Enhanced Photocatalytic Hydrogen Production on TiO$_2$ by Using Carbon Materials

Bashir Ahmmad, Kensaku Kanomata, Fumihiko Hirose

Abstract—The effect of carbon materials on TiO$_2$ for the photocatalytic hydrogen gas production from water / alcohol mixtures was investigated. Single walled carbon nanotubes (SWNTs), multi walled carbon nanotubes (MWNTs), carbon nanofiber (CNF), fullerene (FLN), graphite (GP), and graphite silica (GS) were used as co-catalysts by directly mixing with TiO$_2$. Drastic synergy effects were found with increase in the amount of hydrogen gas by a factor of ca. 150 and 100 for SWNTs and GS with TiO$_2$, respectively. Moreover, the increment factor of hydrogen production reached to 180, when the mixture of SWNTs and TiO$_2$ were smashed in an agate mortar before photocatalytic reactions. The order of H$_2$ gas production for these carbon materials was SWNTs > GS >> MWNTs > FLN > CNF > GP. To maximize the hydrogen production from SWNTs/TiO$_2$, various parameters of experimental condition were changed. Also, a comparison between Pt/TiO$_2$, SWNTs/TiO$_2$ and GS/TiO$_2$ was made for the amount of H$_2$ gas production. Finally, the recyclability of SWNTs/TiO$_2$or GS/TiO$_2$ was tested.

Keywords—Photocatalysis, carbon materials, alcohol reforming, hydrogen production, titanium oxide.

I. INTRODUCTION

THE conventional energy resources such as coal, petroleum, natural gas etc., which are being used to meet most of the world's energy requirements, have been depleted to a great extent. Moreover, CO$_2$ gas which is produced by most combustion processes is believed to be the main culprit involved in global warming. Therefore, it is necessary to search for an alternative fuel, which should in principle be pollution free and storable. As a potential candidate of alternative energy sources scientists are very interested in hydrogen gas because it satisfies all requirements, which are necessary for a sustainable environment. The photocatalytic decomposition of water into hydrogen and oxygen has been regarded as one of the most potential approaches of hydrogen production ever since Fujishima and Honda reported the photo electrochemical water splitting using a TiO$_2$ electrode [1]. Afterward, TiO$_2$ photocatalysis has been extensively studied in terms of hydrogen production from water which is apparent by several review papers and books published in the past several years [2]-[6]. However, despite its several advantages, TiO$_2$ suffers from the unavailability of solar visible light due to a wide band gap of ca. 3.2 eV and the fast charge recombination. Various approaches to overcome such limitations have been attempted including doping [7], sensitization [8], and surface modifications [9]. For surface modification, many researchers have used many noble metals as co-catalysts. For example, Al-Mazroai et al. [10] showed the enhancement of H$_2$ production with various noble metals and found an order of Pt>Pd>Ir> Au> Rh≥Ru> Ni. These metal clusters can trap photo excited electrons, preventing recombination; the hole is then free to migrate to the surface of the TiO$_2$ where it can catalyze oxidation, whilst the electron enables reduction on the metal, producing a physical separation of reaction products. These metals show outstanding performance for photocatalytic hydrogen production, but these are rare and expensive metals. Thus, for practical application low-cost alternatives are preferred.

Carbon materials appear to play multiple and unique roles in TiO$_2$ photocatalysis [11]. Due to their large surface areas (max.> 1000 m^{2}g^{-1}), porosity, and electrical conductivity, carbon materials can increase the binding capability, change photocatalytic mechanism, and boost photocatalytic redox reactions such as H$_2$ production from water and remediation of environmental pollutants [12]. Carbon materials are diverse from traditional activated carbons (AC), graphite (GP), carbon nanofiber (CNF), single- and multi-walled carbon nanotubes (SWNTs and MWNTs, respectively) etc. Previously, we have shown the application of SWNTs as co-catalyst for photocatalytic degradation of water pollutant on TiO$_2$. Activity of TiO$_2$ was increased by ca. 50 times when only 5 wt% of SWNTs was mixed with TiO$_2$ [13]. Later, we have shown the enhance effect of SWNTs on photocatalytic hydrogen production on TiO$_2$ dispersed in alcohol/water mixture [14]. Recently, Khan et al. [12] have reported the catalytic effects of carbon materials on the photocatalytic degradation and hydrogen production on TiO$_2$. They used both virgin or nitric acid treated carbon materials and it was found that TiO$_2$ composites with virgin SWNTs and MWNTs exhibit the enhanced H$_2$ amounts by a factor of ca. 17 and 12, respectively as compared to bare TiO$_2$ in 10 vol% aqueous methanol solution. Hydrogen production increment was enhanced by 4 with acid treated a-MWNTs compared to virgin MWNTs. However, they did not report the optimized condition of maximum amount of hydrogen production on TiO$_2$ and also the recyclability of composite materials. The aim of this study is to compare the effect of virgin carbon materials on photocatalytic hydrogen production on TiO$_2$ and to optimize the rate of hydrogen production. We show that amount of hydrogen production can be optimized by changing the ratio of carbon materials to TiO$_2$ and water to alcohol, type of alcohol, amount of catalyst mixture etc. We also show the photocatalytic hydrogen production on TiO$_2$ using GS, which is a slightly

