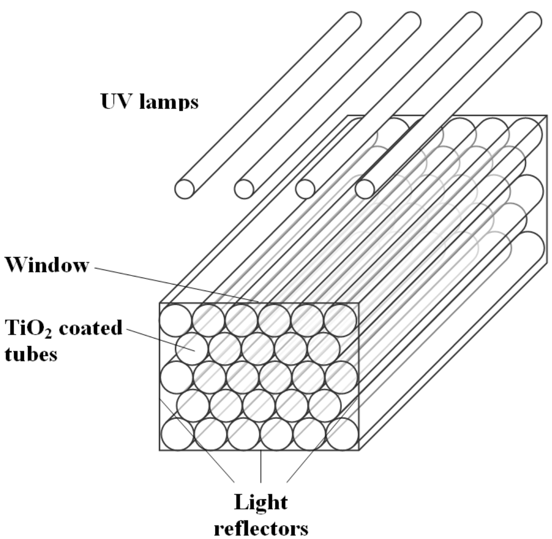
C.H. Ao[a], M.K.H. Leung[a,*], Ringo C.W. Lam[a], Dennis Y.C. Leung[a], Lilian L.P. Vrijmoed[b], W.C. Yam[c], S.P. Ng[c]

Photocatalytic decolorization of anthraquinonic dye by TiO_2 thin film under UVA and visible-light irradiation

Chemical Engineering Journal 129 (2007) 153–159

Photocatalytic Air Purification





Patent: *Light-transmitting tubular-honeycomb photocatalytic reactor*, Inventors: M.K.H. Leung, Y.C. Leung, W.C. Yam, P.S.P. Ng, L.L.P. Kwan, Hong Kong short-term patent, publication no.: 1099477, publication date: 10 Aug 2007.

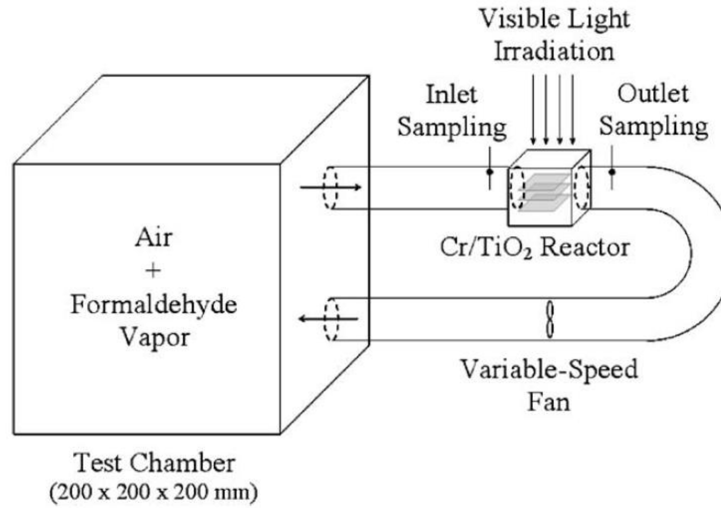
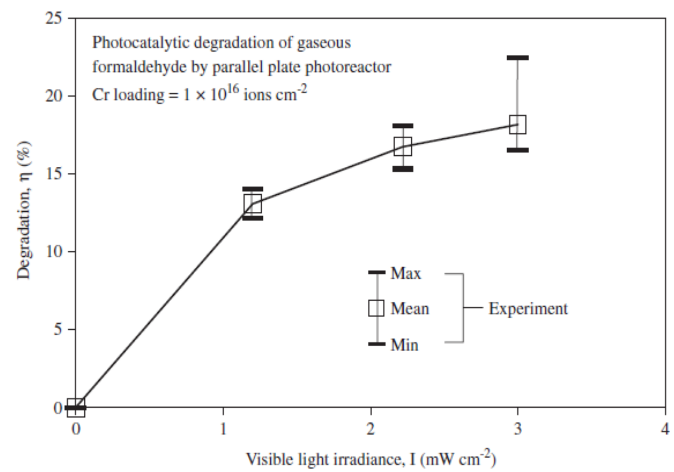


Fig. 6. Experimental setup for testing parallel-plate Cr/TiO_2 photoreactor.



Ringo C.W. Lam[a], Michael K.H. Leung[a,*], Dennis Y.C. Leung[a], Lilian L.P. Vrijmoed[b], W.C. Yam[c], S.P. Ng[c]

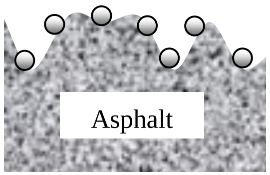
Visible-light-assisted photocatalytic degradation of gaseous formaldehyde by parallel-plate reactor coated with Cr ion-implanted TiO_2 thin film

Solar Energy Materials & Solar Cells 91 (2007) 54–61

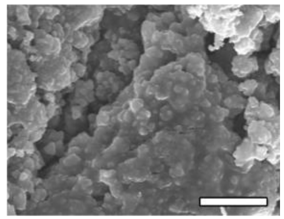
Photocatalytic Asphalt for Removal of Roadside Pollutants

Application: Photocatalytic degradation of vehicle exhausts: NOx and SOx

Photocatalytic Nanoparticles



Spray coating



SEM

Heat Treatment

$$TiO_2 \xrightarrow{h\nu} h^+ + e^-$$

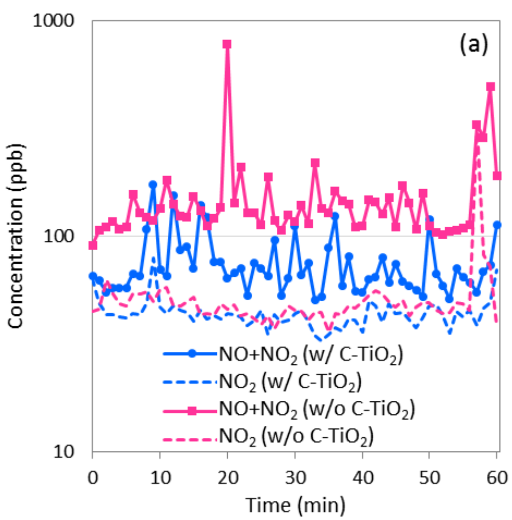
$$h^+ + OH^- \rightarrow OH^*$$

$$e^- + O_2 \rightarrow O_2^{*-}$$

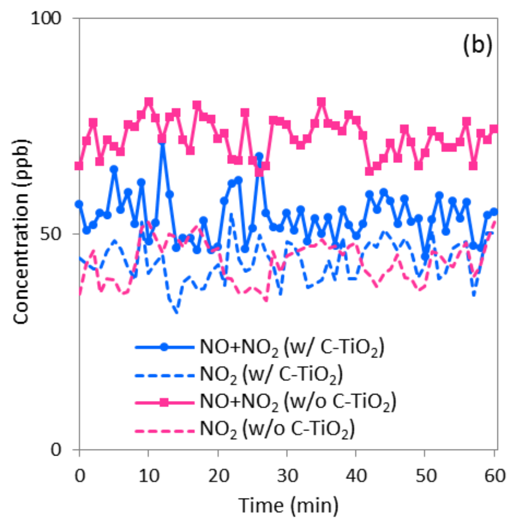
$$H^+ + O_2^{*-} \rightarrow HO_2^*$$

$$NO + HO_2^* \rightarrow NO_2 + OH^*$$

$$NO_2 + OH^* \rightarrow HNO_3$$



Gasoline-powered vehicle



Diesel-powered vehicle

Photocatalytic Marine Antifouling

Conventional heavy metal based antifouling paint

After 3 months
Biofouling by barnacles and tubeworms
30-40% more fuel consumption due to friction

