플라즈마 반응기의 수소발생에 미치는 TiO_2, Cu, Ni 촉매제 영향

論 文
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The co-effect of TiO_2, Cu and Ni Powders for Enhancing the Hydrogen Generation Efficiency using Plasma Technology

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(Jae-Yoon Park · Jong-Suk Kim · Jang-Gun Jung)

Abstract - The research was conducted in order to improve the hydrogen generation efficiency of the electrical plasma technology from tap water by using TiO_2 photocatalyst, mixed Cu - TiO_2 powder, and mixed Ni - TiO_2 powder as the catalysts. Experiments were performed with the pulsed power and nitrogen carrier gas. The result has shown that the hydrogen concentration with the presence of TiO_2 powder was created higher than that of without using photocatalyst. The hydrogen concentration with using TiO_2 was 3012ppm corresponding to the applied voltage of 16kV, while it without using the TiO_2 was 1464ppm at the same condition . The effect of TiO_2 powder was strongly detected at the applied voltages of 15kV and 16kV. This phenomena might be resulted from the co-effect of the pulsed power discharge and the activated state of TiO_2 photocatalyst. The co-effect of the mixed catalysts such as Cu-TiO_2 and Ni-TiO_2 (the mixed photocatalyst TiO_2 and transition metals) were also investigated. The experimental results showed that, Cu and Ni powder dopants were greatly enhancing the activity of the TiO_2 photocatalyst. Under these experimental conditions the extremely high hydrogen concentrations at the optimal point were produced as 4089ppm and 6630ppm, respectively.

Key Words : Hydrogen generation, photocatalyst, TiO_2 powder, Ni-TiO_2 catalyst, Cu-TiO_2 catalyst.

1. Introduction

Currently, the demand for hydrogen and hydrogen-rich gas usage in industrial processes as well as for transportation is growing rapidly [1]. The advantage in using the hydrogen fuel is that, during combustion, it binds itself with the oxygen in the air, and creates water [2]. The remain problem is how to decrease production cost and avoid the unexpected effects on the environment during the producing processes. To avoid the emissions of the environmentally hazardous byproducts from commercial hydrogen production plants, it is essential to produce hydrogen in large scale from water, which is an abundant and clean source of hydrogen [3]. Direct production of hydrogen from photocatalytic splitting of water over various kinds of oxide semiconductors has gained much attention to search a sustainable source of energy supply. Recently, photocatalytic hydrogen evolution using organic compounds such as simple molecule of alkyl alcohol, organic pollutants and even biomass as sacrificial reagent has also been extensively investigated [4-6]. However, in the absence of sacrificial reagent, the efficiency of photocatalytic hydrogen evolution is very low and semiconductor photocatalyst can deactivate after long-term irradiation [7]. Breaking down water to hydrogen and oxygen is a process that requires energy. Heat, electricity, light or chemical energy can be used for this purpose [8-11]. The method of decreasing the electron-hole recombination processes is thought to be through the loading of dispersed metal cocatalyst on the TiO_2, which drives the transportation of electrons produced by the photo excitation to the outer system that is photocatalytic reaction [12]. Electrolytic hydrogen production involves the use of electricity to decompose the water catalytically into hydrogen and oxygen [13].

The total energy required to decompose water was given by plasma pulsed discharge in water-gaseous phase, and this process is promoted by the effect of the TiO_2 photocatalyst. In this paper, the authors used the electricity as a supplied energy source for supporting the non-thermal plasma reactor and generated hydrogen in the various conditions such as the use of mono photocatalyst TiO_2, and the use of mixed catalysts.

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2. Experiment

2.1 Experimental setup

The schematic of the hydrogen production plasma system is shown in the Figure 1. It consists of high voltage pulse generator, MFC (mass flow controller) that can control the amount of carrier gas, watt meter to estimate the consumption power when hydrogen is generated, oscilloscope to record voltage waveform through a voltage divider and current, and GC system (Gas chromatography - Younglin Instru. Co., Model 600D) for estimating the hydrogen concentration and analysing the by products. The detector system of GC is PDD (pulse discharge detector) type, sample loop used 2 ml, with the diameter of 1.6 mm.