B. Ahmmad is with Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan (phone: +81-238-26-3309; fax: +81-238-26-3309; e-mail: arima@yz.yamagata-u.ac.jp).

K. Kanomata and F. Hirose are also with Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan.

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different carbon based materials composed of mainly silica, alumina and carbon.

II. EXPERIMENTAL METHOD

A. Materials

The photocatalyst was TiO_2 (Degussa P25) with mainly anatase structure (ca. 80%) under the shape of non-porous polyhedral particles of ca. 20 nm mean size with a surface area of ca. 50 m^2g^{-1}. SWNTs and MWNTs with a purity of 20-40% were obtained from Materials Technologies Research Ltd. (USA) and were used without further purification. The SWNTs and MWNTs are "as produced" matrix of amorphous carbon soot that contains traces of C-60, C-70 and higher fullerenes in addition to carbon nanotubes. CNF and FLN were of 98 wt% purity and obtained from Frontier Carbon Co. and Showa Denko Co. (Japan), respectively. GS was collected from Hokkaido prefecture in Japan. Powdered Pt of 99.98% purity (Nilaco) was used without further treatment. Methanol, ethanol and 1-propanol of highest grade (Wako, Japan) available and doubly deionized water were used throughout the experiment.

B. Photoreactor and Light Source

A cylindrical flask (so-called Schlenk's tube) made of Pyrex of ca. 154 cm^3 was used as a photoreactor. The top of the flask was sealed with a silicone rubber septum. A super high-pressure mercury lamp (Ushio 500W USH-500SC) was used as the light source. For filtration of the light a 300-400 nm band pass filter (Toshiba ATG UV-D33S) was used. Care was taken not to heating up the suspension.

C. Procedure and Analysis

Preferred amounts of TiO_2 and carbon materials were put into the flask and then alcohol/water mixtures were added. The photoirradiation was carried out under Ar atmosphere for 1 h, maintaining the reaction mixture in suspension by a magnetic stirrer. Prior to irradiation, the suspension of the catalyst was dispersed in an ultrasonic bath for 5min and Ar gas was bubbled through reaction mixture for 1h to remove oxygen gas. Gas sampling was made through the silicon rubber septum using a locking-type syringe at a constant time interval, usually 15 min. The quantitative analysis of gas sample was performed by gas chromatography (column packing: MS5Å or porapak N, carrier gas: Ar, detector: TCD). To analyze the recyclability of catalyst mixture the suspension used was centrifuged at 1000rpm for 5 min, and then the supernatant was removed. A fresh methanol-water mixture was added to the remaining sediment. Again, the hydrogen production experiment was performed following the procedure described above. These recycling processes were repeated consecutively three times. The particle size was measured by a laser scattering particle size distribution analyzer (Horiba LA-920).

