

Short communication

# Photocatalytic hydrogen production from natural seawater

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## Abstract

Hydrogen could be produced photocatalytically from natural seawater with simple pre-treatments as demonstrated with  $\text{La}_2\text{Ti}_2\text{O}_7$  suspension under ultraviolet light,  $\text{CdS}/\text{TiO}_2$  suspension under visible light, and  $\text{Fe}_2\text{O}_3$  film under photoelectrochemical conditions. In all cases, the formation of harmful chlorine gas was not detected. The role of salts in the seawater was elucidated.

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**Keywords:** Photocatalysis; Hydrogen; Seawater;  $\text{La}_2\text{Ti}_2\text{O}_7$ ;  $\text{CdS}/\text{TiO}_2$ ;  $\text{Fe}_2\text{O}_3$

## 1. Introduction

Realization of hydrogen economy requires the production of hydrogen in an economic and sustainable manner. It is the most ideal to produce hydrogen energy from the most abundant energy source available on earth (which is the sun) and the most abundant natural resource on earth (which is water). The enabling technology for this process is the photocatalytic water splitting (PWS). Since its demonstration in 1972 by Honda and Fujishima [1], PWS has become an area of active research worldwide, particularly due to recent surge of price and uncertainty in the long-term supply of oil. Almost all studies of PWS so far have been performed in pure water (distilled water), although some additives such as NaOH, KOH and  $\text{Na}_2\text{CO}_3$  are dissolved into pure water to enhance the efficiency of hydrogen production [2]. Therefore, availability of pure water is the first consideration for the photocatalytic hydrogen production. Although water is abundant on the earth, pure water is scarce because 93% of the earth's water is present in oceans and inland seas and most of the remaining water is isolated as glacier in the polar regions [3]. Thus, it is difficult to obtain pure water from our surroundings without expensive water purification processes. Seawater is the most available water on the earth although it is not pure.

Hydrogen production methods from seawater via electrolysis or marine photosynthetic bacteria have been proposed [4]. Yet, these methods are disadvantageous because of harmful chlorine evolution, low efficiency and high cost. Here, we report that hydrogen could be produced photocatalytically from natural seawater with simple pre-treatments.

There is no unique system or photocatalyst with high efficiency to demonstrate PWS. Thus we employed three systems to evaluate the photocatalytic hydrogen production from seawater;  $\text{La}_2\text{Ti}_2\text{O}_7$  suspension under ultraviolet light,  $\text{CdS}/\text{TiO}_2$  suspension under visible light, and  $\text{Fe}_2\text{O}_3$  film under photoelectrochemical conditions.

## 2. Experimental

The layered-perovskite  $\text{La}_2\text{Ti}_2\text{O}_7$  is a typical photocatalyst efficient under UV light irradiation and has been studied extensively by us for PWS and decomposition of toxic organic compounds such as  $\text{CH}_3\text{Cl}$  [5–7]. The  $\text{La}_2\text{Ti}_2\text{O}_7$  photocatalyst was synthesized by the conventional solid-state reaction method. A stoichiometric mixture of  $\text{La}_2\text{O}_3$  (Aldrich 99.999%) and anatase- $\text{TiO}_2$  (Aldrich 99.99%) was mixed and ground in a mortar in the presence of ethanol and dried in an oven. Pelletized powders were calcined at 1323 K for 10 h in static air. Synthesized  $\text{La}_2\text{Ti}_2\text{O}_7$  was converted to the efficient photocatalyst ( $\text{NiO}/\text{Ni}/\text{La}_2\text{Ti}_2\text{O}_7$ ) by loading 2.0 wt.% of Ni metal from nickel nitrate solution by the incipient-wetness

