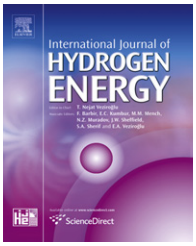
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 15136–15144

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/he



Generation of hydrogen from aluminum and water – Effect of metal oxide nanocrystals and water quality

Hong-Wen Wang [a,*], Hsing-Wei Chung [a], Hsin-Te Teng [a], Guozhong Cao [b]

[a] Department of Chemistry, Master Program of Nanotechnology, Center for Nanotechnology, Chung-Yuan Christian University, Chungli 320, Taiwan, ROC
[b] Department of Materials Science and Engineering, University of Washington, Seattle, WA, USA

ARTICLE INFO

Article history:
Received 19 June 2011
Received in revised form
16 August 2011
Accepted 23 August 2011
Available online 16 September 2011

Keywords:
Hydrogen generation
Aluminum
Modification agent
TiO_2 nanocrystals

ABSTRACT

Metal Oxides nanocrystals such as TiO_2, Co_3O_4, Cr_2O_3, Fe_2O_3, Mn_2O_3, NiO, CuO and ZnO were used as modifiers on the metallic aluminum (Al) powders for the production of hydrogen in deionized water or tap water at room temperature. In particular, the influences of TiO_2 nanocrystals with various crystal sizes on the production of hydrogen from the reaction in tap water under ambient condition were investigated in details. It was found that hydrogen was barely generated from metal Al powders in tap water at 25–45 °C but significantly produced in deionized water above 35 °C without any modifiers. TiO_2, Co_3O_4, and Cr_2O_3 nanocrystals were very effective to promote hydrogen generation from the reaction of Al and deionized water at 25 °C. In addition, while other oxide nanocrystals were ineffective to promote hydrogen generation in tap water, TiO_2 nanocrystals (P90, ~14 nm in diameter) were found to be highly effective in facilitating the production of hydrogen from the reaction of Al with tap water, comparable to the well-known γ-Al_2O_3. The production of hydrogen over time was found to be dependent on the passive layer of metal Al, where $Al(OH)_3$ plays an important role during reaction. Pitting is proposed as the major mechanism behind the production of hydrogen in the nanocrystals TiO_2 (P90)-modified Al/tap water system, which is thought to be originated from point defects, and differ considerably from the uniform corrosion model.

1. Introduction

Hydrogen is considered the best clean energy carrier, due to its light weight, high energy density and zero pollution [1]. However, the low-cost production and safe storage of hydrogen pose considerable technical challenges. Hydrogen can be produced in many different ways, such as through direct decomposition or partial oxidation of hydrocarbon compounds [2,3], the steam reforming of hydrocarbons [3,4], chemical hydrides reacting with water [5], splitting water using metal-oxide catalysts under solar energy [6–10], and metallic aluminum reacting with aqueous alkaline solutions [11]. However, all of the above production methods suffer from various drawbacks. For example, the direct decomposition or partial oxidation of hydrocarbon reactants requires elevated temperatures and produces considerable quantities of CO and other byproducts. The reforming of methanol produces hydrogen at lower temperatures, with considerably less CO than the oxidation of hydrocarbons [3,4]; however, this process is endothermic, and externally supplied heat is

---

* *Corresponding author*. Tel.: +886 955285268; fax: +886 3 2653399.
E-mail address: hongwen@cycu.edu.tw (H.-W. Wang).

doi:10.1016/j.ijhydene.2011.08.077

required to maintain the reaction. Chemical hydrides such as $LiBH_4$, $NaBH_4$, NaH, and MgH_2 react with water directly and generate large quantities of hydrogen under ambient conditions [5]; however, the deactivation of the catalysts (Pt, Ru), the treatment of hydroxide byproducts, control of the reaction rate, and the high price of reactants are all impediments to the commercialization of this process. Splitting water using metal-oxide photocatalysts such as TiO_2 is a promising route for the production of hydrogen [6–8]; however, the efficiency of producing hydrogen using bare TiO_2 is low, due mainly to the fast recombination of electron/hole pairs [7,8]. Noble metals such as Pt or semiconductors such as CdS-modified TiO_2 have proven highly effective in overcoming this problem [9,10].

The reaction of aluminum (Al) with aqueous alkaline solutions to generate hydrogen is well known [11]. One gram of Al can produce 1.36 L of H_2 when completely reacted with water in ambient conditions. A direct reaction of metallic Al with pure water is difficult however, due to a dense Al_2O_3 film (3–6 nm in thickness) that passivates the surface of the Al [12]. Metallic Al reacts continuously with water when the passive Al_2O_3 layer is exposed to acid or alkaline solutions; however, the environmental pollution and the easy passivation of metallic Al are major concerns using this method. Several novel alternative processes permitting the direct reaction of metallic Al and pure water under ambient conditions were proposed by Woodall [13,14], Chaklader [15,16], and Czech [17]. The method invented by Woodall takes advantage of Al–Ga eutectic reaction to generate hydrogen in a straight- forward manner [13,14]. The gallium is a critical component hindering the formation of the aluminum oxide skin on the surface of the Al. In the same manner, other metals such as Bi, Sn, and In could also be used for the formation of alloys with Al to generate hydrogen gas on demand; however, caution must be exercised to prevent hydrogen gas explosions. The cost of materials is also a critical concern for the practical implementation of this process. Chaklader [15,16] patented the direct reaction of metallic Al with tap water by using α-Al_2O_3 and γ-Al_2O_3 powders as modifiers through mechanical mixing. Czech [17] reported similar direct reactions of metallic Al with tap water through the mechanical mixing of Al with chloride salts such as KCl and NaCl. The latter two methods generate hydrogen easily under ambient conditions. Zeng et al. [18–20] reconfirmed the role of the catalyst/modifier γ-Al_2O_3 and the enhancement of hydrogen production enabled by elevated temperatures. Zeng et al. [19,20] also explained the mechanism behind the production of hydrogen using γ-Al_2O_3-modified Al powders (referred as “GMAP”) in a (GMAP)/water system based on the uniform corrosion model, illustrated in a report by Bunker [12].

In addition to the well studies in tap water outlined above, the experiments using deionized water as the media for corrosion of aluminum are not well revealed. Especially, effective modifiers other than γ-Al_2O_3 and α-Al_2O_3 were not known. This study demonstrates that many metallic oxides such as TiO_2, Co_3O_4, and Cr_2O_3 nanocrystals could be used as effective modifiers on aluminum powders for the production of hydrogen in tap water or deionized water through a simple mixing process. Neither heat treatment nor compaction is required for the modification of Al, as required in the reports [19,21]. It is considered that the pitting mechanism originating from point defects [12] is essential in the nanosized TiO_2-modified Al/water system, which considerably varies from that of γ-Al_2O_3-modified Al/water system [19].