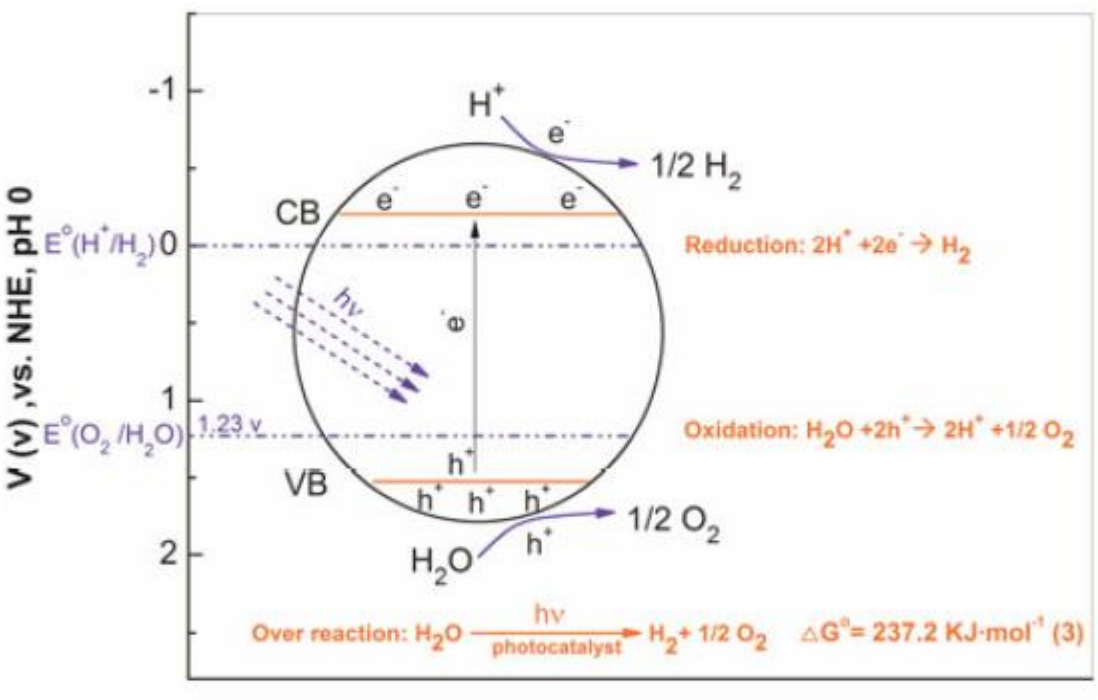
Photocatalytic antifouling paint

After 12 months
No fouling

Photocatalytic antifouling

Seawater cooled condenser intake screen after 3 months

Solar Photocatalytic Water-Splitting Hydrogen Production

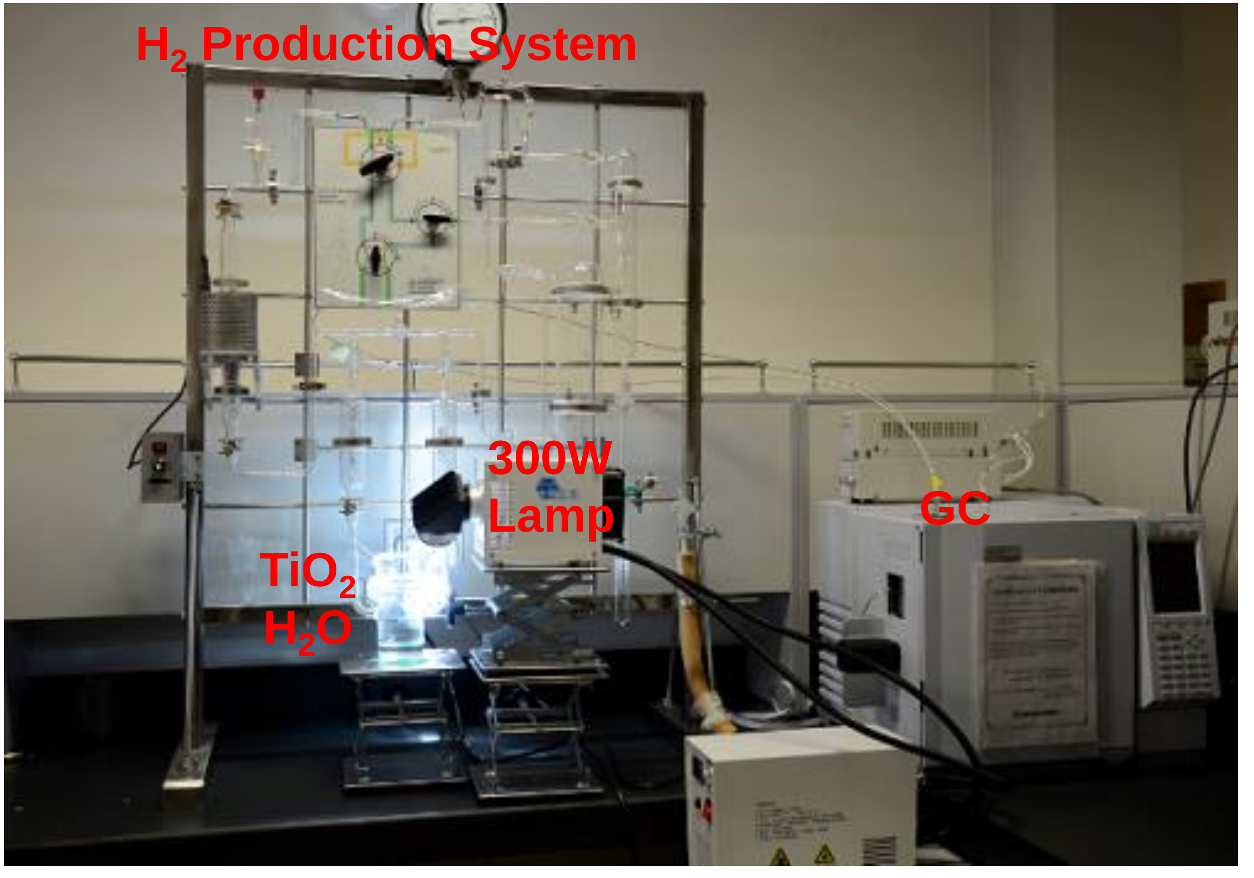


Ref.: A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production

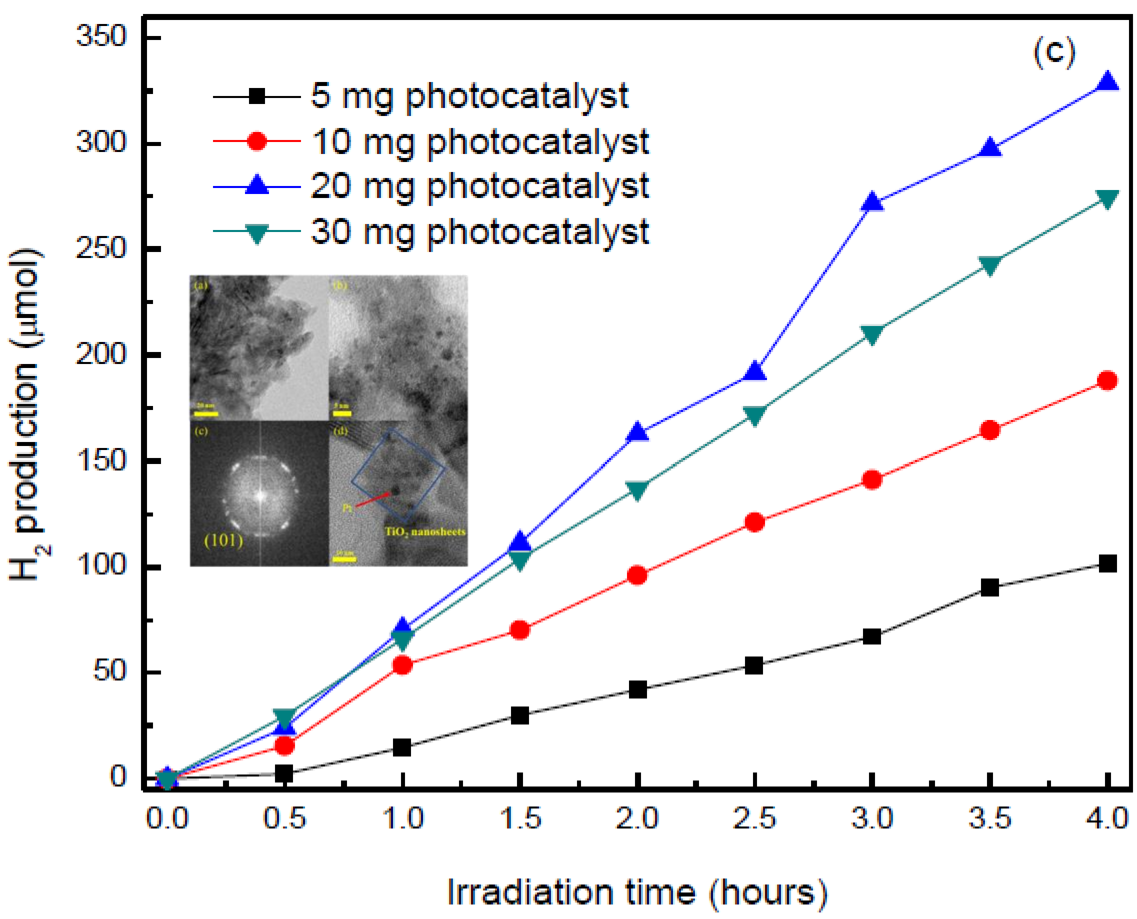