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impregnation method, followed by reduction in  $H_2$  at 773 K for 2 h, and then reoxidation in air at 473 K for 1 h [5,6]. The photocatalytic hydrogen/oxygen production was carried out at room temperature in an upper-irradiation-type Pyrex-casing reaction vessel with a Quartz-window under UV light irradiation with 400 W Mercury-arc lamp equipped with a liquid filter to remove IR light. The photocatalyst (0.1 g) was suspended in natural (or simulated) seawater (100 ml) by magnetic stirring. The amount of hydrogen/oxygen, gaseous by-products evolved and chloride ion ( $Cl^-$ ) in a solution was determined by a gas chromatography equipped with TCD (molecular sieve 5 Å column, Ar carrier gas), GC-MSD system (HP GC 6890 and 5973 Mass Selective Detector) and Ion Chromatography (DX-120, DIONEX Co.), respectively. Natural seawater (NSW) sample was taken from the Korea's east coast. It contained suspended matter and planktons as well as various kinds of ionic salts (electrolytes) such as  $Na^+$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ , etc. Therefore, it was filtered through a filter paper (Whatman 40, pore size: 4–5  $\mu m$ ) and a polymer membrane filter (Advantec MFS, Inc., pore size: 0.45  $\mu m$ ) to remove suspended matter and planktons, respectively [3]. For comparison, simulated seawater (SSW) was synthesized by dissolving the chemicals (NaCl, 27.21 g;  $MgCl_2$ , 3.81 g;  $MgSO_4$ , 1.66 g;  $CaSO_4$ , 1.404 g;  $K_2SO_4$ , 0.577 g;  $K_2CO_3$ , 0.2124 g;  $MgBr_2$ , 0.08 g) in 1 L of distilled water. We identified seven major dissolved components which make up 99.9% of the soluble ionic species of seawater. The salinity of the simulated seawater was 34.95 per mill (‰), which is very close to the global average salinity of ca. 35‰.

### 3. Results and discussion

Fig. 1 shows typical time courses of hydrogen/oxygen evolution for the photocatalytic reduction of pure water, NSW and SSW over  $NiO/Ni/La_2Ti_2O_7$  under UV light irradiation. Hydrogen and oxygen were produced steadily in a stoichiometric ratio ( $H_2/O_2 = 2:1$ ) in all cases. Especially, hydrogen was produced continuously from both NSW (69.6  $\mu mol/h$ ) and SSW (59.8  $\mu mol/h$ ) by photocatalytic reaction, although  $H_2$  evolution rate from both seawaters was lower than that from pure

water (137.2  $\mu mol/h$ ). The reduction of photocatalytic hydrogen/oxygen production from seawater should be caused by the various dissolved ionic components of seawater [8]. In all cases, there was no indication of catalyst deactivation during three runs separated by purging of the gas phase. In addition, another UV-light-driven photocatalyst,  $NiO/Ni/Sr_2Nb_2O_7$  [5], showed the same tendency in hydrogen production from pure water and NSW ( $H_2$  evolution rate was 42.6 and 26.9  $\mu mol/h$ , respectively). Thus, photocatalytic  $H_2$  production from seawater can occur independently of photocatalyst materials. Moreover, although seawater is more complicated than pure water because of various salt ions in seawater, only hydrogen and oxygen was evolved stably without any gaseous by-products or precipitates via photocatalytic reaction. Especially, unlike electrolysis of seawater, the harmful chlorine gas did not evolve and the concentration of chloride ion in solutions (NSW and SSWs) did not decrease during photocatalytic reaction for 6 h as evidenced by the analysis of evolved gases and reaction solutions. In addition, the variation of pH value of solutions after reaction for 12 h was very small ( $pH = 8.5 \rightarrow 8.3$  at 25 °C). From these results, it could be concluded that chloride ions in NSW and SSWs are not oxidized under the conditions of our photocatalytic reaction. The oxidation potential of chloride ion (1.397 eV) is more positive than that of  $H_2O$  (1.23 eV). The valence band position of  $La_2Ti_2O_7$  (2.714 eV) is positive enough to oxidize the chloride ion, yet it appears that this oxidation reaction does not occur because of insufficient overpotential to drive this reaction kinetically.

The effect of the seven ions contained in seawater was examined by preparing SSW containing the each individual ionic component and the results are summarized in Table 1. The hydrogen evolution rate over  $NiO/Ni/La_2Ti_2O_7$  varied significantly with the nature of ionic species contained in the SSW. All the dissolved ions reduced the rate of hydrogen production, but the exception was potassium sulfate that increased the hydrogen production rate by ca. two times. The most detrimental component was magnesium chloride, which decreased the evolution rate by a factor of ca. 2. This magnesium chloride solution contained  $Mg^{2+}$  and  $Cl^-$  corresponding to 73.8 and 14.7% of the amount present in NSW, respectively. In addition,  $H_2$  evolution rate from SSW containing six salts omitting only  $MgCl_2$  showed a much improved rate compared to SSW containing seven salts, and the rate corresponded to ca. 76% of pure water. These results show that magnesium ion is the main culprit of decreased  $H_2$  evolution rate from NSW. Recently, Toutianoush et al. reported that 98% of magnesium ions can be rejected from seawater in a single step through polyelectrolyte multilayer membrane of polyvinyl alcohol and polyvinyl sulfate [9]. It is expected that hydrogen could be produced more efficiently from natural seawater pretreated with this simple ion exchange membrane.