III. RESULTS AND DISCUSSION

Different series of experiments were carried out in order to compare the amounts of H_2 gas evolved by different compositions of TiO_2 and carbon materials as co-catalysts. The amounts of carbon materials were changed from 0 to 100 wt% and the maximum rate of H_2 evolution were found at 9, 40, 40, 30, 50 wt% for SWNTs, MWNTs, CNFs, FLN, GP and GS, respectively (Fig. 1). With an increase in the amount of carbon materials, the surface area for reduction of H^+ ion increases and therefore hydrogen production increases. However, larger amounts of carbon materials will impair the absorption of UV light by TiO_2. This results a decrease in the evolution rate of H_2 gas. Appearance of maximum H_2 yield at a relatively lower SWNTs content (9.0 wt%) is due to that the specific surface area of TiO_2 (P25) is 50 m^2g^{-1} whereas that of as-grown SWNTs ranges from 400 to 900 m^2g^{-1} [15]. Thus, higher loading of TiO_2 is required coming into contact with the large surface of SWNTs.
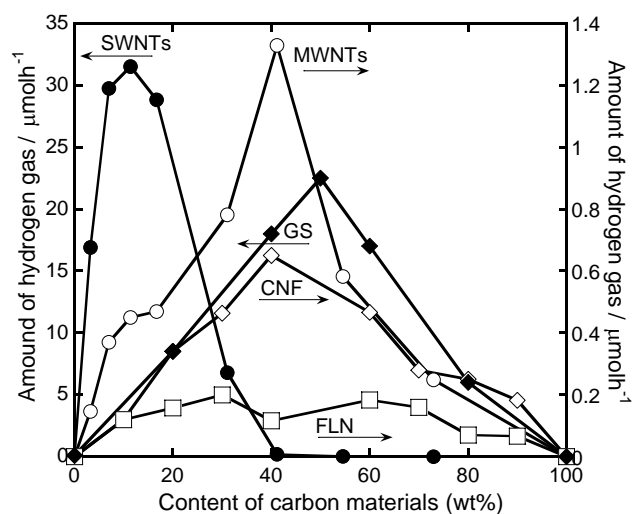

Fig. 1 Plots of the evolution rate of H_2 gas vs. the content of carbon materials to TiO_2 (Total amount of catalyst: 30 mg, methanol content: 50 vol%)

The highest rates of H_2 generation with above amounts of carbon materials are shown in Fig. 2. As seen from the figure the increasing order was found to be SWNTs > GS >> MWNTs > CNFs > FLN > GP. We can see a drastic increase in the amount of evolved H_2 gas when SWNTs or GS are used with TiO_2. This is due to the synergy effect of SWNTs and GS to TiO_2. In the case of noble metal such as Pt, an electron from photoexcited TiO_2 is transferred to Pt and then it reduces H^+ ion to produce H_2 gas. Depending on the tube helicity and diameter carbon nanotubes can be either semi-conducting, semi-metallic or metallic, in nature [16]. Thus, based on the above results, we proposed a mechanism [14] as follows: Photoexcited electrons in TiO_2 are transferred to SWNTs through collisions which then reduce the proton available in the system. Although MWNTs have also a larger surface area ranging from 200 to 400 m^2g^{-1} [15], it showed a lower effect on the photocatalytic activity of TiO_2 than SWNTs (see Fig. 2). It is found that the rolling direction of simple graphite sheet has a large effect on the electrostatic characteristics of tubes and the presence of defects (other than hexagon) on the tube also affects its electric conductivity, considerably [17]. The structures of MWNTs are

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complex. It is commonly known that there are some defects on the surfaces of the tubes and the direction of the rolled graphite sheets is not controlled [15]. These complexities might affect the photocatalytic effect of MWNTs on TiO_2. CNFs, FLN and GP have a large surface area but their electrical properties are different from that of SWNTs and MWNTs and thus they have negligible effect on hydrogen production on TiO_2.

carbon-to-carbon bond breaking. The extend of carbon-to-carbon bond breaking decreases with the increase in chain elongation and complexity as these factors contribute to enhancing the steric hindrance in the molecule [20]. This order is consistent with the hydrogen production using different electron donors (hydrocarbons) over suspended modified TiO_2photocatalysts reported by Lin et al. [21].
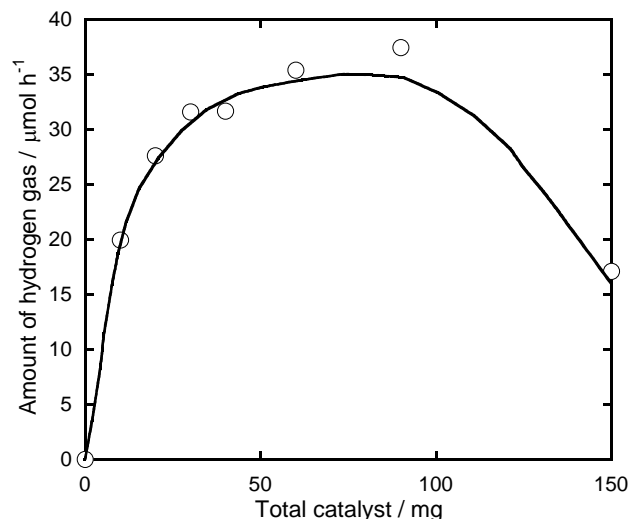

