Enhanced Hydrogen Production at Optimum pH for the Recovery Cycle of β-FeOOH

Younghwa Yoon, Ken-ichi Katsumata, Sangbin Park, Akira Fujishima, and Jeongsoo Hong*

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ABSTRACT: In the photo-Fenton reaction, highly reactive oxygen species are generated on UV irradiation of β-FeOOH, which contributes significantly to hydrogen production. The production process was performed by adjusting the pH of the solution. The effect of acid concentration on hydrogen production was analyzed in this study, and the difference in the amount of hydrogen gas produced in each sample with different pH values was determined. X-ray powder diffraction (XRD) measurements of the samples corresponding to the peaks of β-FeOOH were compared with the reference data, and crystallite sizes were calculated by the Scherrer equation using XRD patterns. The rod-like structure of the sample particles was revealed by scanning electron microscopy. A higher amount of hydrogen was produced at lower pH, and these results confirmed that pH plays an important role in hydrogen production.
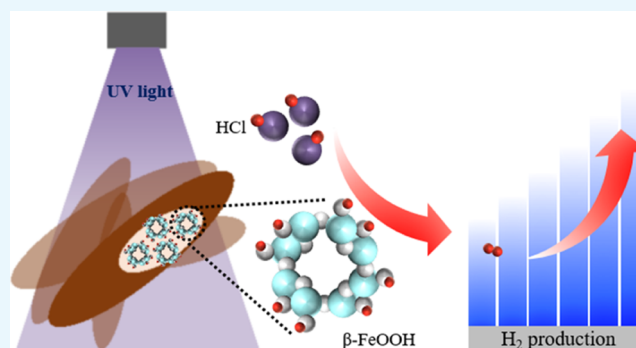
INTRODUCTION

Fossil fuels have been a major source of energy since the industrial revolution in the 18th century and they are indispensable for maintaining civilization. However, the depletion of fossil fuels and adverse environmental effects, such as global warming and air pollution, caused by the use of fossil fuels have prompted the search for alternative sources of energy.[1] Utilizing renewable energy resources, such as solar energy,[2−4] to replace fossil fuels as the primary energy source has become the focus of global attention to ensure sustainable development of future energy supply.[5−7] Hydrogen production from an infinite source, that is, water, is considered as "a clean energy for the future", which does not cause environmental pollution; hence, research has been conducted to increase the efficiency of hydrogen production.[8−11] In a previous study, we produced hydrogen from β-FeOOH, which is an iron oxide, through the photo-Fenton reaction.[12] β-FeOOH is a type of rust that is considered a waste resource and is readily available in nature at a low cost. The use of β-FeOOH is advantageous because it not only generates hydrogen energy by recycling waste resources but also decomposes pollutants that cause environmental pollution.[13−15] In addition, the photo-Fenton reaction is a photoreduction process that generates OH radicals based on the electrochemical properties of the iron complex, and the ligand−metal charge transfer excitation occurs under the presence of ultraviolet light.[16,17] The generation of OH radicals through the redox reaction between Fe^{3+} and Fe^{2+} occurs under acidic conditions, and the reaction equations of Fenton (eq 1) and photo-Fenton (eq 2) reactions are as follows[14,18]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (2)$$
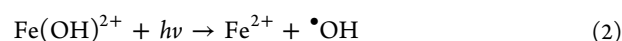
The possibility of producing hydrogen through the photo-Fenton reaction has been confirmed, and further studies are required to enhance the catalytic activity. Numerous theoretical and experimental studies are being conducted to determine the optimal conditions for maximizing the efficiency of hydrogen production using the photo-Fenton reaction. The typical experimental factors that affect the reaction are temperature, additives, and pH,[19,20] which can promote redox reactions. Therefore, based on the reported maximum efficiency of the Fenton reaction at pH 3,[21,22] the pH was adjusted as an operating parameter in this study to increase the activation efficiency of the photo-Fenton reaction. The experiment was conducted by setting the pH conditions of the solution at four values, from initial pH to pH 1, and the
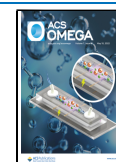
efficiency of the catalytic activity was determined based on the amount of hydrogen produced.