Photocatalytic hydrogen evolution from seawaters with different salinities was investigated. As stated above, a global average salinity of seawater is ca. 35‰. Salinity of prepared SSWs was varied from 35 to 3.5‰. Hydrogen evolution rate increased as salt concentration (salinity) decreased. In particular, hydrogen evolution rate increased up to ca. 59.5 and 90.3% of that from pure water when salinity of seawater was reduced

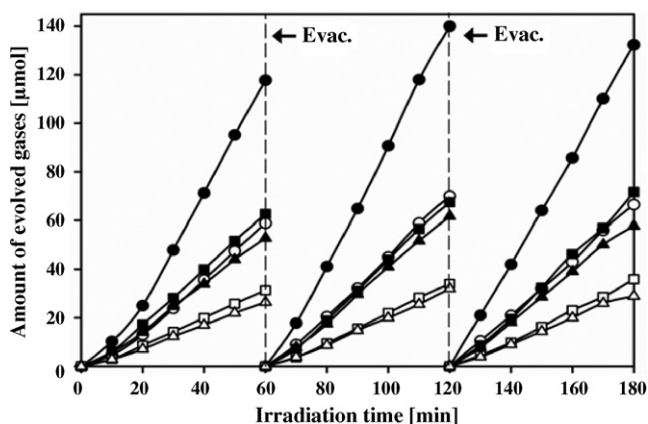


Fig. 1. Time courses of  $H_2$  (solid symbols) and  $O_2$  (open symbols) evolution from pure water (●), natural seawater (■) and artificial seawater (▲) over  $NiO/Ni/La_2Ti_2O_7$ .

Table 1  
H<sub>2</sub> evolution rate from pure water, NSW and several sea electrolyte solutions over Ni(2.0 wt.%)/La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

Solution or electrolyte	Weight (mg)	Concentration (mmol)	Ions in solution				pH at 25 °C	H <sub>2</sub> evolution rate <sup>a</sup> (μmol h <sup>-1</sup> )
			Cation	% <sup>b</sup>	Anion	% <sup>b</sup>		
Pure Water	–	–	–	–	–	–	–	137.2
Natural seawater	–	–	–	–	–	–	–	69.6
NaCl	27.21	465.586	Na <sup>+</sup>	100	Cl <sup>-</sup>	85.3	6.69	119.7
MgCl <sub>2</sub>	3.81	400.166	Mg <sup>2+</sup>	73.8	Cl <sup>-</sup>	14.7	9.00	59.4
MgSO <sub>4</sub>	1.66	13.791	Mg <sup>2+</sup>	25.4	SO <sub>4</sub> <sup>2-</sup>	50.3	7.60	95.3
CaSO <sub>4</sub>	1.404	10.313	Ca <sup>2+</sup>	100	SO <sub>4</sub> <sup>2-</sup>	37.6	6.32	110
K <sub>2</sub> SO <sub>4</sub>	0.577	3.311	K <sup>+</sup>	68.3	SO <sub>4</sub> <sup>2-</sup>	12.1	7.41	282.5
K <sub>2</sub> CO <sub>3</sub>	0.2124	1.537	K <sup>+</sup>	31.7	CO <sub>3</sub> <sup>2-</sup>	100	10.62	99.6
MgBr <sub>2</sub>	0.08	0.435	Mg <sup>2+</sup>	0.8	Br <sup>-</sup>	100	6.76	88.3

<sup>a</sup> Reaction conditions: photocatalyst 0.1 g; electrolyte solution 100 ml; 400 W Mercury-arc lamp.

<sup>b</sup> The percentage of each ion in solution per total amount of each ion in natural seawater.

to 17.5 and 3.5%, respectively. The concentration of salt ions in seawater can be reduced easily through conventional and simple desalination processes [10] such as reverse osmosis, electro-dialysis, etc. Thus the activity of photocatalytic hydrogen production from natural seawater can be enhanced also by pretreatment of mild desalination.