Table 1 Photocatalyst and characteristics

Type	Conductivity	Size	Surface area
TiO_2	-	0.035μm	27.2043 m^2/g
Cu	5.98×105Ω.m-1	1.29×102μm	0.2734 m^2/g
Ni	0.89×105Ω.m-1	84.6μm	0.4959 m^2/g

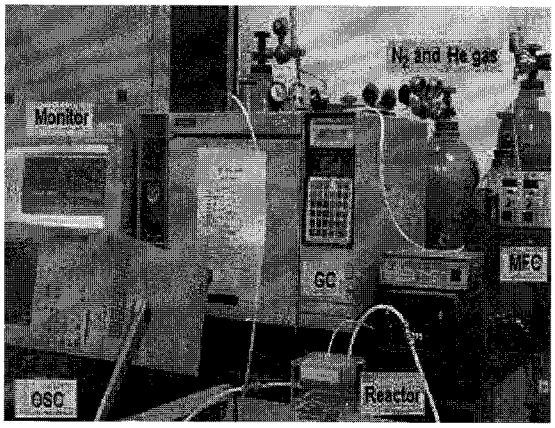


Fig. 1 Schematic of the experiment

The schematic of the plasma reactor is shown in figure 2. The discharge system includes of the reactor chamber made of acrylic insulator with the dimension as 30mm in high and 60 mm in inner diameter, quartz tube electrode made of quartz, the needle high voltage electrode inside the quartz tube made of stainless steel with the diameter of 1mm. Meanwhile, the ground electrode made of copper film is sunk into the water and grounded with a connecting wire. The gap between the tip of the inner electrode and the lowest point of quartz tube was fixed at 5mm, it is also 5mm for the gap between that point to the water surface inside the discharge chamber of the reactor. Three kinds of photocatalyst and catalysts are used as TiO_2, mixed Cu-TiO_2, mixed Ni-TiO_2 (photo 1 of the SEM images).

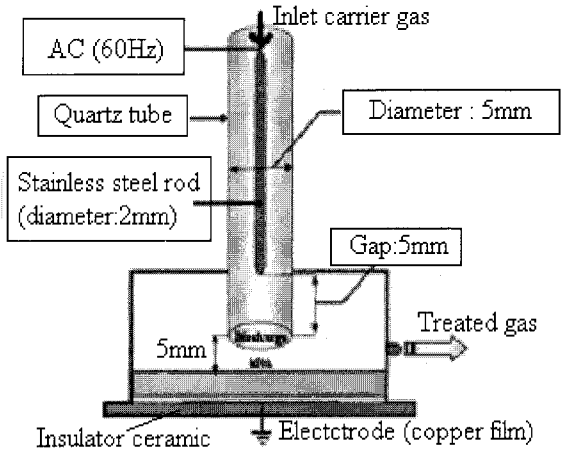
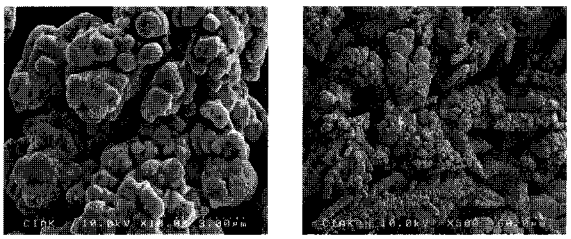
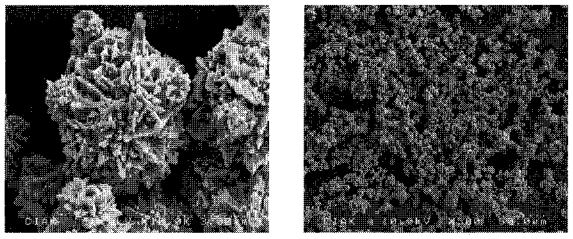