2. Experimental procedure

A list of suppliers, the purity of the chemicals, and size of the particles used in this study are listed in Table 1. Tap water (pH = 6.3–7.5, resistivity < 4.5 kΩ•cm) and deionized (DI) water (pH = 6.5–7.0, resistivity > 18 MΩ•cm) were used throughout this study. Metallic Al powders with particle size of 45 μm were used for all experiments. 1 g of metallic Al powder was hand-mixed (HM) with 1 g modifier powders such as TiO_2 (reagent), Cr_2O_3, Co_3O_4, NiO, CuO, ZnO, Mn_2O_3, or Fe_2O_3 nanocrystals for 3 min, respectively. The modified Al powder with the modifiers were added to 200 ml of tap water or deionized water, and sealed in a conical flask. All experiments were carried out at 25 °C±1 °C and 35 °C±1 °C by placing the reaction flask in a circulation water bath. No magnetic stirring was employed within the reaction flask. The hydrogen generated was measured using a precision gas flow meter (Alicat Scientific, Inc.), in which the output data was automatically recorded in a notebook computer every second till the reaction reached 100% yield of hydrogen (1360 ml/g•Al) or stable.

For the further study on the TiO_2-modified Al powders in tap water, TiO_2 nanocrystals such as P90, P25, PT501A, and reagent powders with particles of various sizes were used for comparison. Hand-mixing using mortar and pestle or ball-mixing (BM) process using plastic bottles were employed for the mixing process of Al and TiO_2 modifiers. ZrO_2 balls were used as the mixing media for ball-mixing process. Mixing duration varied from 3 min to 64 h. Following the mixing process, the Al powder (1 g) with its modifier (1 g) were added to 200 ml of tap water, and sealed in a conical flask. All

Table 1 – The specification and suppliers of precursors used in this study.

Precursors	Supplier	Purity (%)	Particle size
Al powder	Alfa Aesar (325 mesh)	>99.5	45 μm
AlO(OH)	Genesis Nanotech Corp.	>99.5	15 nm
$Al(OH)_3$	Acros	>99	600–700 nm
γ-Al_2O_3	Alfa Aesar	>99.97	1.6 μm
TiO_2 (P90)	Degussa Ltd.	>99.5	14 nm
TiO_2 (P25)	Degussa Ltd.	>99.5	22 nm
TiO_2 (PT501A)	Ishihara Sangyo Kaisha	>99	100 nm
TiO_2 (Reagent)	Shimakyu’s Pure Chemicals	>99	300–450 nm
Co_3O_4	NanoAmor	>99	30 nm
Cr_2O_3	NanoAmor	>99	50 nm
Mn_2O_3	NanoAmor	>99	50 nm
NiO	NanoAmor	>99	50 nm
Fe_2O_3	NanoAmor	>99	20 nm
ZnO	NanoAmor	>99	20 nm
CuO	NanoAmor	>99	40 nm

experiments were carried out at room temperature (25 °C±1 °C). The hydrogen generated was measured using a precision gas flow meter, in which the output data was automatically recorded in a notebook computer every second for 18 h.

After reacting with water, the specimens of modified Al powder were characterized with a Rigaku D/MAX-3C X-ray diffractometer, with the Cu Kα radiation and a Ni filter, over the angular range of 15°–80° (2θ) at a scanning rate of 4° min^{-1} and a step size of 0.01°. Field-emission scanning electron microscopy (FESEM, Jeol JSM 7600F) was employed to characterize the morphology of the powders. Particle size of four TiO_2 nanoparticles in water was measured using a particle size analyzer (Brookhaven Instrument Corp. 90 plus). The trace Al element in tap water or deionized water after dissolving Al_2O_3 powders in the water for 8 h was detected using inductively coupled plasma mass spectrometer (ICP-MS, PE-SCIEX ELAN 6100 DRC). Secondary ion mass spectrometer (SIMS IV, ION-TOF, Germany) was carried out on an aluminum foil which was previously immersed in tap water or deionized water for 8 h at 35 °C and subsequently freeze-drying in order to reveal the oxide profile on the surface of metallic Al.

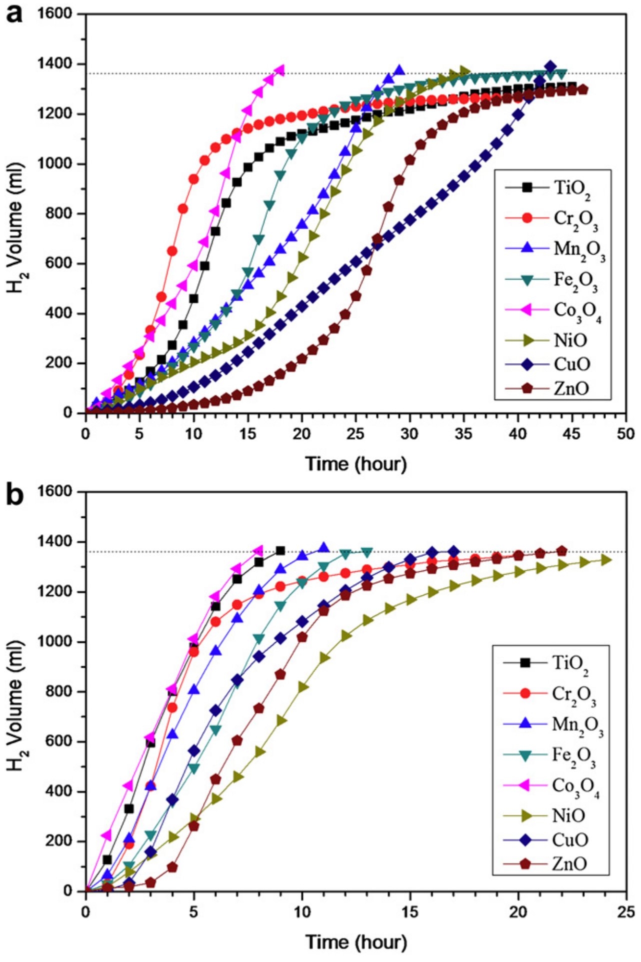


Fig. 1 – Hydrogen generation from the oxide-nanocrystal-modified Al in deionized water (a) at 25 °C, and (b) at 35 °C, respectively. The dot line denotes the ideal 100% yield.