Meng Ni, Michael K.H. Leung*, Dennis Y.C. Leung, K. Sumathy

Renewable and Sustainable Energy Reviews 11 (2007) 401–425

Photocatalytic Hydrogen Production

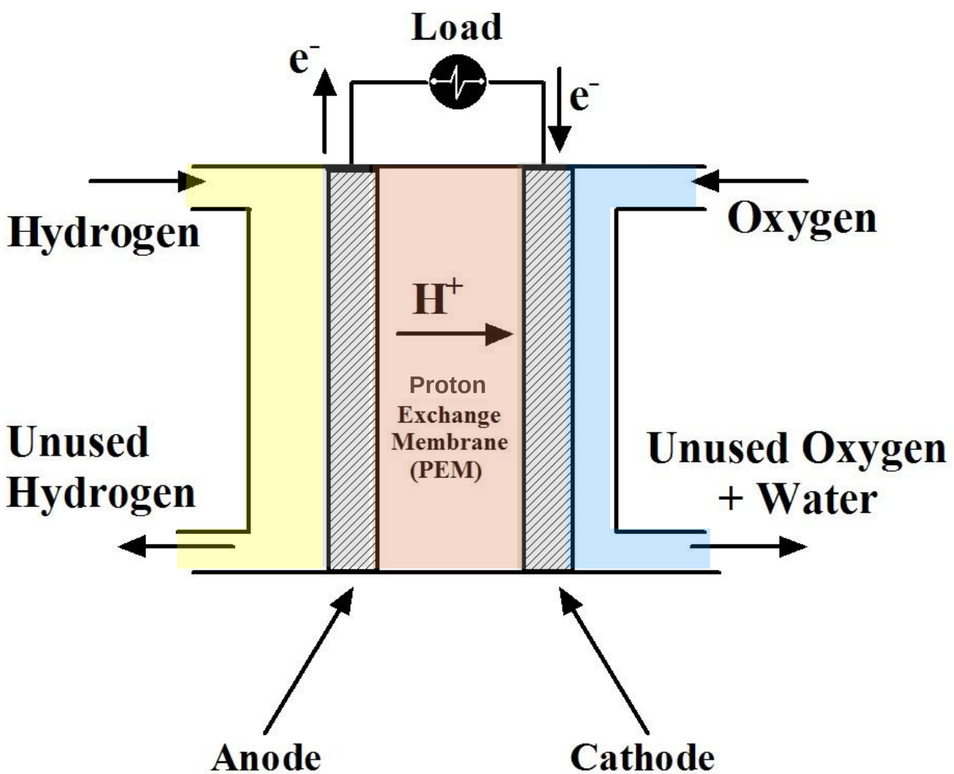


Effect of Photocatalyst Loading



2. Fuel Cell

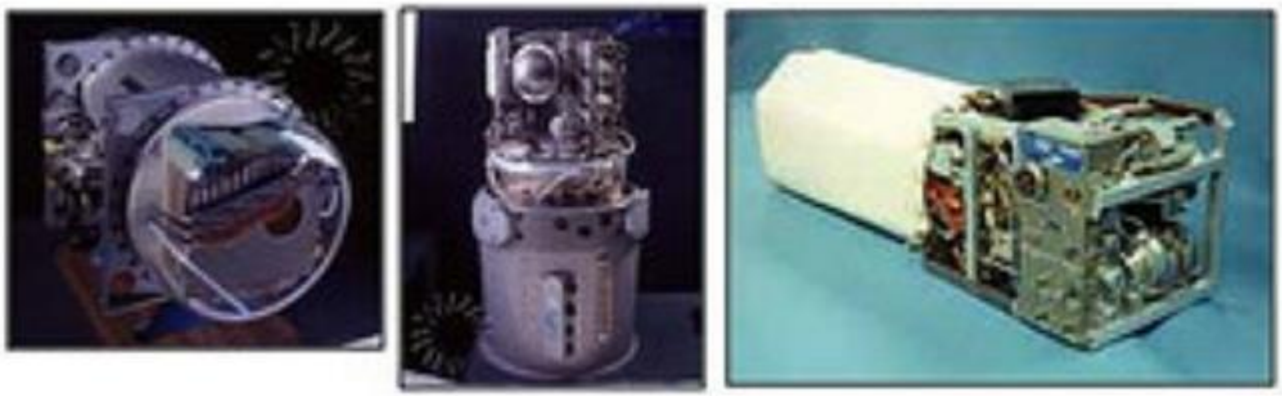
Fuel cell converts hydrogen into electricity by electrochemical reactions. Water and heat are byproducts.