■ EXPERIMENTS

β-Phase iron oxyhydroxide (β-FeOOH) was synthesized using a hydrothermal method. Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$; ferric chloride, >99.0%, Wako Chemicals, Japan) and poly(ethylene glycol) (PEG, $H(OCH_2CH_2)_nOH$, #10000, Yakuri, Japan) were purchased and directly used as reducing agents to synthesize β-FeOOH. In a typical experiment, 3.7 mmol ferric chloride and a pertinent amount of PEG were dissolved in 40 mL of deionized (DI) water in a Teflon vessel at room temperature (RT), that is, 21 °C. The aqueous solution was vigorously stirred for 5 min to obtain a homogenous solution. Then, the Teflon vessel was transferred into an autoclave and heat-treated at 80 °C for 6 h using hydrothermal treatment. The as-synthesized β-FeOOH was used for hydrogen production.

The hydrogen production process was as follows: 100 mL of DI water-based 10 vol % methanol solution was prepared in a 200 mL quartz vessel and 20 mg of β-FeOOH was added.[12] All processes of solution preparation were performed in the dark, and the pH was adjusted before UV irradiation to confirm the change in catalytic activity of the photo-Fenton reaction (Table 1). HCl (36%; Wako Chemicals, Japan) was used for

Table 1. pH Control of Solution with HCl

	HCl (adjuster)			initial pH (without HCl)
pH	1	2	3	3.59

pH adjustment. The process was conducted at room temperature (21 °C) and a He—Xe UV lamp (200 W, Hayashi Watch Works, Japan) was used at an intensity of 2.5 mW/cm². Hydrogen peroxide required for Fe^{2+} oxidation was expected to be generated during the photo-Fenton reaction and thus was not externally supplied.
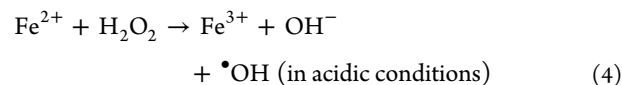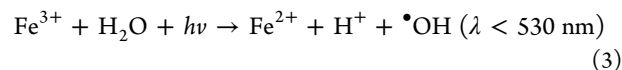
The air composition in the sealed reactor was measured during the experiment. Changes in the composition included a reduction in the amount of oxygen consumed for hydrogen production. The effect of pH on oxygen consumption was also observed.

The morphology of β-FeOOH was analyzed before and after UV irradiation by scanning electron microscopy (SEM, S-4700, Hitachi, Japan) and also verified by X-ray diffraction (XRD, SmartLab, Rigaku, Japan) at 10−80°. A gas chromatography-thermal conductivity detector (GC-TCD-2014, Shimadzu, Japan) was used to measure the amount of hydrogen produced and determine additional air composition changes.

■ RESULTS AND DISCUSSION

Hydrogen production using the photo-Fenton reaction exhibits a mechanism similar to that of photocatalysis (Scheme 1).[9,10,23,24] Highly reactive oxygen species (ROS) such as hydrogen peroxide, hydroxyl radicals, and superoxide radicals play the most important role in this photoreduction process, and have a profound effect on increasing hydrogen production efficiency.[15,25,26]

When β-FeOOH was irradiated by UV light, the Fe^{3+} ions in the solution were reduced to Fe^{2+} ions. However, the reaction did not end even when the consumption of Fe^{3+} ions is complete, and the newly generated Fe^{2+} ions became the main components of the reaction. The circulation continues as Fe^{2+} ions are oxidized to their original form.[22,27] Owing to this semipermanent cycle, hydrogen energy was continuously obtained by generating ROS. The reactions depicting the cycle of the photo-Fenton reaction are as follows[15,17,28−30]

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + {}^\bullet OH \ (\lambda < 530 \ nm) \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^-$$
$$+ {}^\bullet OH \ (in \ acidic \ conditions) \tag{4}$$