3. Results

3.1. *Effect of metal oxides nanocrystals*

Fig. 1 (a) and Fig. 1(b) show the hydrogen generation from the reaction of modified Al and deionized water at 25 °C and 35 °C, respectively. All the reactions at 35 °C are more rapid than their counterparts at 25 °C, as expected. In the reactions at 25 °C,

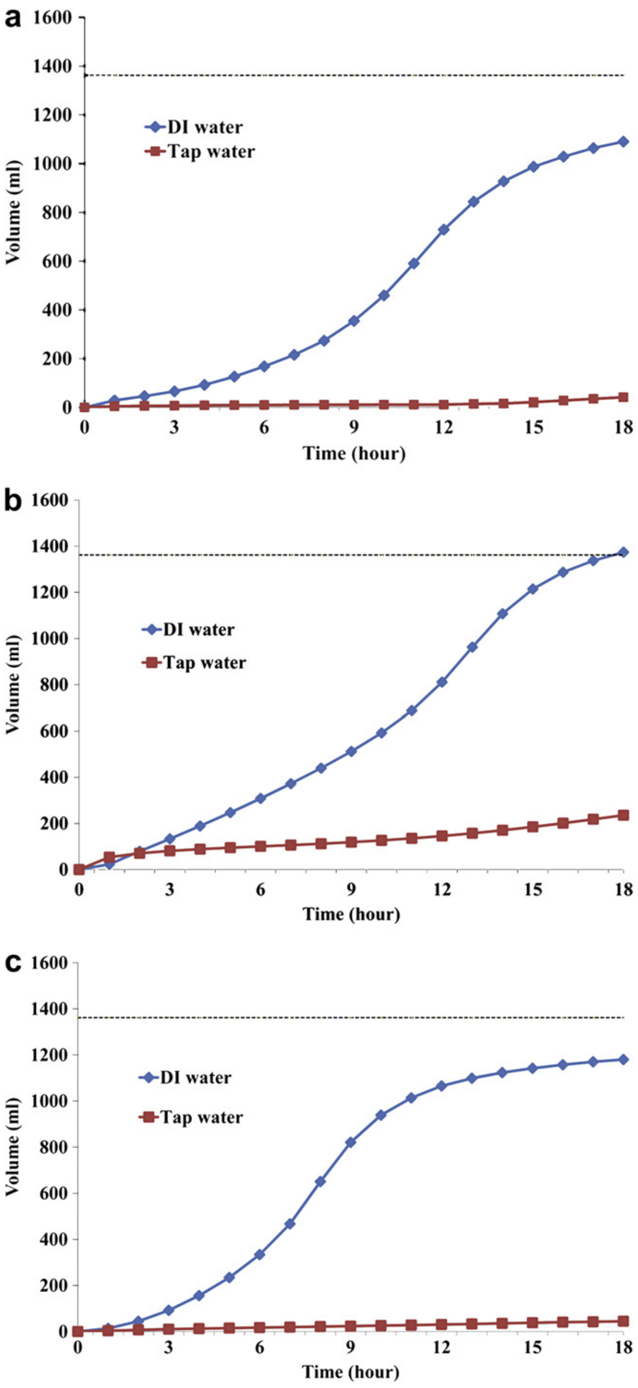


Fig. 2 – The effect of (a) TiO_2 (reagent), (b) Co_3O_4, and (c) Cr_2O_3 modifiers on the hydrogen generation from the metal Al/water system. The dot line denotes the ideal 100% yield.

Table 2 – Total generation of hydrogen in 18 h for oxide nanocrystals modified Al in de-ionized water and tap water at 25 °C, respectively.

	TiO_2 (reagent)	Cr_2O_3	Co_3O_4	Mn_2O_3	Fe_2O_3	NiO	CuO	ZnO
DI water (ml)	**1090**	**1180**	**1362**	655	959	469	355	157
Tap water (ml)	41.7	44.9	236	179	332	32.5	12.2	17.1

modifiers such as TiO_2 (reagent), Co_3O_4, and Cr_2O_3 exhibited higher generation rate than the other five nanocrystals at initial 12 h. However, TiO_2 (reagent) and Cr_2O_3 did not reach the ideal 100% yield even after 45 h Co_3O_4, Mn_2O_3, NiO, Fe_2O_3, and CuO reached the ideal 100% yield at 18 h, 29 h, 35 h, 44 h, and 43 h, respectively, as shown in Fig. 1(a). ZnO exhibited the slowest generation rate for the initial 25 h and produced 1297 ml hydrogen (95% yield) after reaction time of 45 h.

For those reactions at 35 °C, all modifiers produced 100% yield hydrogen out of 1 g Al in deionized water. The durations of 100% yield for TiO_2 (reagent), Co_3O_4, Cr_2O_3, Mn_2O_3, Fe_2O_3, CuO, NiO, and ZnO were 9 h, 8 h, 20 h, 11 h, 13 h, 17 h, 24 h, and 22 h, respectively, as shown in Fig. 1(b). At 35 °C, the hydrogen generation rate for modifiers such as TiO_2 (reagent), Co_3O_4, and Cr_2O_3 is about 200 ml/h·g Al at initial 5 h. Mn_2O_3 becomes more rapid than that of Fe_2O_3 and exhibits a generation rate of 160 ml/h·g Al at first 5 h. The uniqueness of TiO_2 (reagent) is that the size of this reagent powder (rutile) is 300 nm–450 nm, much larger than other nanocrystals. In these experiments, all metal oxide nanocrystals seem to assist metal Al in corrosion and generation of hydrogen in deionized water. Differences in hydrogen generation rate and time to stable (or 100% yield) for these oxide nanocrystals in Al/deionized water system deserved more studies, which will be reported elsewhere later.

3.2. *Effect of water quality*

Fig. 2(a), (b) and (c) shows the hydrogen generation from 1 g modified Al in tap water and deionized water for reagent TiO_2 (rutile), Co_3O_4, and Cr_2O_3 at 25 °C, respectively. All the mixing processes of the oxide nanocrystals modifier and Al powders were accomplished by hand-mixing for 3 min. At room temperature, these oxide nanocrystals facilitate the reaction of Al and deionized water and produce more than 1090 ml hydrogen within 18 h. The same experiments using tap water produced far less amount of hydrogen, as shown in Fig. 2(a)–(c). Other metal oxide nanocrystals such as NiO, Mn_2O_3, Fe_2O_3, CuO, and ZnO also exhibit similar results that the hydrogen generations in tap water are much less than those in deionized water, which are listed in Table 2.

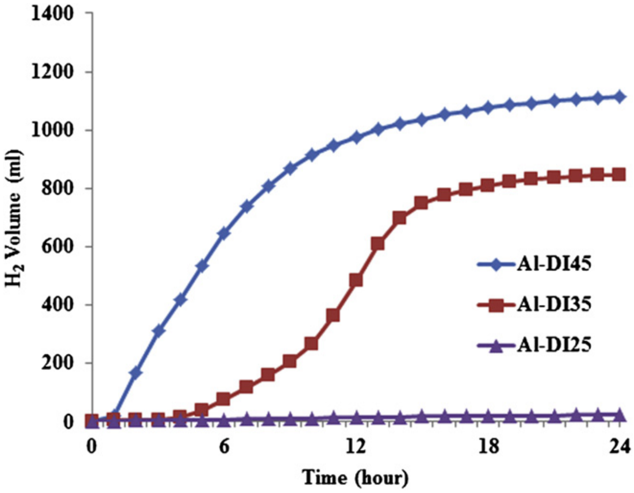


Fig. 3 – Hydrogen generation from the reaction of Al and neutral water without modifiers, DI = deionized water, Tap = tap water. The number denotes the reacting temperatures, i.e. Al-DI45 = Al reaction with deionized water at 45 °C, etc.