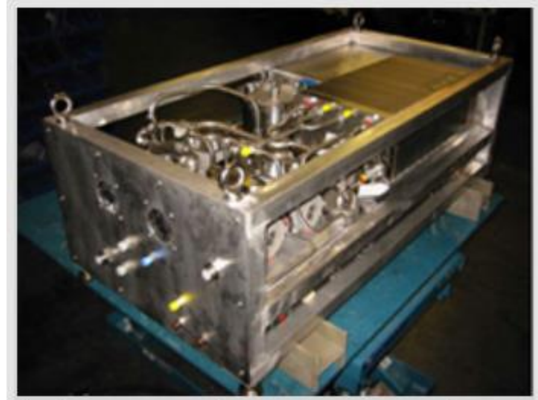
$H_2 \rightarrow 2H^+ + 2e^-$ $\quad$ $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Net reaction: $2H_2 + O_2 \rightarrow 2H_2O$

Originally Designed by NASA for Space Applications



Gemini, Apollo and Space Shuttle alkaline fuel cells (1965 to today)



A phase-one proton exchange membrane fuel cell design for space exploration developed by Teledyne. Credit: NASA

Ref.: www.nasa.gov

Features:

- **Use available hydrogen fuel**
- **Produce drinkable water**
- **Effective hydrogen recycling**

For Commercial Applications

- Reduce greenhouse gas emissions
- Reduce depletion of finite fossil fuels
- Hydrogen is clean and, in practice, it can be produced from water, which is abundant.
- Promote diverse, domestic, and sustainable energy resources
- Increase reliability and efficiency of electricity generation
- Hydrogen technologies can be viable with a transition from conventional technologies

Stationary Electricity Supply

400-kW hydrogen fuel cell plant in Connecticut

200-kW natural gas fuel cell plant in Sydney

Natural gas fuel cell plant in New Jersey

2.4-MW biogas fuel cell plant in San Diego

Stationary & Portable Electricity Supply

400,000-MWh year^{-1} hydrogen fuel cell plant in Seosan

59-MW fuel cell park comprises 21 fuel cell power plants in Pyeongtaek

37-MW natural gas and biogas integrated fuel cell plant in California

Hydrogen, natural gas, and biogas integrated fuel cell plant in Wernau

0.3 to 1-kW domestic hydrogen fuel cell in Fukuoka Prefecture

45-W fuel cell laptop by Antig and AVC

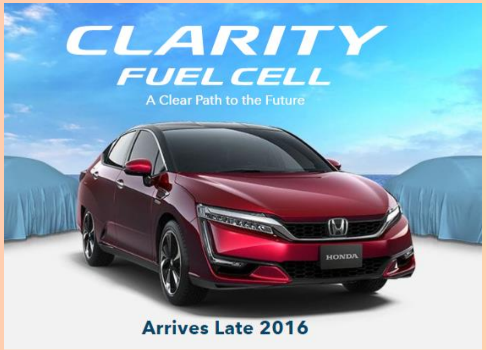
Fuel Cell Cars

Mercedes-Benz plug-in hydrogen fuel-cell

GM Opel HydroGen4

BMW hydrogen fuel-cell vehicle

Honda Clarity fuel cell



Toyota Mirai

Hyundai Tucson Fuel Cell

Fuel Cell Cars and More …

Mercedes-Benz plug-in hydrogen fuel-cell

Gumpert Nathalie Fuel Cell

BMW Hydrogen Fuel-Cell Vehicle

Fuel Cell Tram in Foshan

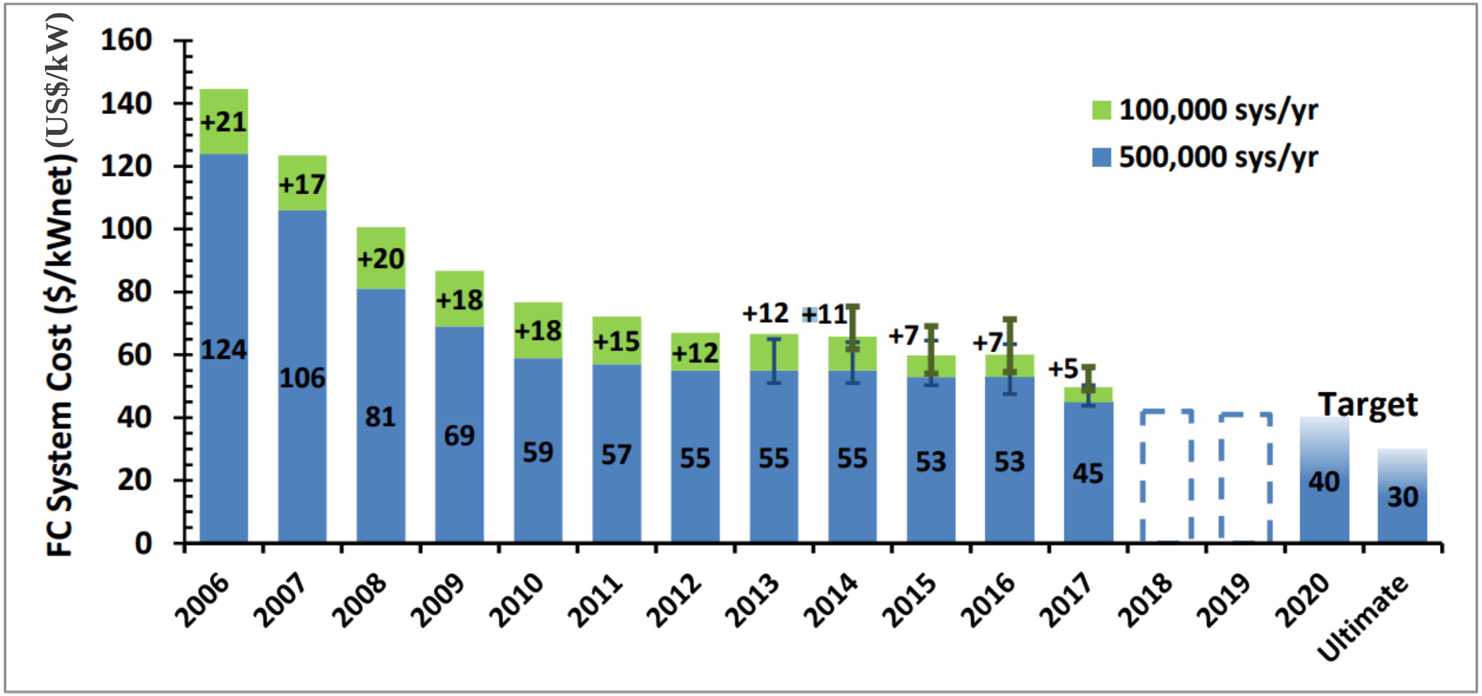
CaetanoBus SA Fuel Cell

Fuel Cell Aircraft

Capital Cost of Fuel Cell

Modeled cost of an 80-kWnet fuel cell system based on projection to high-volume manufacturing (100,000 and 500,000 units/year).