When Fe^{3+} was reduced, ROS were generated via eq 3, and the restoration of Fe^{2+} in eq 4 was achieved through various reactions. This process occurred under acidic conditions. Table 2 shows several steps of the reaction pathway from eqs 3 to 4, which indicate the circulation of FeOOH, and the chain reactions between generated ROS and ions in the photo-Fenton reaction process.[28,31,32]

When FeOOH was irradiated with UV light, electrons in the valence band (VB) were excited into the conduction band

Scheme 1. Schematic Diagram of the Mechanism of the Photo-Fenton Reaction
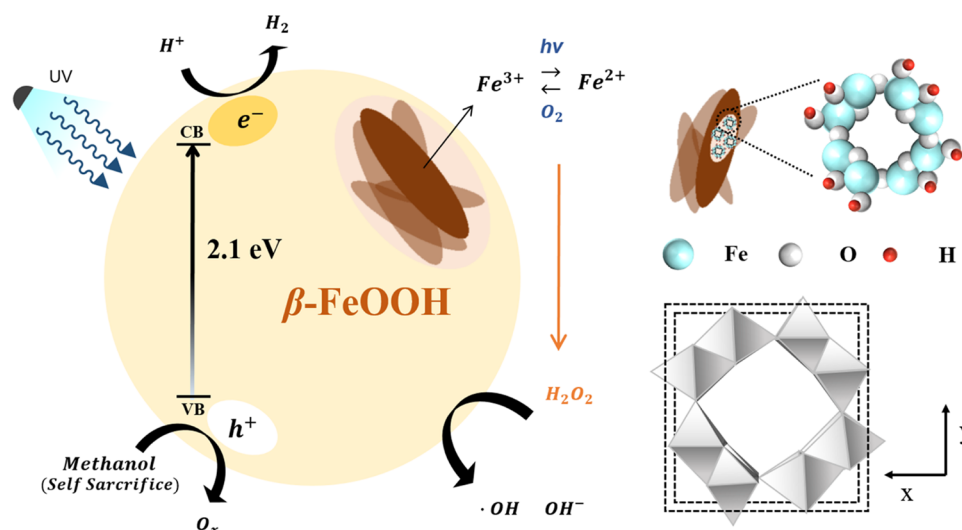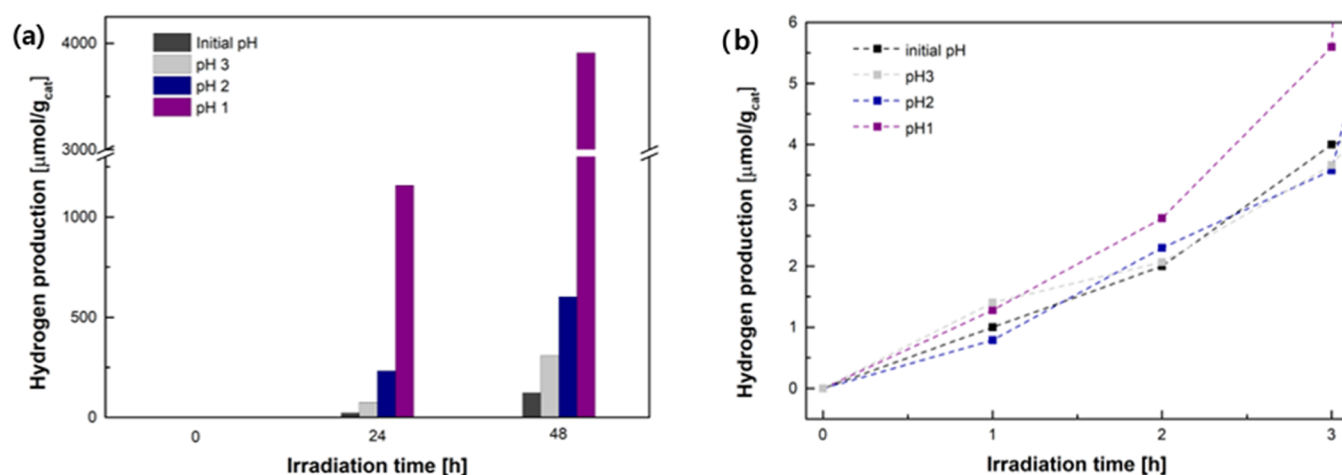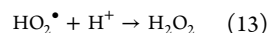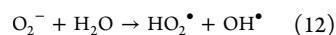
Table 2. Reaction of Active Ions in Solution