Now the photocatalytic hydrogen production was studied under visible light. Table 2 summarizes hydrogen evolution rates from pure water, NSW and SSWs with different salinity over a Pt–CdS/TiO<sub>2</sub> nanocomposite photocatalyst [11] under visible light irradiation ( $\lambda \geq 420$  nm). The reaction solution also contained sulfide/sulfite as electron donors to prevent the photo-corrosion of CdS. In dilute sulfide/sulfite solutions (1/0.2 mmol), H<sub>2</sub> evolution rate from 3.5% ASW was the highest among different electrolyte solutions, and the rate from NSW was also higher than that from pure water. In order to elucidate the source of this promotional effect, we carried out an additional control experiment. Thus, we measured photocatalytic activity over Pt (1.0 wt.%)–CdS/TiO<sub>2</sub> nanocomposite under visible light ( $\lambda \geq 420$  nm) with solution containing 3.5% of NaCl or Na<sub>2</sub>SO<sub>4</sub> in addition to 1 mmol of Na<sub>2</sub>S and 0.2 mmol of Na<sub>2</sub>SO<sub>3</sub>. Compared with the solution without an additional salt (NaCl or Na<sub>2</sub>SO<sub>4</sub>), the rate of hydrogen evolution was higher by 10 and 27% for electrolyte solutions with NaCl and Na<sub>2</sub>SO<sub>4</sub>, respectively. This indicates that alkali salts in seawater help the function of sulfide/sulfite solution as sacrificial agents leading to higher activity. Although it is still not clear how these salts can promote the reaction, this effect is shown not to be specific for any par-

ticular ions. In contrast, with the heavy sulfide/sulfite solution (10/2 mmol), the evolution rate from NSW was much lower than that from pure water. It could be explained by the presence of sulfide and sulfite ions in too high a concentration as electron donors in seawater. It appears to induce a charge unbalance of seawater, impedes their function as sacrificial agents resulting in the formation of precipitates, and reduces the hydrogen evolution rate. Without sulfide/sulfite ions, no activity was observed from NSW and SSW of all concentration.

Finally, the performance of a photoelectrochemical (PEC) half-cell made of a Fe<sub>2</sub>O<sub>3</sub> anode was evaluated in pure water, NSW, and SSW. In this system, a nanostructure film of iron oxide deposited on ITO glass was fabricated by a two-step process. In the first step, the nanocrystals were prepared by thermal decomposition of iron-oleate complex at 593 K [12]. In the second step, thus obtained nanocrystals were used to dip-coat the ITO substrate. The post-drying/annealing was carried out in a temperature range of 473–553 K for several hours. This set up as it is cannot produce hydrogen because there is no bias voltage applied. Yet, we can evaluate its performance by measuring photocurrent generated from oxidation of water. The photogeneration of charge carriers, specifically holes (h<sup>+</sup>) at Fe<sub>2</sub>O<sub>3</sub>, can oxidize water to produce oxygen (2h<sup>+</sup> + H<sub>2</sub>O → 1/2O<sub>2</sub> + 2H<sup>+</sup>). The presence of an added electrolyte (e.g. NaOH) is essential to operate this PEC cell. But, as shown in Table 2, photocurrent was generated from NSW and two SSWs even without added electrolyte under visible light irradiation ( $\lambda \geq 420$  nm). Thus it seems that the existence of various types of metal ions probably

Table 2  
Photoreaction activities from various electrolyte solutions over Pt (1.0 wt.%)–CdS/TiO<sub>2</sub> nanocomposite or iron oxide film under visible light ( $\lambda \geq 420$  nm)

Material	Additive (mmol)		Photoreaction activity			
	Na <sub>2</sub> S	Na <sub>2</sub> SO <sub>3</sub>	NSW (35%)	ASW (17.5%)	ASW (3.5%)	Pure water
Pt (1.0)–CdS/TiO <sub>2</sub>	10	2	41.5 <sup>a</sup>	–	–	221 <sup>a</sup>
	1	0.2	93 <sup>a</sup>	97.5 <sup>a</sup>	132 <sup>a</sup>	83 <sup>a</sup>
Fe <sub>2</sub> O <sub>3</sub>		NaOH	7.2 <sup>b</sup>	219 <sup>b</sup>	112 <sup>b</sup>	1400 <sup>b</sup>
		–	13.4 <sup>b</sup>	15.0 <sup>b</sup>	7.6 <sup>b</sup>	0 <sup>b</sup>

<sup>a</sup> H<sub>2</sub> evolution rate (μmol h<sup>-1</sup>); reaction conditions: photocatalyst 0.05 g; each solution 100 ml with Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as electron donor; 450 W Mercury-arc lamp with cut-off filter ( $\lambda \geq 420$  nm); concentration (mmol) of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub>: 10 and 2, 1 and 0.2.

<sup>b</sup> Photocurrent (μA cm<sup>-2</sup> min<sup>-1</sup>); PEC cell: iron oxide film(working), SCE (reference) and Pt gauze (counter); applied potential: +0.55 V vs. SCE; each solution with or without 50 vol.% 0.1 M NaOH.

favors the faster kinetics of ions transfer across the semiconductor/electrolyte interface. Overall, the performance of the PEC cell in seawater was lower than in pure water containing added NaOH.