U.S. Department of Energy Hydrogen and Fuel Cells Program Record 17007, September 30, 2017, Figure 1.



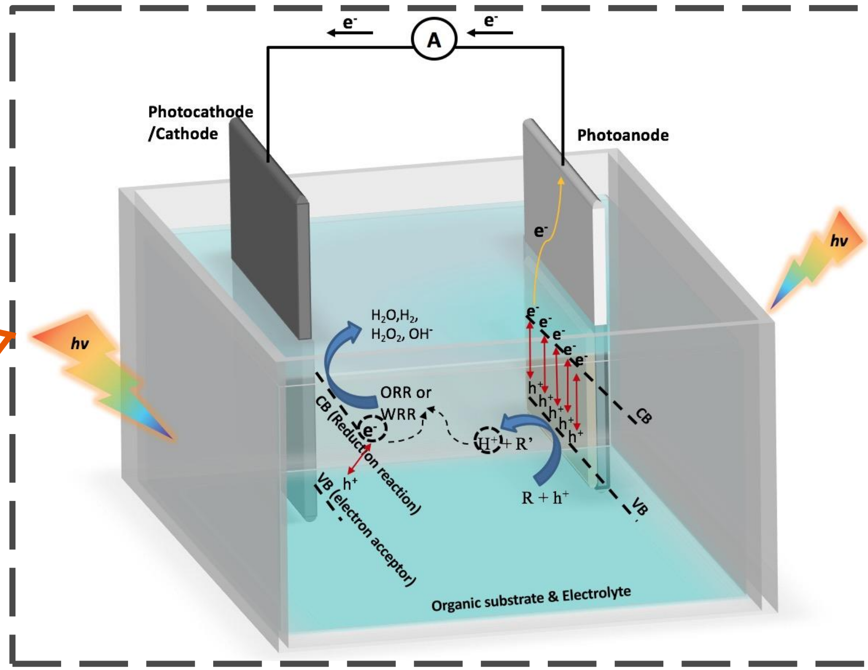
Ref.: U.S. DOE, 2017

Photocatalytic Fuel Cell (PFC)