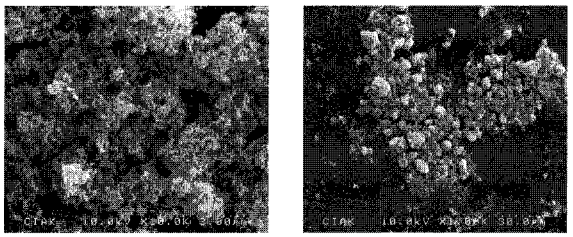
Fig. 2 Schematic of plasma reactor



a. SEM images of the Copper powder



b. SEM images of the Nickel powder



c. SEM image of the TiO_2 powder

Photo 1 The SEM image of the TiO_2 photocatalyst and transition metal powders: Cu and Ni

2.2 Discharge processes

Depending on the related conditions such as the applied

voltage, the flow rates of carrier gase, the water volume inside the reactor, and especially the TiO_2 powder photocatalyst, the discharge phenomena were very different. These phenomena result in the different of the hydrogen generation efficiency. Under the electrical pulsed discharge power in the gas - liquid phase many kind of active spices could be created. When an electrical field (DC, AC or Pulse) is applied to a gas, the energetic electrons transfer their energy to the gas molecules by collision, leading to the excitation, attachment, dissociation or ionization of the molecules [14]. Therefore, the chemical reactions caused by electrical discharge with the presence of TiO_2 would be taken place inside the discharge chamber [15-16] as follow:

TiO_2	→	$h^+ + e^-$	(1)
$h^+ + H_2O$	→	$OH + H^+$	(2)
$O_2 + e^-$	→	O_2^-	(3)
$e^- + H_2O_2$	→	$OH + OH^-$	(4)
$O_2^- + H^+$	→	HO_2	(5)
$H_2O - 2e$	→	$O + 2H^+$	(6)
$H^+ + 2e$	→	$H_2\uparrow$	(7)
$N_2 + e^-$	→	N_2^*	(8)
$N_2^* + 3O^*$	→	$NO + NO_2$	(9)
$N_2^* + O^*$	→	N_2O	(10)

In addition, when an oxide surface is reduced, excess electrons can occupy a variety of states such as surface F-centers in reduced Ti^{3+} (3d1) state in TiO_2 [17]. Thus, under the discharge condition with using TiO_2 other reactions could be happened [18-19] as below:

TiO_2 $+ h\nu(400nm)$	→	$electron(e^-)$ $+ hole(h^+)$	
$e^- + Ti^{4+}$	→	Ti^{3+}	(11)
$h^+ + O^{2-}$	→	O^-	(12)
$O_2 + e^-$	→	O_2	(13)
$H^+ + e^-$	→	$H\cdot$	(14)

3. Result

The results are presented in the Figure 3. The effects of the flow rate were investigated under the operating conditions as the water volume inside the reactor is 10ml; the carrier gase flow rates are 0.1L/min, 0.2L/min, and 0.3L/min, pulsed high voltage is used for the discharge, the discharge time is fixed at 10min for one cycle and the detecting time of the Gas Chromatography system is 4min for one cycle.

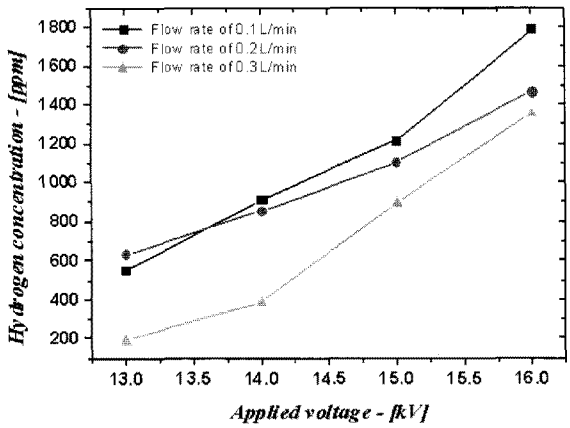


Fig. 3 The relationship between the hydrogen concentration and the applied voltage corresponding to the flow rate of the carrier gase without using the TiO_2

From Figure 3, it is clear that the hydrogen concentration created by using the flow rate of the carrier gas as 0.3L/min is very low. It is resulted from a very weak and unstable electrical discharge. The hydrogen concentration is increased according to the increase of the applied voltage. And in all of the above cases, hydrogen concentration reaches the peak point at the same applied voltage as 16kV. At the applied voltage of 16kV the strongest discharge are obtained. However, when the voltage increases over the 16kV, the discharge becomes weak and very unstable, thus hydrogen concentration decreases. From the Figure 3, the difference of hydrogen concentration in the two cases of flow rates as 0.1L/min and 0.2L/min is insignificant at the range of applied voltage from 13kV to 15kV. When the applied voltage increases over 15kV, the hydrogen concentration at the flow rate of 0.1L/min is higher. The hydrogen concentration with using 0.3L/min is much lower compared to the others.