Fig. 2 Rate of hydrogen evolution from various carbon materials with TiO_2 (total amount of catalyst: 30 mg, methanol content: 50 vol%)

Fig. 3 The dependence of hydrogen production on the amount of catalyst mixtures (TiO_2 and SWNTs) keeping the percentage of SWNTs to TiO_2 constant at 9

Although, GS has neither good electrical properties nor high surface area ($11 m^2 g^{-1}$), interestingly it shows high activity of hydrogen production on TiO_2. The detail mechanism of GS for the enhancement of hydrogen production is not clear yet. But it is assumed that GS exchange its surface metal ions with proton ions from the alcohol/water solution. As a result the pH of the solution is changed and the surface of TiO_2 becomes negatively charged. This negatively charged TiO_2 is then physically adsorbed on GS, which surface is positively charged. Due to this adsorption, electron transfer and charge separation becomes easy and effective. Thus, the rate of proton reduction on GS surface by photoexcited electrons from TiO_2 increases [18], [19]. However, there some points which could not be explained by this assumption and further research is underway in our laboratory.

To optimize the hydrogen production rate over TiO_2 and carbon materials, we changed the amount of catalysts (SWNTs (9%)+TiO_2) from 0 to 150 mg in 40 ml of methanol/water (50vol%). The result shows (Fig. 3) that with increasing the amount of catalysts, hydrogen production also increases. However, above 30 mg of catalyst, enhancement of hydrogen production is slow. Therefore, for all subsequent experiments, amount of total catalyst was fixed at 30 mg.

Fig. 4 shows the dependence of the rate of H_2 gas evolution on the SWNTs content to TiO_2 after 1h irradiation from 50 vol% methanol-, ethanol- and 1-propanol-water mixtures. Maximum amount of hydrogen production was observed for methanol/water solution. However, the hydrogen production decreases with the increase of the carbon number of alcohol. This effect is mainly due to the decrease in the formation of formaldehyde for higher alcohols because it involves
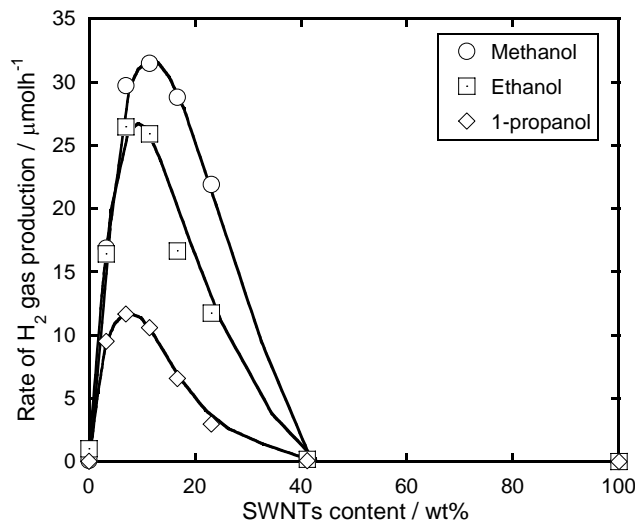

Fig. 4 Rate of hydrogen production from aqueous solutions of various alcohols using SWNTs/TiO_2 (total amount of catalyst: 30 mg, alcohol content: 50 vol%)

