Effective Photocatalytic Seawater Splitting

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Abstract

The photocatalytic (PC) hydrogen production from water splitting is a promising route to fulfill the current energy demand in an eco-friendly and sustainable manner. For photocatalysis to become industrially viable, seawater should be used. This solvent owes its salinity due to various ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, SO_4^{2-}, and CO_3^{2-}). To date, there are contradicting reports in the literature on the influence of these ions on the PC splitting of water. A variety of different neutral transition metal-oxide-based photocatalysts has been exploited. Although they might be effective in splitting deionized water[1], however, thus far, there has been a lack of a well-established route to effectively using any semi-conductor for seawater splitting. Presented here are the details of our work where an intriguing, ionized, low-cost semiconductor has been successfully evaluated for sea-water splitting. The structure consists of a modified carbon nitride such that it forms an ionized organic polymer-based system.[2] A detailed study has been done using this salt-type semiconductor in the presence of various ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}), and their role has been probed in modulating the photocatalytic activity. Photoelectrochemical measurements have provided insight as to how the presence of cations aids advantageously in forming an effective *in-situ* interface between catalyst/co-catalyst for improved charge transfer. This improved interfacial charge transfer rationalizes the 8-fold enhancement in the photocatalytic rate in the presence of simulated seawater compared to deionized water. It provides an impetus for using these carbon nitride structures for sustainable PC splitting of seawater.

Introduction

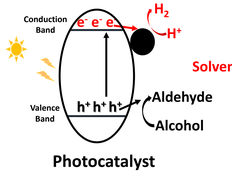
	Fuel	Specific Energy density (MJ/Kg)
	Hydrogen gas	141
Fossil Fuel	Natural gas	53.6
	Gasoline	46.4
	Diesel	45.6
Capacitor	Supercapacitor	0.018
Battery	Lithium ion battery	0.87
	Nickel metal hydride battery	0.41

➢Hydrogen is having the highest specific energy density

➢Combustion of hydrogen has zero carbon emission

❑Photo-catalysis

$2H_2O \rightleftharpoons 2H_2(g) + O_2(g)$ $\Delta G^\circ = 237$ KJ/mole

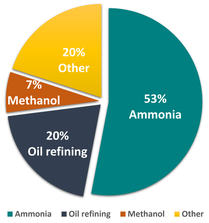


Photocatalyst

Solvent: Deionised water

Current Usage of Hydrogen

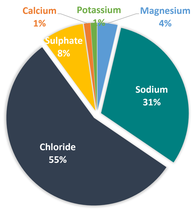
Annually approx. > 800 metric tons of CO_2 emitted into the environment to generate hydrogen only

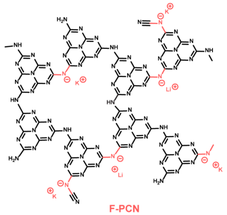


Photocatalyst	Cocatalyst	H_2 Production µmole h^{-1} g^{-1}	Seawater type	Better than Pure water?	% Change in Performance
TiO_2 [3]	CuO	3.1	3% NaCl	No	↓33%
p-GaN/InGaN [4]	Rh/Cr_2O_3, cobalt oxide	5.1 x 10^6	Simulated seawater	Yes	↑35%
$La_2Ti_2O_7$ [5]	Ni	69.6	Natural seawater	No	↓49%
WO_2-Na_2WO_4 [6]	-	5.76	Seawater	Yes	↑15%
$ZnS_{1-x-0.5y}O_y(OH)_y$-ZnO [7]	NiS	354	Simulated water	Yes	↑11%
Covalent organic polymer COP-TP [8]	Pt	4250	Simulated water	No	↓15%
CdS nanosheets [9]	Carbon dots (CDs)	4640	Natural Seawater	No	↓54%

Do these ions affect the rate of photocatalytic water splitting?

Ideal Solvent : Seawater

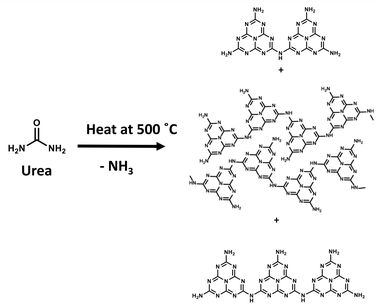




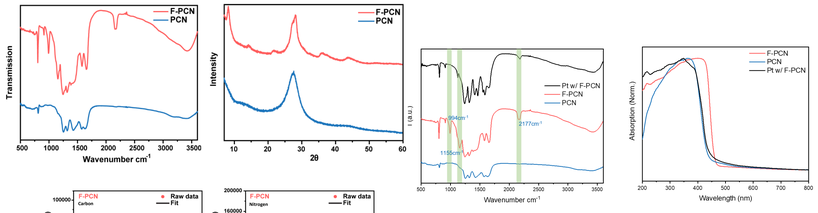
How an ionized carbon nitride photocatalytic water splitting is going to modulate in the presence of ions?