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH \quad (\lambda < 530 \text{ nm}) \quad (3)$$

$$2HO^{\bullet} + 2H_2O \rightarrow 2H_2O_2 + H_2 \quad (5)$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (6)$$

$$HO^{\bullet} + H^+ + e^- \rightarrow H_2O \quad (7)$$

$$HO^{\bullet} + OH^- \rightarrow H_2O \quad (8)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (9)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (\text{in acid condition}) \quad (4)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \quad (10)$$

$$Fe^{2+} + O_2^- + 2H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (11)$$

$$O_2^- + H_2O \rightarrow HO_2^{\bullet} + OH^{\bullet} \quad (12)$$

$$HO_2^{\bullet} + H^+ \rightarrow H_2O_2 \quad (13)$$
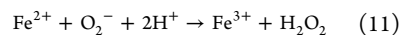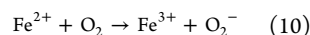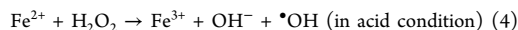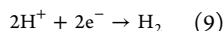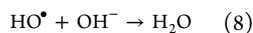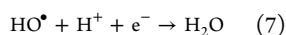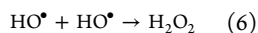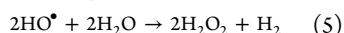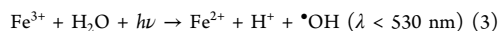
Figure 1. Amount of hydrogen produced at four different solution pH values: (a) amount of hydrogen produced in 48 h and (b) hydrogen production in first 3 h.

(CB), thereby generating electron−hole pairs. The holes created in the VB gain electrons from water and split into OH radicals and H^+ ions. The newly formed electron−hole pair caused two different reactions.

First, simultaneously with the separation of water by electron holes, the electrons in the CB recovered the Fe^{3+} ions through the reaction in eq 4 with H_2O_2 generated in eqs 5,6, 11. Second, the electrons in the CB reacted with oxygen on the surface. Electrons of Fe^{2+} were transferred to oxygen to generate superoxide anions, as shown in eq 10, and Fe^{2+} species were oxidized to Fe^{3+}. The superoxide anion generated hydrogen peroxide via eqs 11−13.[35] The cycle continued with the consumption of newly oxidized Fe^{3+} in eq 3. Therefore, regardless of the reactants of electrons in CB, hydrogen peroxide was generated by both and remained in the circulation process of FeOOH. Furthermore, based on eq 4, the generated hydrogen peroxide during the photo-Fenton reaction was used for the oxidation of Fe^{2+}, and Fe ion circulation was found to occur without adding hydrogen peroxide to the solution.

The pH of the solution was adjusted during hydrogen production to analyze the pH dependence under UV irradiation. Hydrochloric acid was used for pH adjustment, and the pH of the solution was set to four different conditions. The experiment was conducted for 48 h, and the amount of hydrogen produced under the four different pH conditions is shown in Figure 1.

Irrespective of the pH of the solution, hydrogen production occurred immediately when UV light irradiation was started in all of the four samples. In Figure 1b, the rate of hydrogen formation was found to be faster at lower pH, up to the first 3 h. The same trend was also observed in the total hydrogen

produced after 48 h of experiment. The amount of hydrogen produced at pH 3.59 differed by 30 times from that at pH 1. This result indicated that hydrogen production was pH-dependent, and the production increased at high acid concentrations. The role of ROS is important in the photoreduction reaction and its effects on hydrogen production; therefore, the activity of these substances was investigated to determine the cause of the change in the amount of hydrogen produced according to the decrease in pH. Thus, the hydrogen ions enriched by the addition of HCl were used in eqs 7, 11, and 13 to accelerate the circulation of Fe ions and contribute to the generation of hydrogen gas.