#### 4. Conclusion

In summary, we confirmed the possibility of photocatalytic hydrogen production from natural seawater under various conditions and setups. In case of UV-light-driven NiO/Ni/La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> photocatalyst, the H<sub>2</sub> evolution rate from NSW was about half as much as that from pure water. It was shown that Mg<sup>2+</sup> was the main culprit that reduced the hydrogen evolution rate from seawater. Thus, the activity of photocatalytic hydrogen production from NSW could be enhanced by selective removal of magnesium ion through simple pre-treatment. Decrease in salinity by a mild desalination could also improve the performance. For visible-light-driven Pt–CdS/TiO<sub>2</sub> nanocomposite photocatalyst in the presence of sulfide/sulfite as electron donors, H<sub>2</sub> evolution rate from NSW was much higher when a dilute sulfide/sulfite solution was employed. The photoelectrochemical cell with Fe<sub>2</sub>O<sub>3</sub> film anode also demonstrated photocurrent generation in seawater under visible light, although the rate was much reduced from that observed in pure water. Thus, the photocatalytic H<sub>2</sub> production from seawater could be achieved with various photocatalyst materials and reaction conditions. The performance in seawater is lower in general than in pure water, yet could be improved by simple pretreatments.

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#### References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37.
- [2] S. Sato, J.M. White, *J. Catal.* 69 (1981) 128;  
K. Domen, A. Kudo, T. Onishi, *J. Catal.* 102 (1986) 92;  
K. Sayama, H. Arakawa, *J. Chem. Soc. Chem. Commun.* (1992) 150.
- [3] F.J. Millero, *Chemical Oceanography*, 2nd ed., CRC Press LLC, Florida, USA, 2002.
- [4] J.O'M. Bockris, *Energy, The Solar-Hydrogen Alternative*, John Wiley, New York, USA, 1975;  
A.M.A. El-Bassuoni, J.W. Sheffield, T.N. Veziroglu, *Int. J. Hydrogen Energy* 7 (1982) 919.
- [5] H.G. Kim, D.W. Hwang, J. Kim, Y.G. Kim, J.S. Lee, *Chem. Commun.* (1999) 1077;  
D.W. Hwang, H.G. Kim, J. Kim, K.Y. Cha, Y.G. Kim, J.S. Lee, *J. Catal.* 193 (2000) 40;  
J. Kim, D.W. Hwang, H.G. Kim, S.W. Bae, J.S. Lee, W. Li, S.H. Oh, *Top. Catal.* 35 (2005) 295.
- [6] J. Kim, D.W. Hwang, S.W. Bae, Y.G. Kim, J.S. Lee, *Korean J. Chem. Eng.* 18 (2001) 941;  
J. Kim, D.W. Hwang, H.G. Kim, S.W. Bae, S.M. Ji, J.S. Lee, *Chem. Commun.* (2002) 2488;  
D.W. Hwang, K.Y. Cha, J. Kim, H.G. Kim, S.W. Bae, J.S. Lee, *Ind. Eng. Chem. Res.* 42 (2003) 1184;  
D.W. Hwang, J.S. Lee, W. Li, S.H. Oh, *J. Phys. Chem. B* 107 (2003) 4963.
- [7] H.G. Kim, D.W. Hwang, S.W. Bae, J.H. Jung, J.S. Lee, *Catal. Lett.* 91 (2003) 193;  
H.G. Kim, S.M. Ji, J.S. Jang, S.W. Bae, J.S. Lee, *Korean J. Chem. Eng.* 21 (2004) 970.
- [8] K. Sayama, H. Arakawa, *J. Photochem. Photobiol. A* 77 (1994) 243.
- [9] A. Toutianoush, W. Jin, H. Deligöz, B. Tieke, *Appl. Surf. Sci.* 246 (2005) 437.
- [10] S.A. Kalogirou, *Progr. Energy Comb. Sci.* 31 (2005) 242;  
E. Drioli, G.D. Profio, E. Curcio, *Water Sci. Technol.* 51 (2005) 293.
- [11] J.S. Jang, S.M. Ji, J.S. Lee, W. Li, S.H. Oh, *Stud. Surf. Sci. Catal.* 159 (2006) 201.
- [12] J. Park, K. An, Y. Hwang, J.G. Park, H.J. Noh, J.Y. Kim, J.H. Park, N.M. Hwang, T. Hyeon, *Nat. Mater.* 3 (2004) 891.