In order to clarify the mechanism of hydrogen generation from Al and water, experiments without any modifiers were carried out. Fig. 3 shows the generation of hydrogen from pristine metal Al powders in tap water and deionized water at temperature of 25 °C, 35 °C, and 45 °C, respectively. It is clear that metal Al readily reacts with deionized water and produces hydrogen at a temperature only above 35 °C without any modifiers (sample Al-DI35 and Al-DI45). However, the production of hydrogen from 1 g of Al-DI35 and Al-DI45 samples were slow down at a yield of 58% (800 ml) and 73% (1000 ml) after an initial significant reaction, respectively. In tap water, there was little hydrogen generated at temperatures from 25 °C to 45 °C. The volume of hydrogen generated from Al and tap water without any modifiers was 10 ml, 8 ml and 5 ml for temperature at 45 °C, 35 °C, and 25 °C after 24 h, respectively, which were within experimental variations due to the interference of water vapor. It is clear that metal Al exhibits higher reactivity in deionized water, and temperature enhances the reactivity. However, metallic Al would not significantly generate hydrogen through corrosion in deionized water until temperature over 35 °C. The curve of hydrogen generation for Al-DI35 agrees with the reported reacting stages of Al-water split reaction, i.e. an initial induction period, fast reaction, and slow reaction [21,25]. However, Al-DI45 is more reactive than Al-DI35 and its initial induction period is rather short, resulting in a more rapid production rate and higher maximum volume of hydrogen. We will discuss the mechanisms behind these curves in the discussion section. At 25 °C, the hydrogen generated from the reaction of Al and deionized water was only 25 ml (Al-DI25, overlapped in Fig. 3) after reaction for 24 h. The significance and advantage of adding nanocrystalline modifiers to metal Al powder at 25 °C is clear.

3.3. *TiO_2 modifier with different particle sizes*

Table 3 summarized the effect of different modifiers tested in this study on the production of hydrogen from Al and tap water. $Al(OH)_3$ exhibited little effect on hydrogen production while AlO(OH) was very effective when no mixing process was employed. The results in Table 3 also revealed that though TiO_2 (reagent) possessed insignificant catalytic effect on the production of hydrogen in tap water, TiO_2 (P25) and TiO_2 (P90)

Table 3 – Effect of modifiers on hydrogen generation from Al and tap water. The total reaction time of Al and tap water in this table was 18 h.

Oxide powder	Weight ratio of 1 g Al to modifier	Ball-mixing	Total H_2 volume (ml) in 18 h	Average H_2 generation rate (ml/h·1g Al)	Remark[a]
$Al(OH)_3$	1 : 1	No[a]	0	0	Little effective
	1 : 10	No	1.6	0.1	Little effective
	1 : 20	No	6.1	0.34	Little effective
$AlO(OH)$	1 : 1	No	364.8	20.3	Effective
	1 : 10	No	1057.5	58.8	Effective
	1 : 20	No	1249.8	69.4	Effective
TiO_2 (Reagent, rutile)	1: 1	3 min (HM[a])	147.9	8.22	Less effective
	1 : 1	1 h	155.0	8.61	Less effective
	1 : 1	24 h	162.5	9.03	Less effective
TiO_2, (PT501A, anatase)	1: 1	3 min (HM)	109.4	6.08	Less effective
	1 : 1	1 h	57.5	3.19	Less effective
	1 : 1	24 h	183.2	10.18	Less effective
TiO_2, (P25)	1: 1	3 min (HM)	443.3	24.6	Effective
	1 : 1	1 h	303.7	16.9	Less effective
	1 : 1	24 h	211.4	11.7	Less effective
TiO_2, (P90)	1 : 1	No[a]	381.7	21.2	Effective
	1 : 1	3 min (HM)	1021	56.7	Effective
	1 : 1	7.5 min	872.6	48.5	Effective
	1 : 1	15 min	784.0	43.6	Effective
	1 : 1	30 min	638.6	35.5	Effective
	1 : 1	1 h	602.5	33.5	Effective
	1 : 1	2 h	499.3	27.7	Effective
	1 : 1	3 h	414.5	23.0	Effective
	1 : 1	24 h	342.8	18.0	Less effective
	1 : 1	64 h	315.8	17.5	Less effective
γ-Al_2O_3	1 : 1	No[a]	449.0	24.9	Effective
	1 : 1	3 min (HM)	601.3	33.4	Effective
	1 : 1	7.5 min	657.4	36.5	Effective
	1 : 1	1 h	764.7	42.5	Effective
	1 : 1	24 h	511.6	28.4	Effective
	1 : 1	64 h	390.8	21.7	Effective

a We labeled "effective" for the H_2 generation rate greater than 20 ml/h per g Al, and "No" for the reactions without mixing process. "HM" means hand-mixing.

were found to be quite effective when hand-mixing process for 3 min was employed. As shown in Fig. 4, TiO_2 (P90) nanocrystals with a diameter of ~14 nm (anatase/rutile = 80/20) greatly facilitated the production of hydrogen, larger TiO_2 particles, such as P25 (~22 nm, anatase/rutile = 75/25), PT501A (~100 nm, anatase) and reagent powders (300–450 nm, rutile) did not exhibit as strong a catalytic effect in the production of hydrogen from tap water. However, the behavior of P25 was very similar to that of P90, in which the HM = 3 min exhibited the slowest initial production of hydrogen (will be shown in next section) but the highest volume of hydrogen produced in 18 h, as shown in Table 3. This behavior was not observed with the PT501A or the reagent powders, with considerably larger particles at 100 nm and >300 nm, respectively. According to the results obtained from all TiO_2 materials used in this study, the particle size (or surface area) of the modifier was considered to play an important role in the production of hydrogen of Al/tap H_2O system. We will discuss this in the discussion section.