The investigations are conducted under the experimental conditions as the water volume inside the reactor is 10ml the carrier gases' flow rates are 0.1L/min 0.2L/min, and 0.3L/min, and the weight of the TiO_2 powder is 0.3g. The experimental results are presented in the Figure 4. From Figure 4, the effect of the flow rates of the carrier gas on the hydrogen generation efficiency is very strong and clear at high applied voltage. The hydrogen concentrations with using 0.2L/min are much higher when the applied voltage increases over 14kV. At this high voltage, strong UV (ultraviolet) could be generated from the discharge, thus the photocatalyst could

be excited. Therefore, 0.2L/min is the most efficient flow rate of the carrier gas in this system.

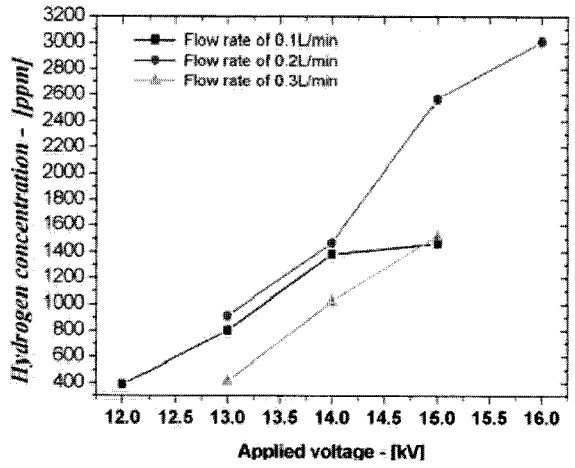


Fig. 4 The relationship between the hydrogen concentration and the applied voltage corresponding to the flow rates of the carrier gase with using TiO_2

In order to investigate the effect of TiO_2 photocatalyst quantity on the hydrogen production efficiency, the experiments are conducted with changing TiO_2 quantity at the flow rate of 0.2L/min. The results are shown in the Figure 5:

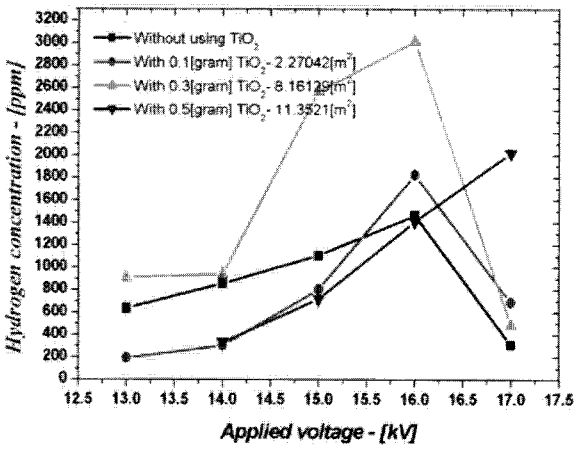


Fig. 5 The relationship between the hydrogen concentration and the weight of the TiO_2 photocatalyst

In Figure 5, the highest hydrogen concentration is obtained in the case of using 0.3g TiO_2 at the applied voltage of 16kV as 3012ppm. The discharge is unstable at 17kV in all cases except the case of using 0.5g TiO_2. The reason might be resulted from the resistance of the TiO_2. At the low range of the applied voltage from 13kV to 15kV, the photocatalyst has shown its negative effect to the discharge because of its resistance, thus the discharge was rather weak, this leads to the very low concentration of hydrogen.

For the purpose of improving hydrogen generation efficiency, the copper powder (M=63.54, and 300 mesh) is used in order to enhance the TiO_2 effect. The result is shown in the Figure 6. This experiment was conducted at the TiO_2 weight of 0.3g. The Cu powder is varied from 0.1g to 0.5g and at the same condition.