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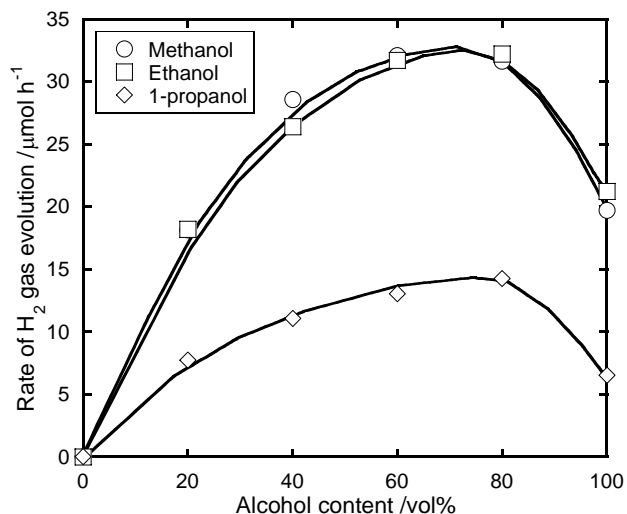International Journal of Energy and Power Engineering
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Fig. 5 Plots of the evolution rate of H_2 gas vs. alcohol content (Total amount of catalyst: 30 mg; SWNTs content: 9 wt%)

Fig. 5 shows the effect of the alcohol content in the production of H_2 gas, keeping the total amount of SWNTs/TiO$_2$ catalysts and the content of SWNTs constant. In the absence of water hydrogen production rate is observed to be almost zero and with increasing the alcohol content, hydrogen production gradually increases. However, after a maxima at around 60-80 vol % of alcohol, hydrogen generation decreases. At 100% of alcohol, hydrogen production decreased by ca. 50% for all alcohols. The reason of this result is discussed later part in this manuscript.
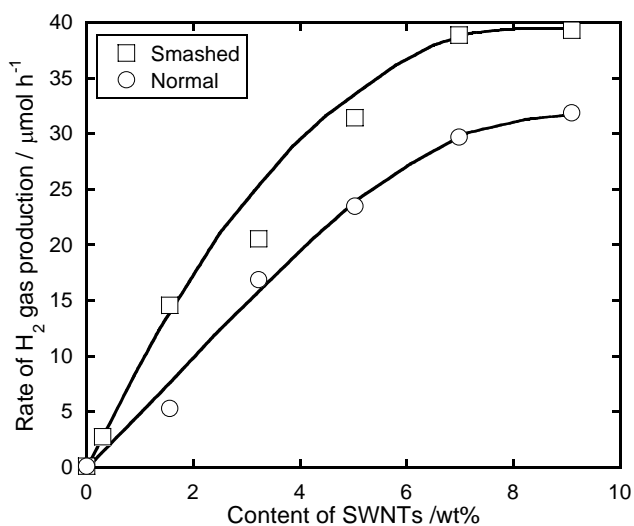

Fig. 6 Comparison curve for H_2 production from smashed and normal (non-smashed) mixtures of SWNTs and TiO$_2$

It is known that Na$_2$SO$_3$ is a good sacrificial agent. But with a similar concentration of Na$_2$SO$_3$ (0.1M) and methanol (0.1M), the rate of H_2 production was found to be 0.15 and 5.5 μmolh^{-1}, respectively. From this result it can be concluded that the protons necessary for hydrogen production is coming from the decomposition of alcohol molecules of alcohol/water mixtures.

Therefore, with increasing the amount of alcohol content more protons are produced in the system, which are then reduced by the photoelectrons on the surface of carbon materials. Although water molecule has negligible contribution to proton formation, when there is no water in the system, hydrogen production decreases for all type of alcohol. This is because, water molecule in this system works as diffusion media of proton and thus when there is not water molecule in the system diffusibility of proton decreases. That is why hydrogen production decreases with 100 vol% of alcohol (Fig. 5).
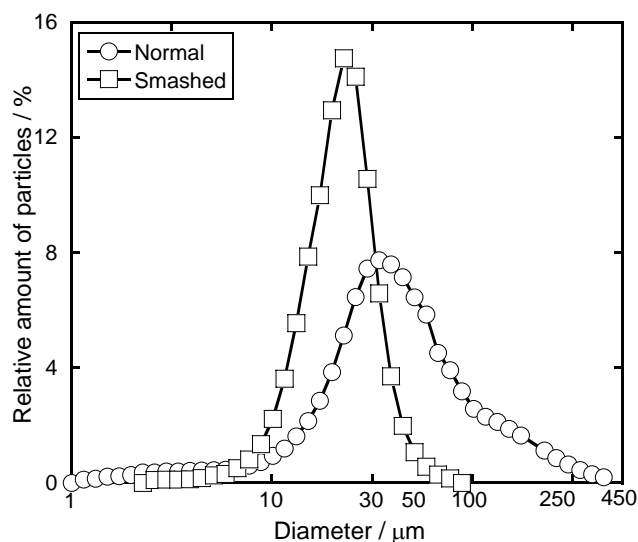