3.4. *Effect of mixing-duration for TiO_2 (P90)*

TiO_2 nanocrystals (P90) have never been previously reported to be as effective as that of γ-Al_2O_3 [18–21] in promoting hydrogen production, as shown in Fig. 5 (a), (b). The effect of γ-Al_2O_3 has been well demonstrated by Chaklader [14,15] and Zeng et al. [18–21] and has been reproduced in our experiment for the sake of comparison, as shown in Fig. 6. Fig. 5 (a) shows that ball-mixing duration significantly deteriorated the

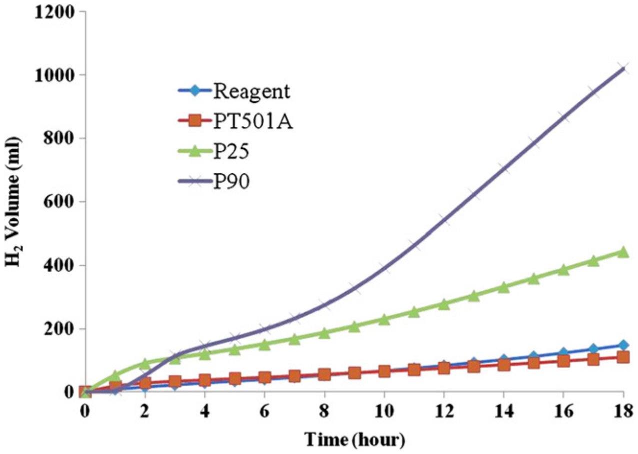


Fig. 4 – Effect of various TiO_2 nanocrystals on the generation of hydrogen from Al corrosion in tap water at 25 °C. Mixing was accomplished by hand-mixing for 3 min.

effectiveness of TiO_2 (P90) in the total production of hydrogen over 18 h, in which hand-mixing for 3 min (HM = 3 min) provided the highest hydrogen production. However, γ-Al_2O_3 showed a distinct enhancement of hydrogen production when the duration of dry ball-mixing was increased to 1 h. The effectiveness of γ-Al_2O_3 decreased when the duration of dry ball-mixing was increased to 24 h or longer.

The results of TiO_2 (P90) are further detailed in Fig. 5 (b). Extended ball-mixing resulted in a decrease in total production of H_2 over 18 h, as shown in Fig. 5 (a); however, it enhanced the generation rate in the first hour of reaction, as shown in Fig. 5 (b). This was an interesting phenomenon, not found in the case of γ-Al_2O_3 for ball-mixing less than 1 h. It has generally been believed that the ball-mixing process distributed the modifier over the surface of metal Al powders in a uniform manner, wore out the initial passive Al_2O_3 layer and thereby enhancing the production of hydrogen [15,16]. However, this might be true only at the early stages of the reaction in the case of TiO_2 (P90) modified-Al powders. Extended periods of ball-mixing (ball-mixing over 7.5 min) increased the hydrogen production rate in the first hour; however, the reaction rate slowed following this early burst, resulting in a decrease in the total production of hydrogen over 18 h, as shown in Fig. 5 (a) and (b). It is considered that the quick build-up $Al(OH)_3$ product layer slowed the reaction, as will be discussed in the discussion section.

The most intriguing case was observed when the mixing was performed using a mortar and pestle for only 3 min (HM = 3 min), which showed the slowest initial generation rate, but gradually increased over the 18 h to provide the highest average generation rate of hydrogen, as calculated and listed in Table 3. The incubation time to produce the first 5 ml H_2 generated in the HM = 3 min case was approximately 50 min, while the cases involving longer ball-mixing durations were considerably shorter, as shown in Fig. 5 (b). The label "No" in Table 3 represents the samples in which modifiers were simply added to metal Al powders in a flask of 200 ml tap water without any ball-mixing or hand-mixing actions. The generation of hydrogen over 18 h for "No" experiments was slightly low but still quite effective (>20 ml/h·g) using either γ-Al_2O_3 or TiO_2 (P90) in tap water.

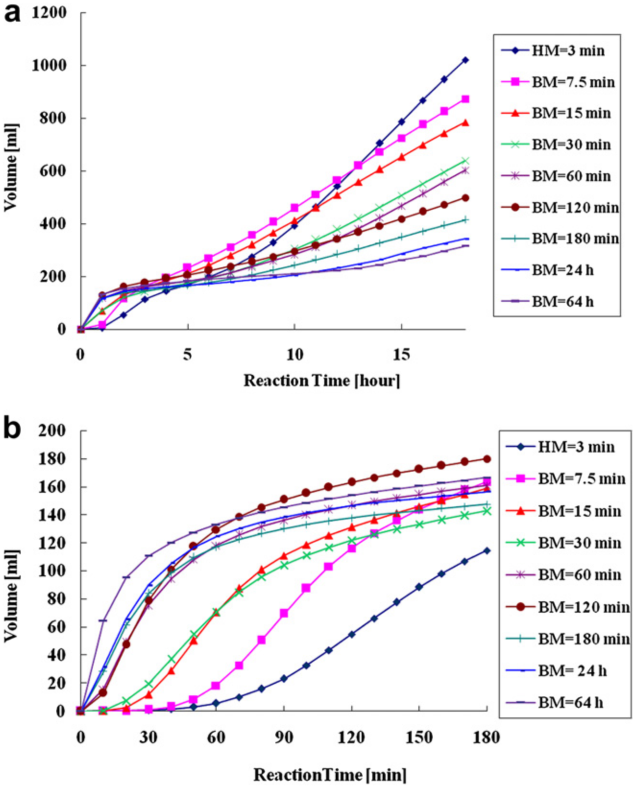


Fig. 5 – Effect of mixing duration of modifier TiO_2 (P90) on the Al powders for the promotion of hydrogen generation in tap water. (a) 0–18 h, (b) 0–3 h, which is the enlarged view of (a).

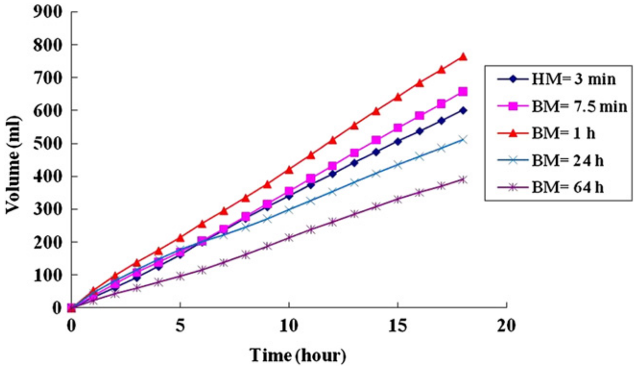


Fig. 6 – Effect of mixing duration of modifier γ-Al_2O_3 on the Al powders for the promotion of hydrogenation in water. (0–18 h).

3.5. *Characterization of Al powders*

It's well known that little hydrogen can be generated when pure Al powder is immersed in tap water at room temperature. However, through either the use of deionized water at temperature over 35 °C or various metal oxide nanocrystals modifiers in tap water at room temperature, we are able to generate hydrogen in an effective way. Although the rutile TiO_2 reagent powders were a poor catalyst in tap water for metal Al, they were very effective to facilitate the reaction of hydrogen generation from Al in deionized water. Experiments on other nanocrystals of metal oxides showed similar effect, which the deionized water rendered these nanocrystals exhibit enhanced hydrogen production behavior. These results evidence that the deionized water impose some significant influences on the metal Al than that of tap water. The key is the passive layer Al_2O_3 on the surface of metal Al powder.