Energy Generation

Solar energy → Chemical energy

Solar energy → Electricity

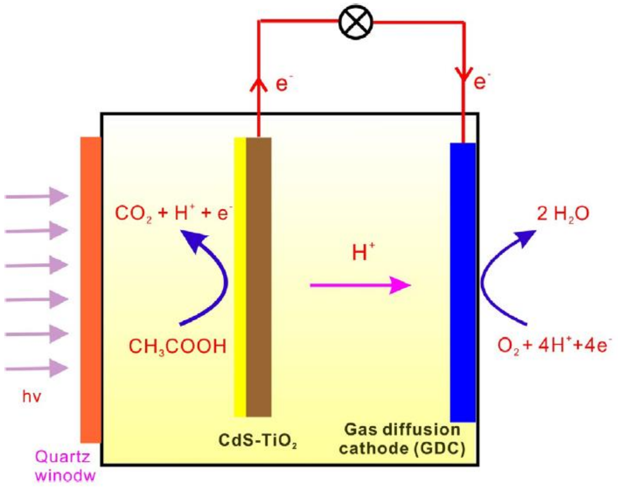


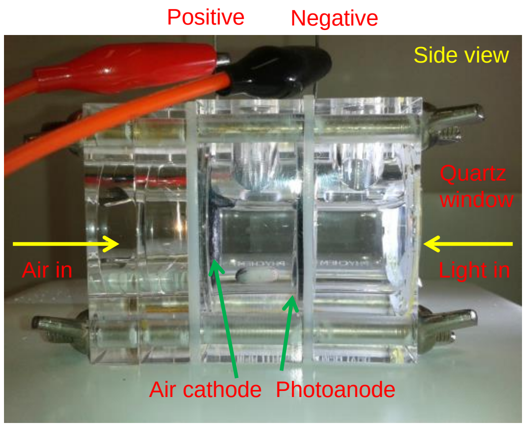
Environmental Remediation

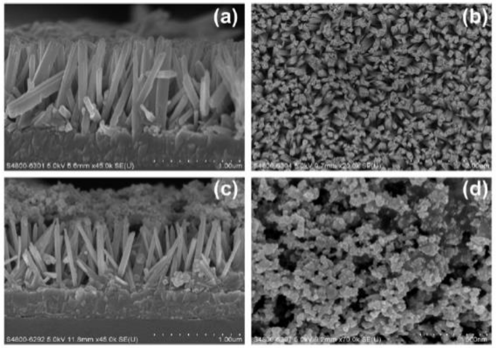
Pollutants Treatment

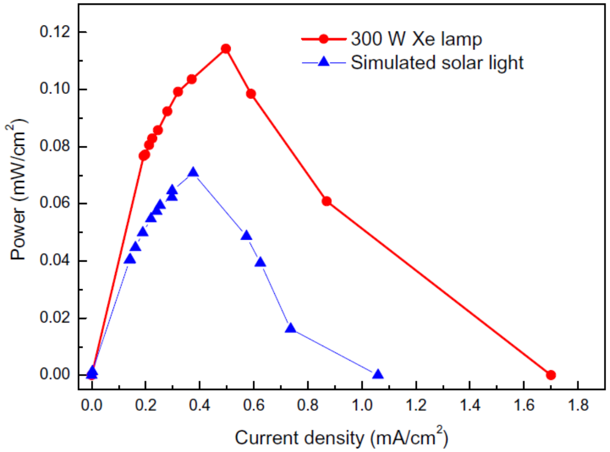
Photocatalytic detoxificaion

PFC Wastewater Treatment





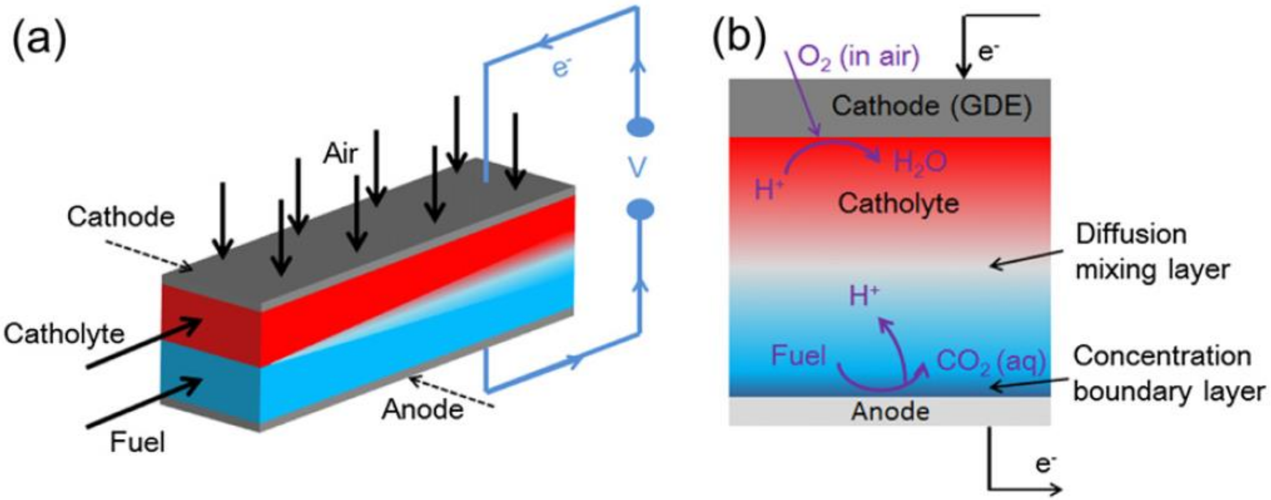




- **Effective wastewater treatment and simultaneous production of electricity**
- **Low-cost fabrication**
- **Environmental-friendly operation**

Ref.: Bin Wang, Hao Zhang, Xiao-Ying Lu, Jin Xuan, **Michael K.H. Leung**, Solar photocatalytic fuel cell using CdS–TiO_2 photoanode and air-breathing cathode for wastewater treatment and simultaneous electricity production, Chemical Engineering Journal, Volume 253, 2014, Pages 174-182.

Membraneless Microfluidic Fuel Cell



Why can be membraneless?

- Laminar microchannel flow
- Naturally separate two streams
- Good ionic conductivity

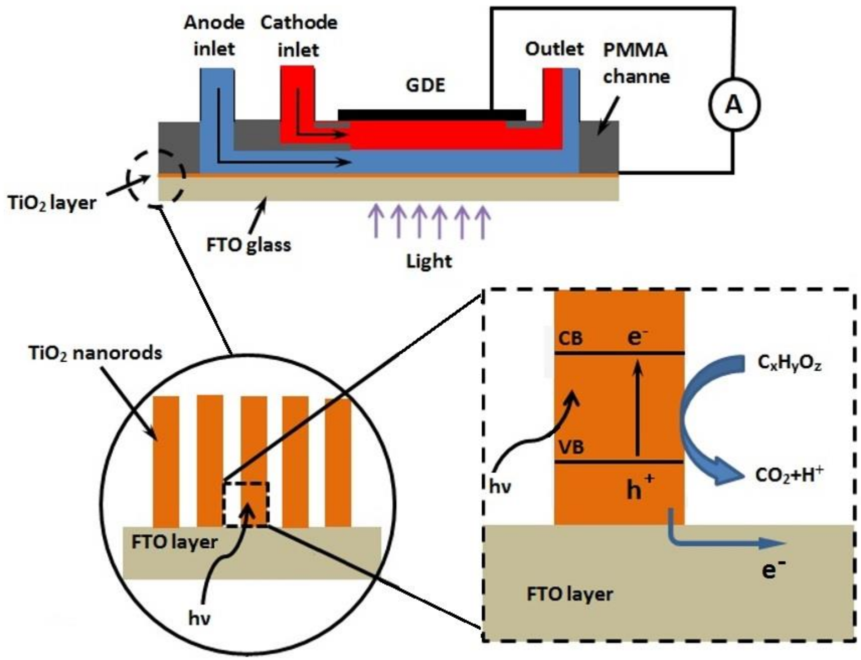
Ref.:

Jin Xuan, Huizhi Wang, Dennis Y.C. Leung, **Michael K.H. Leung**, Hong Xu, Li Zhang, Yang Shen, Theoretical Graetze-Damköhler modeling of an air-breathing microfluidic fuel cell, Short Communication, Journal of Power Sources 231 (2013) Pages 1-5.

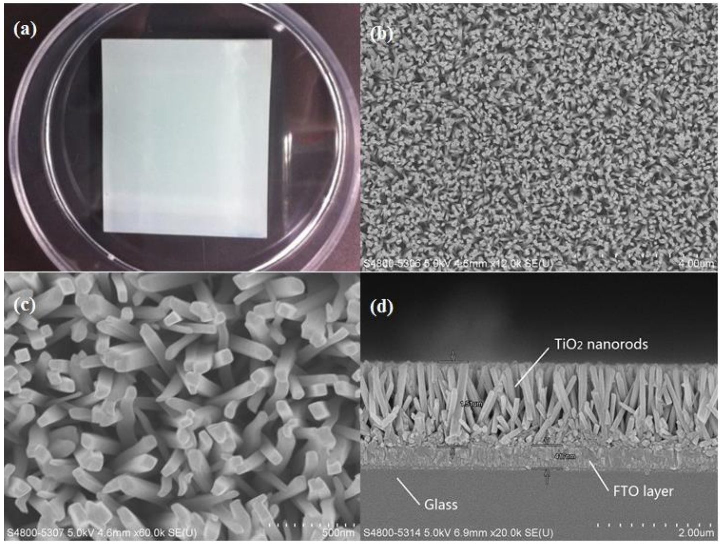
Jin Xuan, **Michael K.H. Leung**, Dennis Y.C. Leung, Huizhi Wang, Laminar flow-based fuel cell working under critical conditions: The effect of parasitic current, Applied Energy, Volume 90, Issue 1, 2012, Pages 87-93.

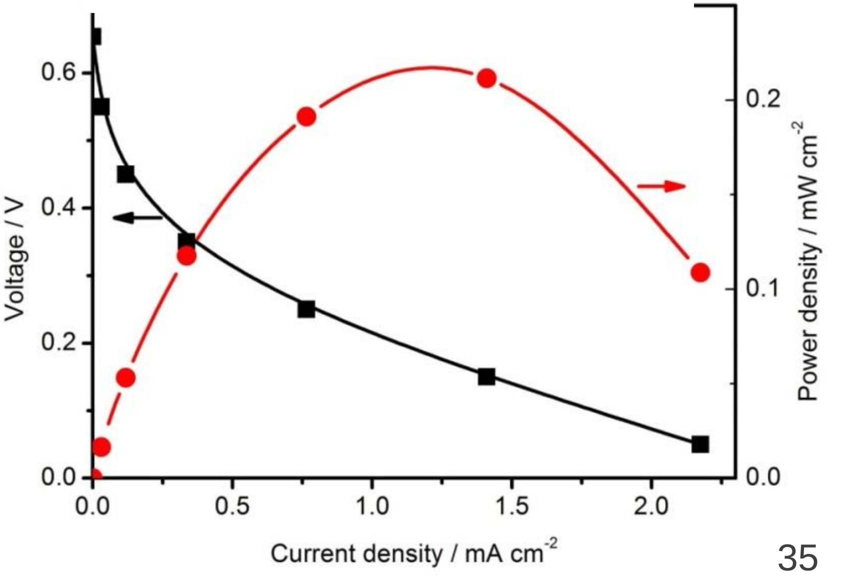
Jin Xuan, **Michael K.H. Leung**, Dennis Y.C. Leung, Huizhi Wang, Towards orientationindependent performance of membraneless microfluidic fuel cell: understanding the gravity effects, Applied Energy, 90(1), 2012, pp 80-86.