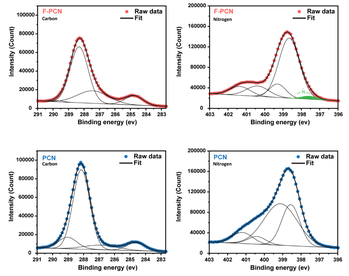
- ❑ Metal-free photocatalyst
- ❑ Visible absorption cross-section
- ❑ Proper band alignment for water splitting
- ❑ Stable in acidic and basic conditions
- ❑ Ease of preparation, inexpensive

Synthesis



Characterization



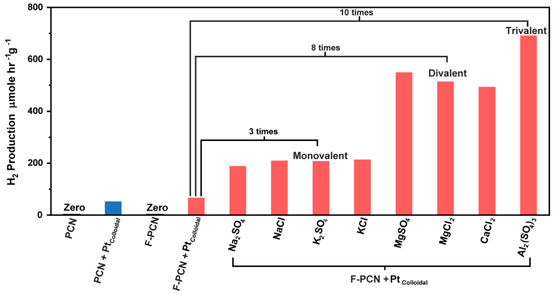


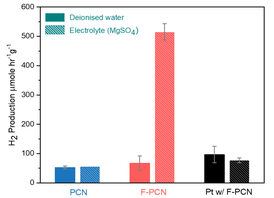
Material	Carbon (wt%)	Nitrogen (wt%)	Hydrogen (wt%)	Potassium (wt%)	Lithium (wt%)	C/N atomic ratio	N/H atomic ratio
PCN	29.1 ± 0.0	50.1± 0.1	2.9 ± 0.3	0.0	0.0	0.68	1.23
F-PCN	25.9 ± 0.0	38.7 ± 0.5	2.1 ± 0.2	9.5 ± 0.9	0.8 ± 0.1	0.78	1.31
Pt w/ F-PCN	27.0 ± 0.1	40.6 ± 1.0	2.9 ± 0.2	0.6 ± 0.1	0.0	0.78	1

Photodeposition of Pt cocatalyst removes the negative charged from the framework

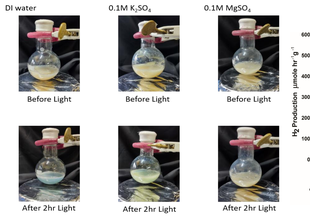
XPS confirms F-PCN has a negatively charged framework

Photocatalytic Water Splitting





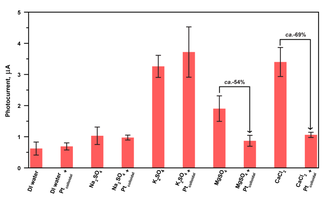
Only the cationic part of the electrolyte plays a role in augmenting the H_2 production.



Catalyst	K^+ (µmole)	Li^+ (µmole)	Na^+ (µmole)	Mg^{2+} (µmole)
F-PCN	2.4 ± 0.2	1.1 ± 0.2	-	-
F-PCN in DI water	1.2 ± 0.1	0.1 ± 0.0	-	-
F-PCN in Na_2SO_4	0.2 ± 0.1	-	1.7 ± 0.1	-
F-PCN in K_2SO_4	2.2 ± 0.4	-	-	-
F-PCN in $MgSO_4$	0.5 ± 0.0	-	-	0.9 ± 0.0

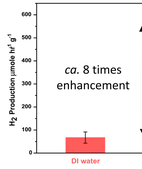
Cationic part of the electrolyte is exchanged with the cations of the framework

The formation of blue species in DI water and K_2SO_4 show that electrons are stored on the material



Reduction in photocurrent with Bi-valent cation showcases an effective interface formed between catalyst/cocatalyst.

Conclusion & Future Direction



- ❑ The augmentation in photocatalysis for Ionized structure is substantially high compared to neutral transition metal oxide.
- ❑ The Presence of cations improves the electron transfer ability from the catalyst to the cocatalyst.
- ❑ Ionized carbon nitride showcases the promising behavior for seawater splitting.

Reference

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