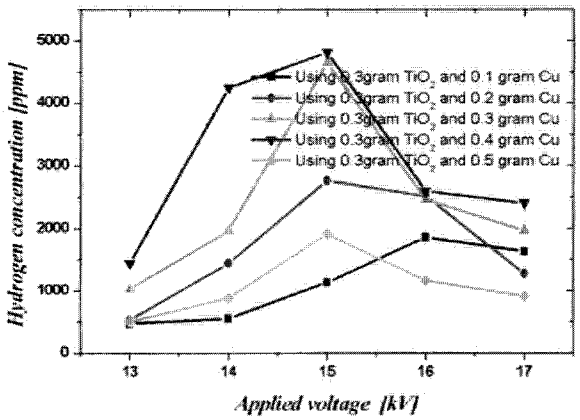


Fig. 6 The hydrogen concentration with the simultaneous use of TiO_2 and Cu powder

From the Figure 6, the hydrogen concentrations increase following the increase of the Cu powder weight up to 0.4g. The peak concentration of 4809ppm is obtained at 15kV. The discharge phenomenon is very strong. The Cu powder particles themselves gathered together and created a layer on the surface of the water. The effect of Cu particles is found to greatly enhance the photocatalytic activity of TiO_2 toward hydrogen production [4]. The Cu particles were oxidized and self-regulated to achieve the optimum valence for the maximum activity during the course of reaction. On the other hand, doping with Cu ions in TiO_2 lattice was found to enhance the activity. Except the weight of Cu powder of 0.1g, the peak concentrations are obtained at 15kV. Therefore, the present of Cu could reduce the resistance of TiO_2 and increase the discharge power. However, this positive effect decreases when the weight of Cu powder increases up to 0.5g.

The effect of the mixed Ni-TiO_2 photocatalyst is investigated under same condition to the previous experiment with the mixed Cu-TiO_2. The Ni powder used for this experiment is Cica-reagent, AW. 58.69, purify minimum 99%. The weight of the nickel powder was varied from 0.1g to 0.5g. The results are shown in the Figure 7. From the results of Figure 6, the optimal condition of Ni - TiO_2 mixed photocatalyst is obtained when the weight of Ni powder and TiO_2 power is same as 0.3g (50%-50%). Under this condition, the hydrogen concentrations strongly increase with the increase of the applied voltage. The discharge phenomenon is vehement stable. Thus, the arc- streamer discharge was occurred.

It reaches the peak point when the applied voltage is 17kV, and an extremely outstanding hydrogen concentration is 6630ppm. The reasons might be origined from the nickel's effect on the TiO_2. After thoroughly mixed with the TiO_2 and water inside the reactor chamber, the Ni particles were thoroughly dispersed on the bottom surface of the reactor. Ni might change the capacitance and therefore change the discharge.

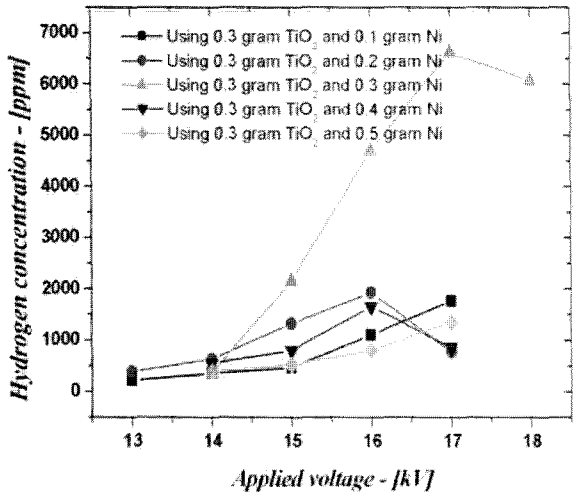


Fig. 7 The hydrogen concentration with the simultaneous use of TiO_2 and Ni powder

D. Jing et al. reported that, it was found that Ni^{2+}doping played an important role in improving the thermal stability and controlling the morphology of the mesoporous photocatalyst. More importantly, existence of Ni^{2+} greatly suppressed recombination of the electron-hole pairs (e^-/h^+) on the surface of the mesoporous photocatalyst, hence enhancing its activity [20]. However, in other cases when the weight of Ni is lower (0.1g and 0.2g) or higher (0.4g and 0.5g) than TiO_2, it has shown that the discharge was much weaker. D. Jing et al. reported that the dopant again becomes recombination center for photo generated e^-/h^+ pairs. This is believed to be the reason for the existence of an optimal Ni concentration for highest activity for the doped mesoporous photocatalyst [20].However, this optimal point was found out at the high applied voltage of (17kV), so it may use a large energy consumption.