Photocatalytic Fuel Cell + Microfluidics

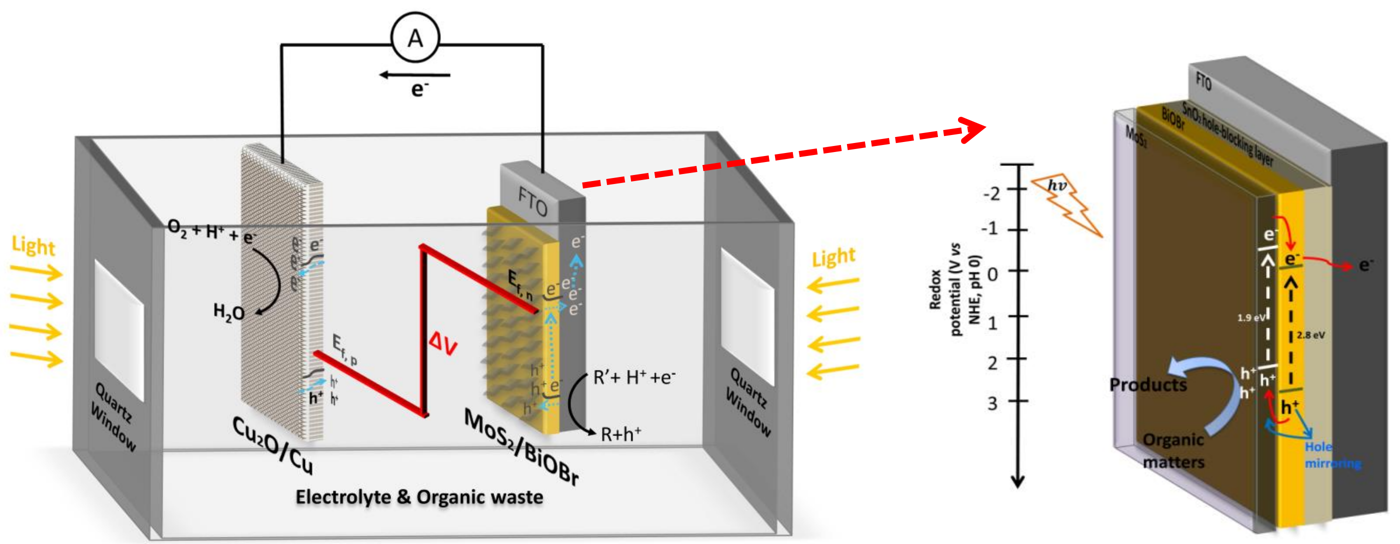


The innovative membraneless photocatalytic fuel cell can purify and use wastewater to generate power.



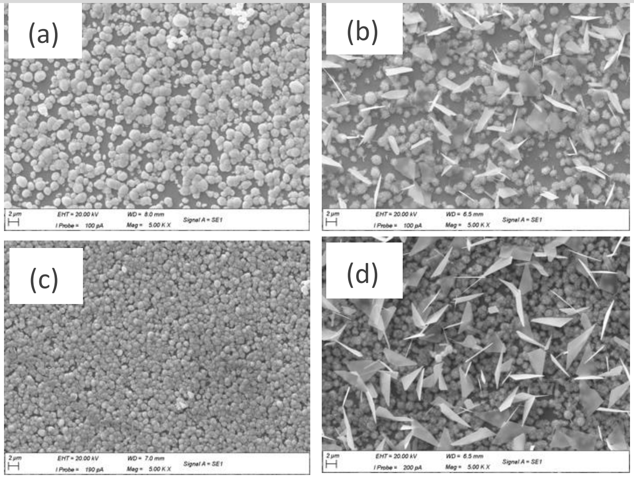


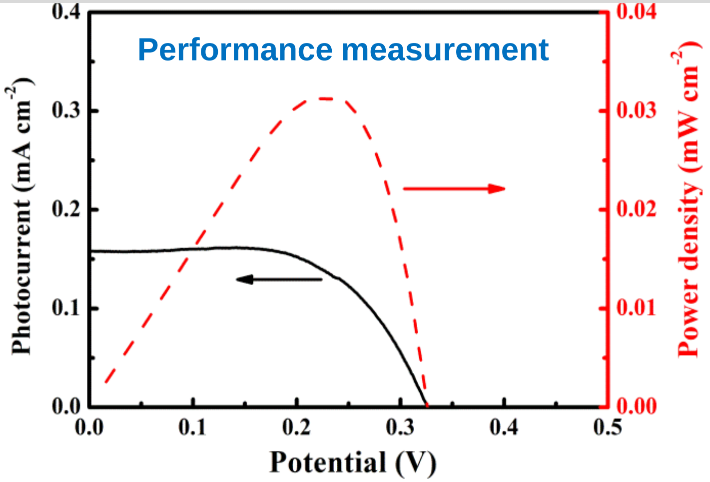
Dual-photoelectrode PFC



SnO$_2$ hole-blocking layer is a promising conductive scaffold
B$_{i2}$S$_3$ has been acted as a sensitizer due to its ability to absorb a large part of visible light up to 800 nm

SEM images





Yun He, Jue Hu, Yizheng Zhang, Ronghua Yuan, Wei Xiong, Chengxu Zhang, **Michael K.H Leung,** A superior heterojunction photoanode with efficient synergetic effect for enhancing photoelectrochemical activity of dual-photoelectrode PFC. (In preparation)

3. Hydrogen Storage

High-pressure gas compression to low volume and high pressure is a commonly used storage method for fuel gases. Ideal gas law can be used to derive the mass-volume relationship of fuel gas stored in a pressure tank.

$$PV = \left(\frac{m}{M}\right)\bar{R}T$$

where

$\bar{R}$ = universal gas constant = 8.314 kNm/(kmol K)
M = molecular weight of a particular gas
m = mass of gas
V = volume
T = absolute temperature in K
P = absolute pressure in N/m^2 (1 atm = 101,325 N/m^2)

Energy Consumption for High-pressure Gas Compression

Energy consumption is needed for the fuel gas compression process. Hydrogen has a low specific gravity than other fuel gases so it takes more energy to compress hydrogen for given mass and compression ratio. The energy needed, *E*, for an ideal isothermal compression of hydrogen can be expressed by