Fig. 7 Particle size distribution for the normal and smashed SWNTs/TiO$_2$ powder mixtures

Mechanically blended SWNTs/TiO$_2$ composite was also used to optimize the H_2 gas generation. For the preparation of the composite, SWNTs and TiO$_2$ were weighed in different amounts and blended adequately by smashing with an agate mortar. After 1 h of irradiation, the hydrogen evolution rate for smashed powder was considerably higher than that of normal powder (simple mixture) as shown in Fig. 6. For 9 wt% of normal powder of SWNTs to TiO$_2$, hydrogen evolution rate of about 32 μmolh^{-1} was observed, whereas the same rate was observed for 5.0 wt% of SWNTs to TiO$_2$ in the case of smashed mixture. For 9wt% of smashed SWNTs/TiO$_2$ mixture, the highest evolution rate was found to be ca. 39 μmolh^{-1}and hydrogen production increment factor was enhanced by 30 as compared to simply mixed SWNT/TiO$_2$.

The "as-received" SWNTs contained many aggregates, which were covered by amorphous carbon and shoot. Due to smashing, the aggregates were broken down and the particle size became smaller resulting increase in the surface area of the catalyst. This fact could be confirmed by the particle size distribution of the mixture of TiO$_2$ and SWNTs, measured after photoirradiation of the mixtures, and the results are shown in Fig. 7. We can see that in case of normal mixtures the particle size was found to be inhomogeneous, ranging from ca. 10 to 400 μm. But in the case of smashed mixtures the particle size is homogeneous, ranging from ca. 10 to 50 μm. Moreover, due to

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smashing of the samples, TiO_2 particles can be deposited on the surface of SWNTs by physical adsorption. Therefore, electron transfer can take place not only by collision between TiO_2 and SWNTs but also by the deposition of TiO_2 on SWNTs, which might result higher H_2 gas evolution.
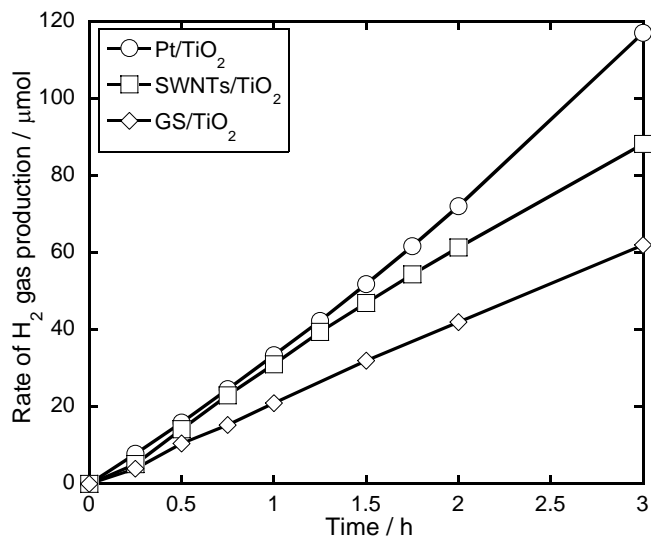

Fig. 8 Plots of amount of H_2 gas vs. irradiation time with SWNTs/TiO_2 and Pt/TiO_2 systems