As shown in Fig. 7 (a), the surface morphology of metal Al before reaction was smooth and evidenced with many mechanical scratches. After reacting with deionized water (without modifiers) for 6 h, the surface morphology of metal Al was porous and cracked, full of standing petals as shown in the center of Fig. 7 (b). The blocks and particles scattering around the porous petals were likely to be $Al(OH)_3$, which were the reaction products and confirmed by XRD analysis. Fig. 7 (c) shows the surface morphology of P90-moidified metal Al after reaction with tap water for 6 h at room temperature. It is clear that many pits and holes appear on the surface, which is

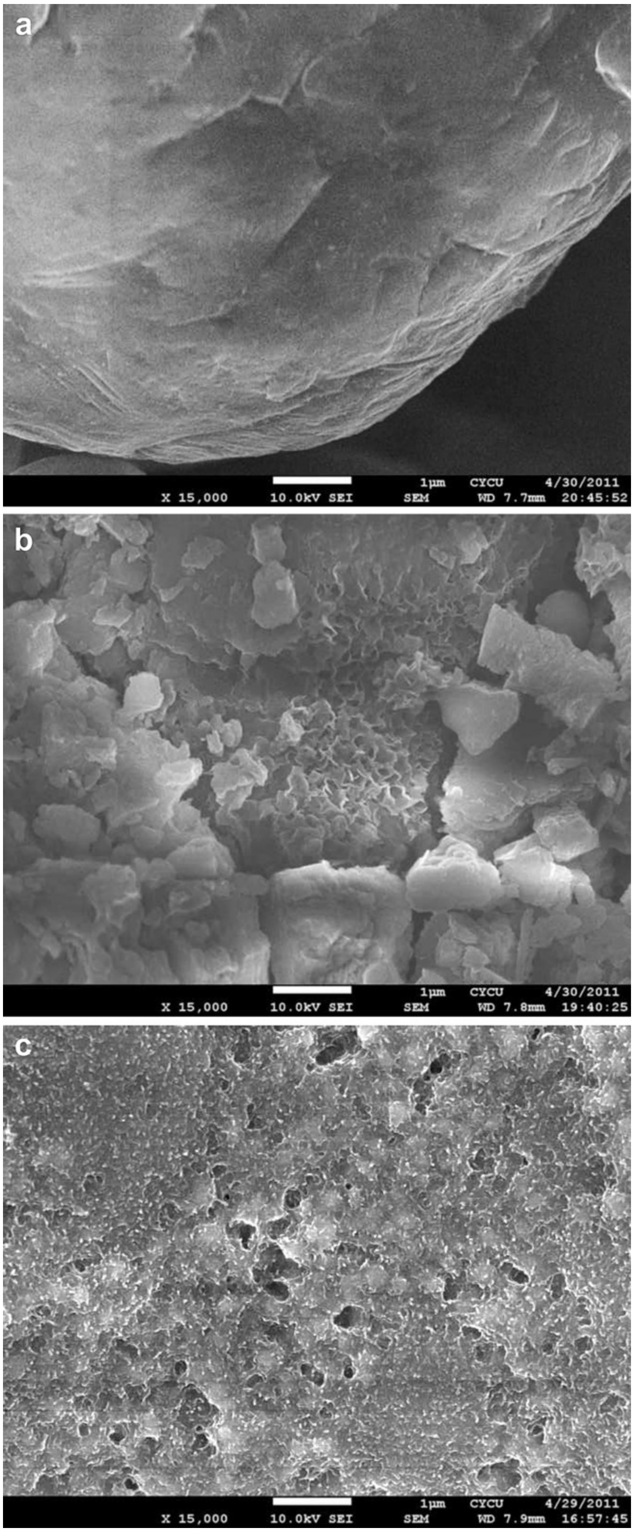


Fig. 7 – Surface of Al powders for three conditions, (a) without reaction, (b) after reacting with deionized water for 6 h at 45 °C, (c) after modification using TiO_2 (P90) and reacting with tap water for 6 h at 25 °C.

dramatically different from those of Fig. 7 (b). The pits and holes indicate implicitly that some different corrosion behavior other than the well-known uniform corrosion mechanism may take place.

XRD analysis (Fig. 8 (a), and (d)) shows that both HM = 3 min and BM = 64 h exhibited only Al and anatase phase after 1 h reaction for the P90-modified Al specimen. However, after 18 h reaction, $Al(OH)_3$ and a very small Al peak was observed in HM = 3 min sample in addition to the anatase, while abundant Al remained in BM = 64 h sample, as shown in Fig. 8 (b) and (e), respectively. $Al(OH)_3$ became very clear when the metal Al was consumed, as shown in Fig. 8 (c) and (f). i.e. Prolonged reaction time up to 48 h eventually consumed all metal Al, producing $Al(OH)_3$.

To reveal the different solubility of Al_2O_3 in deionized water and tap water, ICP analysis were carried out for the trace Al element in the deionized water and tap water after dissolving Al_2O_3 powders for 8 h, as shown in Fig. 9. It was found that deionized water exhibited higher solubility of Al_2O_3 than those of tap water at 25–35 °C. This dramatic difference in solubility of Al_2O_3 may likely to be the major cause for the significant enhancement of hydrogen generation from the corrosion of pristine metal Al in deionized water.

Fig. 10 shows the oxygen profile detected using SIMS on the surface of aluminum foils, where the thickness of oxygen-containing layer on the surface of Al was in the order of "deionized water" > "tap water" > "pristine Al". The data of SIMS indicated that after reaction with deionized water, Al exhibited thicker $Al(OH)_3$ product layer on the surface than that of Al in tap water.

4. Discussion

When γ-Al_2O_3 is in contact with Al powder, either through ball-milling [15,16] or by compact porous pellets [18–21], the following reactions (1) and (2) occur in water, resulting in a significant generation of hydrogen [12,19]. The uniform corrosion mechanism states that the entire native oxide film is hydrated at room temperature in the initial stage [12,19,20], according to reaction (1).

$$Al_2O_3 + H_2O \rightarrow 2\ AlO(OH) \qquad (1)$$

When the AlO(OH) (boehmite) front meets the Al metal surface, they react to produce hydrogen, according to reaction (2).

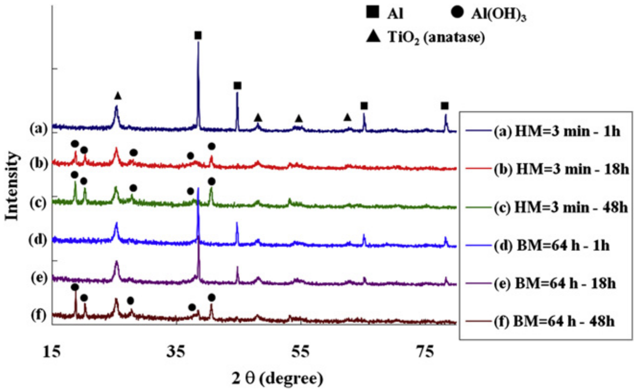


Fig. 8 – XRD analysis for HM = 3 min and BM = 64 h specimens of P90-modified Al in tap water for 1 h, 18 h, and 48 h.