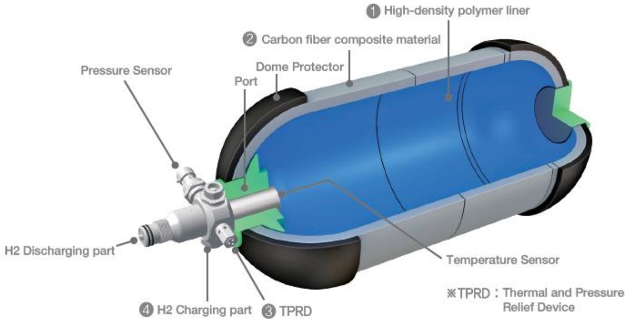
$$E = RT \ln(r_p)$$

where
R **= Specific gas constant of hydrogen (4.157 kJ/kgK)**
r_p **= Compression pressure ratio (ratio of final pressure to original pressure)**
T **= Temperature in degree Kelvin (K)**

Pressure Vessels

Steel vessels are commonly used for high-pressure gas compression storage with operating pressure as high as 700 bars. However, for hydrogen storage, steel is not a desirable material. It is because **hydrogen embrittlement** failure as diffusion of hydrogen into steel may occur, especially when the vessels are frequently charged and discharged. In the case of rupture, steel projectiles may cause serious injuries.

Furthermore, the **gravimetric storage density**, defined as the ratio of the mass of stored gas to the mass of vessel, is low, normally in an order of 0.01 H_2-kg/kg. Steel vessels are too heavy for practical use in vehicles. The hydrogen embrittlement problem can be resolved by using vessels made of composite materials comprised of **polyethylene**, or **carbon fiber** and **epoxy resin with thin aluminum liner**.

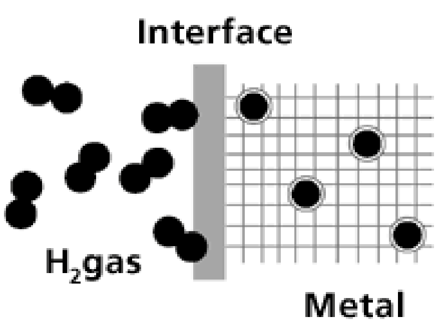


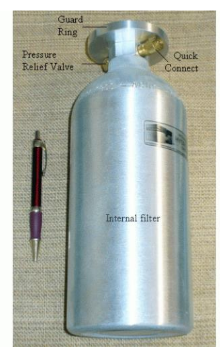
Metal Hydrides

Hydrogen molecules are chemically bonded with metals or alloys to form metal hydrides. When the hydrogen to metal ratio is small (< 0.1), the hydrogen can be exothermically dissolved into the metal. The hydrogen atoms occupy the interstitial sites of the metal lattice structure to form interstitial hydrides. The chemical reactions of the charging and discharging of hydride storage are:

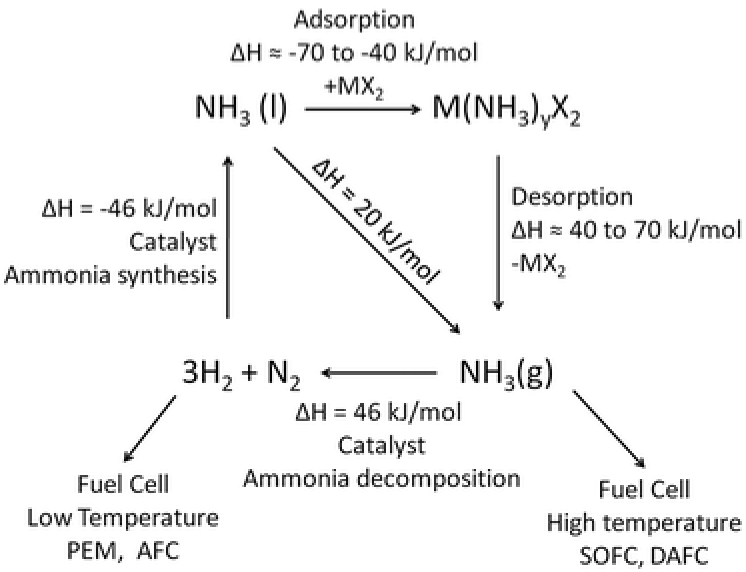
$$aM + (b/2)\ H_2 \Leftrightarrow M_aH_b + heat$$

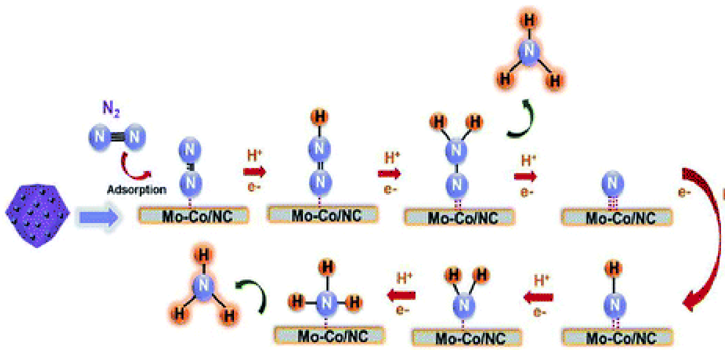
where M is a metal. Heat is generated during hydrogen charging of the hydride storage (absorption of hydrogen) and the same heat is needed to discharge the hydrogen (desorption of hydrogen). The metal hydride formed must be chemically and thermally stable under frequent charging and discharging cycles. Storage materials include Mg, Ti, Ti_2Ni, Mg_2Ni, MgN_2, NaAl, and various combinations.





Ammonia for Hydrogen Storage





Features:

- **The mass percentage of hydrogen is 17.6%.**
- **At normal temperature and pressure, it can be easily converted to liquid.**
- **Easy to store and transport.**
- **Hydrogen can be easily obtained by pyrolysis.**

Ref: Zhang, Yizhen, Jue Hu, Chengxu Zhang, Yizhe Liu, Mengyuan Xu, Yujia Xue, Lifen Liu, and **Michael KH Leung**. "Bimetallic Mo–Co nanoparticles anchored on nitrogen-doped carbon for enhanced electrochemical nitrogen fixation." *Journal of Materials Chemistry A* 8, no. 18 (2020): 9091-9098.
Klerke, Asbjørn, Claus Hviid Christensen, Jens K. Nørskov, and Tejs Vegge. "Ammonia for hydrogen storage: challenges and opportunities." *Journal of Materials Chemistry* 18, no. 20 (2008): 2304-2310.

Demonstration Projects

- **H21 Project**
  Conversion of the UK gas networks to carry 100% hydrogen.

- **Hydrogen Park South Australia (HyP SA)**
  Renewable electricity drives mega-watt PEM electrolyzer for hydrogen production.

- **Gaoming Tram Project in Foshan City**
  World’s first hydrogen fuel cell-powered fixed rail electric tram.

Conclusion

- Renewable hydrogen production methods are available.
- Fuel cell energy conversions are clean and zero-GHG emission.
- Ammonia is a potential solution to hydrogen storage.
- Overall, hydrogen power is a promising approach to achieve Advancing Net Zero.

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