The comparison of the photocatalytic activity for the production of H_2 gas between Pt/TiO_2, SWNTs/TiO_2, and GS/TiO_2 powders was made by using equal quantity of Pt powder and SWNTs or GS together with TiO_2, keeping the methanol content constant at 50 vol% in the solution. The amount of H_2 gas evolved with irradiation time is shown in Fig. 8. The amount of hydrogen production from GS/TiO_2 is lower compared to Pt/TiO_2 and SWNTs/TiO_2. However, the amount of H_2 gas evolved from Pt/TiO_2 and SWNTs/TiO_2 systems are nearly same until 1 h irradiation, although after 1 h the amount of H_2 gas in the Pt/TiO_2 system increases a little over the SWNTs/TiO_2 system. It is known that Pt itself, at the same time acts as light reflector and thus can remarkably improve the photocatalytic efficiency [22]. The lower H_2 production (Fig. 8) by SWNTs/TiO_2 partly attributable to H_2 adsorption, due to pressure increase in the gas phase, to carbon nanotubes and amorphous carbon present in SWNTs used [23]. This amorphous carbon contains graphitic carbon and soot that are unavoidable byproducts of the synthesis processes. These impurities also could decrease the amount of hydrogen generation by hindering light absorption of TiO_2 photocatalyst. For the determination of catalytic effect of this amorphous carbon, investigation was carried out with the mixture of TiO_2 with active carbon (AC) and graphitic (GP). After 1h irradiation, the amount of H_2 gas evolved from the mixtures of (AC+GP)/TiO_2 was 0.45 $\mu mol h^{-1}$. This results indicates that amorphous carbon in not effective to increase the photocatalytic activity of TiO_2.
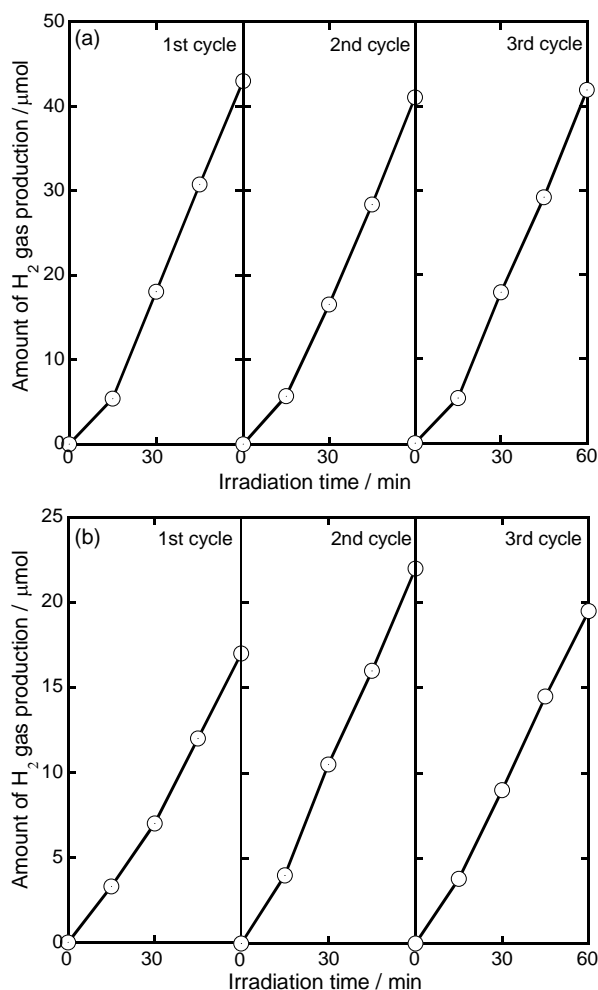

Fig. 9 Hydrogen production from the recycled (a) SWNTs/TiO_2 (smashed) and (b) GS/TiO_2 in aqueous methanol 50 vol%

Fig. 9 shows the hydrogen production by recycled SWNTs/TiO_2 and GS/TiO_2. The amount of hydrogen production from TiO_2/SWNT had no changes. However, in case of GS/TiO_2, the 2nd and 3rd cycle shows a little higher amount of hydrogen production. The cleaning effect and wettability might be the reason of increased hydrogen generation. These results indicate that both SWNTs/TiO_2 and GS/TiO_2 are recyclable and reusable for photocatalytic hydrogen production.

IV. CONCLUSION

We have shown the application of various carbon materials for hydrogen production on TiO_2 from water/alcohol mixture. All of the carbon materials were used without any treatment or purification. The maximum amount of hydrogen production was observed for SWNTs/TiO_2 system and among various alcohols, methanol was found to show the highest amount of hydrogen production. Mechanical blending of the catalyst mixture and concentration of alcohol also can increase the rate of hydrogen production. Both SWNTs/TiO_2 and GS/TiO_2 catalyst mixtures are found to be recyclable and reusable for photocatalytic hydrogen production. These studies show that

low-pure and low-cost carbon based materials or natural mineral, GS could be potential alternatives of metal based co-catalysts in terms of photocatalytic hydrogen production on TiO₂.

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