From the experiment results, it could be assumed that, the enhancing effect of activity of the photocatalyst TiO_2 from Cu and Ni is clear. The energy yields are shown in the figure 8. N. Nakajima et al. reported that, at the electron rich surface of TiO_2 with oxygen vacancies, the excess electrons occupy Ti 3d-states localized on the TiO_2 ions near to vacancy. The resulting Ti^{3+} (3d1) in-gap states are produced also by transition metal adsorption (Ni-TiO_2 Cu-TiO_2) on TiO_2 surface. The interactions of the transition metal with TiO_2 involving significant charge transfer between Ni and the substrate are much stronger compared to Cu [21]. Futhermore, from the photo 1 and the table 1, the size of the Cu particle is about 1.5 time bigger compared to Ni particle. This leads to the surface area of the Ni particle is about 2 times larger compared to Cu particle. Therefore, the surface interactions between Ni particles and TiO_2 are much stronger than those of Cu.

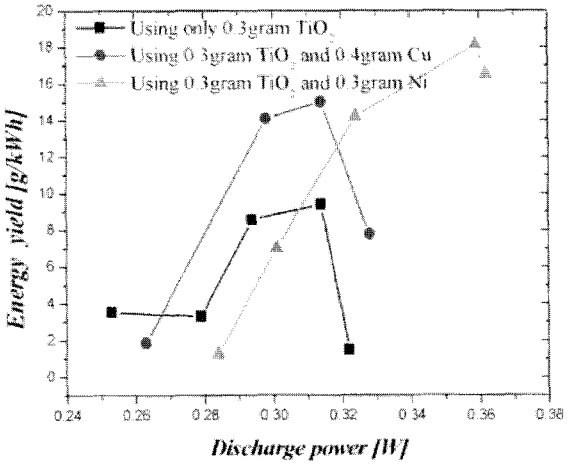


Fig. 8 The comparison of energy yield of the three cases of using photocatalyst

From the Figure 8, at the low applied voltage from 13kV to 15kV corresponding to the discharge power from 0.25W to 0.3W, Cu powder has shown its good ability of promoting the activity of TiO_2 photocatalyst as well as enhancing the hydrogen generation efficiency. The energy yields with Cu-TiO2 are varying from 14.5 to 15.5g/kW · h. While with using only TiO_2, those are from 3.5 to 9g/kW · h. In this applied voltage range, Ni powder has shown its negative effect and thus, the energy yields are obtained from 1.5 to 7g/kW · h which is even lower than that of using only TiO_2. When the applied voltages increase over 16kV corresponding to the discharge power of 0.32W, the energy yields of Cu-TiO_2 decreases because of the over shooting discharge, meanwhile, those with the Ni-TiO_2 are linearly increase up to 17kV and the best energy yield is about 18.5g/kW · h. The discharge was over shooting when the applied voltage was increased up to 18kV, however, at this applied voltage the energy yield is also rather high as 16g/kW · h.

4. Conclusion

Based on the whole above results of the research, the following conclusions are drawn:

1. The hydrogen generation efficiency is considerably

depended on the flow rate of the nitrogen carrier gas.

2. TiO_2 photocatalyst has shown its promising ability on enhancing the hydrogen generation efficiency from tap water using plasma discharge.

3. Copper powder (M=63.54, and 300 mesh) is strongly recommended for its capability of enhancing the activity of TiO_2 in order to improve the energy yield of the hydrogen production processes.

4. Nickel power (Cica-reagent, AW. 58.69, purify min. 99%) is the most suitable for improving the activity of the TiO_2 photocatalyst with its outstanding obtained energy yield as 18.5g/kWh.

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