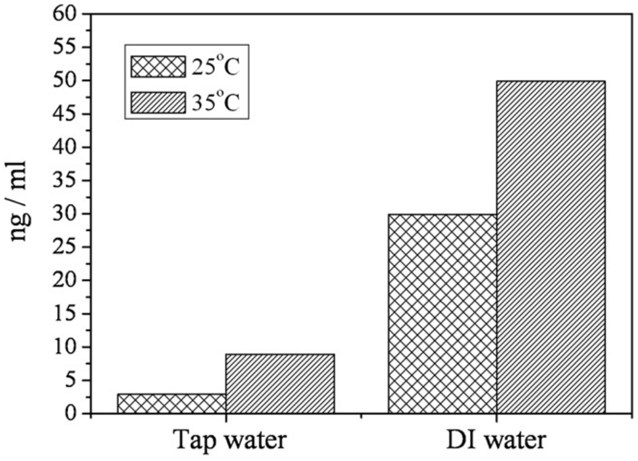


Fig. 9 – Dissolution of Al from Al_2O_3 powder in tap water and deionized water.

$$2Al + 6AlO(OH) \rightarrow 4Al_2O_3 + 3H_2 \quad (2)$$

In fact, the combination of (1) × (4) + (2) results in reaction (3), which is thermodynamically unfavorable at room temperature but favorable between 277 °C and 477 °C [22].

$$2Al + 4H_2O \rightarrow 2AlO(OH) + 3H_2 \quad (3)$$

In Chaklader's patent [15,16], the Al and γ-Al_2O_3 powder mixtures had to be heavily ball-milled together to produce hydrogen. Ball-milling or high impact milling was employed to ensure the contact of γ-Al_2O_3 powders to metallic Al. Regrinding the reacted Al powders after the initial 1 h of reaction also generated hydrogen due to the exposure of unreacted Al [15,16]. The direct water splitting of fresh Al can be achieved with a thermodynamically favorable reaction at room temperature (R.T.~277 °C), which is reaction (4) [22].

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad (4)$$

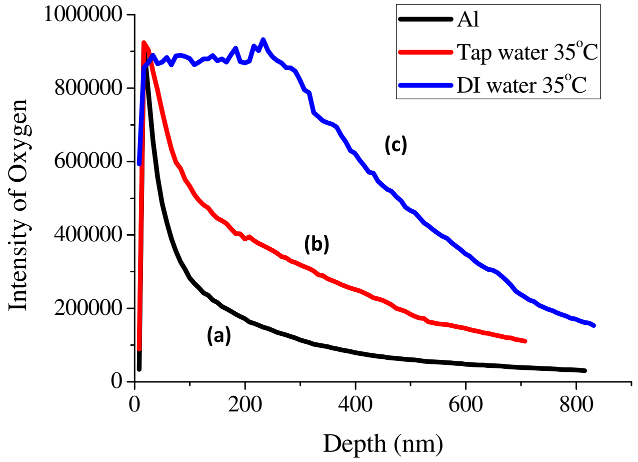


Fig. 10 – SIMS oxygen profile on the aluminum foils at three different conditions, i.e. (a) pristine Al without reaction, Al reacted with (b) tap water, and (c) deionized water at 35 °C for 8 h, respectively.

In this study, modifiers $Al(OH)_3$ and AlO(OH) were also tested for their influence on the production of hydrogen in an Al/H_2O system without mixing. It was confirmed that AlO(OH) (boehmite) greatly facilitates the production of hydrogen in the Al/H_2O system at room temperature but $Al(OH)_3$ did not, as shown in Table 3. The production of hydrogen from Al in deionized water at temperature over 35 °C (Fig. 3) will soon cease due to the cover of $Al(OH)_3$ layer at room temperature. The poor production of hydrogen from Al in tap water could be due to the low dissolving capability of tap water for Al_2O_3 layer.

Although the uniform corrosion model adequately explains the system of γ-$Al_2O_3/Al/H_2O$, it seems inadequately to describe the behaviors of TiO_2 (P90) modifiers. In the HM = 3 min sample, TiO_2 (P90) nanocrystals were in loose contact with Al powders and yet they produced the highest volume of H_2 after 18 h. Even no mixing process was employed (Table 3), hydrogen was produced in an effective way in tap water. An alternative mechanism such as a pitting process originating from point defects [12] is considered to be important in this case, as evident from Fig. 7 (c). In other words, the pitting mechanism can be initiated when nanosized TiO_2 particles were in contact with the surface of Al during the brief mixing process (i.e. HM = 3 min). The diminished effectiveness of larger TiO_2 nanocrystals was thought to be the reduction in the surface area as well as a lack of contact with the surface of Al. The surface area of P90, P25, PT501A, and reagent TiO_2 powders was ~90 m^2/g, ~50 m^2/g, ~16.5 m^2/g, and ~4.1 m^2/g, respectively. P90 possessed the highest surface area among these TiO_2 modifiers, allowing the P90 nanocrystals to remain in intimate contact with the surface of the Al. The anodic polarization at the contact point of TiO_2:Al_2O_3 layer rendered the defect species more mobile and increased reactivity (reaction (1)). Once the AlO(OH) (boehmite) was formed, the front of it reacted with the Al to produce Al_2O_3 and hydrogen in the contact area (reaction (2)). Reactions (1) and (2) continued until all of the Al metal had been completely consumed, as long as the nanosized TiO_2 crystals remained in contact with the oxide layers. The results of Bunker et al. [12] suggested that OH^- ions (or H_2O molecules) are the mobile species in the films (rather than H^+, O^{-2}, or Al^{+3}), and the transport rate of these ions is sufficiently rapid to account for the kinetics involved in the Al corrosion process. Pitting of Al due to localized hydrogen-vacancy defect condensation was observed after immersion of Al in NaOH solution for only 3 min [23]. Pitting corrosion was also a common phenomenon in the stainless steel and other metals [24]. However, pitting mechanism has long been overlooked its importance in corrosion of Al for hydrogen generation behavior.

With an increase in the duration of the ball-mixing process, such as 24 h or 64 h, the thin Al_2O_3 passive layer on the surface of the Al powders became worn-out and intimate contact with water, whereupon the intensive reactions of (4) occurred. The strong reaction resulted in a burst in the production of hydrogen, with the potential to disperse all of the P90 TiO_2 nanocrystals, leaving the metallic Al powder with a thick $Al(OH)_3$ product layer. In other words, the product of $Al(OH)_3$ from reaction (4) covered the surface of the Al significantly slowing down the reaction producing hydrogen. This explains the cases of heavy ball-mixing.

In summary, the corrosion of metallic Al in water to generate hydrogen is an excellent way to produce clean fuel on demand. However, it was found that the size of the metallic Al particles, the modifier materials, the size of the modifier particles, the mixing duration, the reaction temperature, and the purity of water all influenced the production of hydrogen. Despite the research efforts have been made [25–27], modifiers on metallic Al powders still deserve more investigations to fully explore their influences and the mechanisms behind the production of hydrogen in metal Al/H_2O systems.

5. Conclusions

We have demonstrated that the quality of water and the metal oxide nanocrystals such as TiO_2, Co_3O_4, and Cr_2O_3 strongly enhanced the production of hydrogen from the corrosion of metallic Al powder in neutral water at room temperature. However, longer ball-mixing duration detracted from its effectiveness. Extensive ball-mixing seriously catalyzed the passive layer causing a strong initial reaction between the Al and tap water to produce hydrogen, however, slowed down after 1 h. Using the modifier, TiO_2 P90, in the Al/tap water system enabled a new controllable mean of producing hydrogen with reagents other than γ-Al_2O_3, chloride salts modifiers, or the Al–Ga alloy system. We propose that the high surface area of TiO_2 (P90) nanocrystals induces pitting on the surface of the Al, thereby accelerating the mobile defect species in the Al_2O_3 layer to maintain a continuous reaction with the water. The pitting process originating from point defects is considered to be a very important factor in the early stages of hydrogen production in the nanosized TiO_2-modified Al/tap water system.

Acknowledgements

This work was supported financially by National Science Council (NSC96-2113-M-033 -005 –MY3), and the funding of the CYCU Distinctive Research Area project as grant CYCU-98-CR-CH.

REFERENCES

[1] Bromley BP. Tomorrow's energy: hydrogen, fuel cells, and the prospects for a cleaner planet. In: Hoffman Peter, editor. Health Physics, 82; 2002. p. 401. issue 3.

[2] Cheng WH, Shiau CY, Liu TH, Tung HL, Lu JF, Hsu CC. Promotion of Cu/Cr/Mn catalyst by alkali additives in methanol decomposition. Appl Catal A: Gen 1998;170(2):215–24.

[3] Brown LF. A comparative study of fuels for on-board hydrogen production for fuel-cell-powered automobiles. Int J Hydrogen Energy 2001;26(4):381–97.

[4] Palo DR, Dagle RA, Holladay JD. Methanol steam reforming for hydrogen production. Chem Rev (Washington, DC, United States) 2007;107(10):3992–4021.

[5] Wee JH. Which type of fuel cell is more competitive for portable application: direct methanol fuel cells or direct borohydride fuel cells. J Power Sources 2006;161(1):1–10.

[6] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972;238:37–8.

[7] Kitano M, Tsujimaru K, Anpo M. Hydrogen production using highly active titanium oxide-based photocatalysts. Top Catal 2008;49(1â€"2):4–17.

[8] van de Krol R, Liang Y, Schoonman J. Solar hydrogen production with nanostructured metal oxides. J Mater Chem 2008;18(20):2311–20.

[9] Jang JS, Kim HG, Joshi UA, Jang JW, Lee JS. Fabrication of CdS nanowires decorated with TiO2 nanoparticles for photocatalytic hydrogen production under visible light irradiation. Int J Hydrogen Energy 2008;33(21):5975–80.

[10] Li C, Yuan J, Han B, Jiang L, Shangguan W. TiO2 nanotubes incorporated with CdS for photocatalytic hydrogen production from splitting water under visible light irradiation. Int J Hydrogen Energy 2010;35:7073–9.

[11] Belitskus D. Reaction of aluminum with sodium hydroxide solution as a source of hydrogen. J Electrochemical Soc 1970; 117:1097–9.

[12] Bunker BC, Nelson GC, Zavadil KR, Barbour JC, Wall FD, Sullivan JP, et al. Hydration of passive oxide films on aluminum. J Phys Chem B 2002;106:4705–13.

[13] Woodall JM, Hydrogen Fuel generation from solid aluminum. US Patent 2008; No. 0056986.

[14] Woodall JM, Power generation from solid aluminum. US Patent 2008; No. 0063597.

[15] Chaklader A, Hydrogen generation from water split reaction. US Patent 2002; No. 0048548 A1, 6440385 B1 and 6582676 B2.

[16] Chaklader A. Hydrogen generation by reaction of water with a metal in presence of a catalyst. PCT Int Appl; 2002. WO 2002014213.

[17] Czech E, Troczynski T. Hydrogen generation through massive corrosion of deformed aluminum in water. Inter J Hydrogen Energy 2010;35(3):1029–37.

[18] Deng ZY, Liu YF, Tanaka Y, Ye J, Sakka Y. Modification of Al particle surfaces by γ-Al2O3 and its effect on the corrosion behavior of Al. J Amer Ceram Soc 2005;88(4):977–9.

[19] Deng ZY, Ferreira JMF, Tanaka Y, Ye J. Physicochemical mechanism for the continuous reaction of γ-Al2O3-modified aluminum powder with water. J Amer Ceram Soc 2007;90(5): 1521–6.

[20] Deng ZY, Ferreira JMF, Sakka Y. Hydrogen-generation materials for portable applications. J Amer Ceram Soc 2008; 91(12):3825–34.

[21] Deng ZY, Tang YB, Zhu LL, Sakka Y, Ye JH. Effect of different modification agents on hydrogen-generation by the reaction of Al with water. Inter J Hydrogen Energy 2010;35(18):9561–8.

[22] Digne M, Sautet P, Raybaud P, Euzen P, Toulhoat H, Artacho E. Structure and stability of aluminum hydroxides: a theoretical study. J Phys Chem B 2002;106:5155–62.

[23] Adhikari S, Chumbley LS, Chen H, Jean YC, Geiculescu AC, Hillier AC, et al. Interfacial voids in aluminum created by aqueous dissolution. Electrochim Acta 2010;55:6093–100.

[24] ASM Handbook, vol. 13, "Corrosion", ISBN 0-87170-007-7, ASM International, 1987.

[25] Dupiano P, Stamatis D, Dreizin EL. Hydrogen production by reacting water with mechanically milled composite aluminum-metal oxide powders. Inter J Hydrogen Energy 2011;36:4781–91.

[26] Mahmoodi K, Alinejad B. Enhancement of hydrogen generation rate in reaction of aluminum with water. Int J Hydrogen Energy 2010;35:5227–32.

[27] Rosenband V, Gany A. Application of activated aluminum powder for generation of hydrogen from water. Int J Hydrogen Energy 2010;35:10898–904.