During the photo-Fenton reaction, a decrease in oxygen in the sealed reactor was observed. As the hydrogen production varied according to the pH of the solution, oxygen content should also be affected by the pH. According to the reaction presented in eq 10, oxygen is used for the oxidation of Fe^{2+} to Fe^{3+} and is reduced by gaining electrons and converted into highly reactive ions in CB. To elucidate this phenomenon, the amount of oxygen consumed during the photo-Fenton reaction was measured while blocking the inflow of external air into the reactor during the experiment (Figure 2). The air composition was measured using a gas chromatograph, and the internal air was evacuated using a syringe. However, a small inflow of air was inevitable when the syringe passed through the rubber stopper. Nevertheless, the amount of oxygen shown in Figure 2 decreased steadily, and in the case of the sample at pH 1, which showed the highest decrease in oxygen content, only a third of the original amount remained after 48 h.

Therefore, oxygen was consumed, as shown in eq 10, and similar to hydrogen production, the consumption increased proportionally as the rate of the redox cycle rate increased
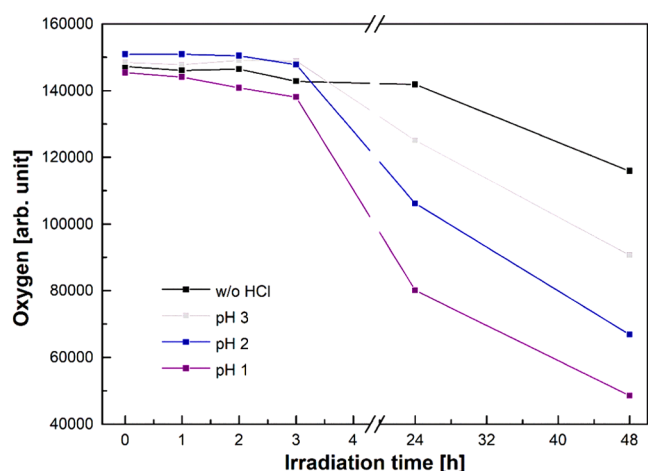
Figure 2. Oxygen consumption during the photo-Fenton reaction.

under the influence of the high acid concentration. When all of the oxygen in the reactor was consumed, the reaction terminated, and to further continue the reaction, external oxygen must be supplied. From the results confirmed in Figures 1 and 2, it was confirmed that the photo-Fenton reaction occurred more actively at low pH. It is presumed that H^+ released from HCl added for pH control affects several reactions shown in Table 2. As there are many steps involving H^+, the cycle of the photo-Fenton reaction is accelerated as a result due to enriched H^+. A follow-up study on the effect of pH on each step is required.

Previous studies have reported positive results for the recovery of FeOOH.[12,27] According to the photo-Fenton reaction pathway, oxidation of Fe^{2+} occurs via ROS generation in the reduction process, which results in the recombination of FeOOH. Herein, we investigated whether the recovery of FeOOH, which is considered as the highest advantage of the photo-Fenton reaction, could be achieved even with a change in pH. As shown in Figure 3, the structural properties of β-FeOOH, which would recombine, were evaluated in comparison with the as-synthesized β-FeOOH.

The XRD patterns of the samples were compared with those of the reference data (JCPDS 34-1266). All major peaks were detected, but only subtle changes in residual peaks were observed at lower pH. Additionally, the changes in structural intensity indicate a change in the crystallinity of β-FeOOH particles, which might be due to the repetition of decomposition and recovery during the photo-Fenton reaction. The cause of the changes in crystallinity according to pH is that, as previously described, the acid concentration and the cycle rate of iron ions are proportional. The main peaks of β-FeOOH were still observed after several circulations, and the results of previous studies showed that it can be used semipermanently, which showed that the same amount of hydrogen can be obtained in the hydrogen production experiment even with the powder that has already been used.[23] The crystallite sizes of the samples were calculated using the Scherrer equation.[33,34] Unlike in a previous study where the crystallite size changed according to the synthesis time or the temperature of the hydrogen production
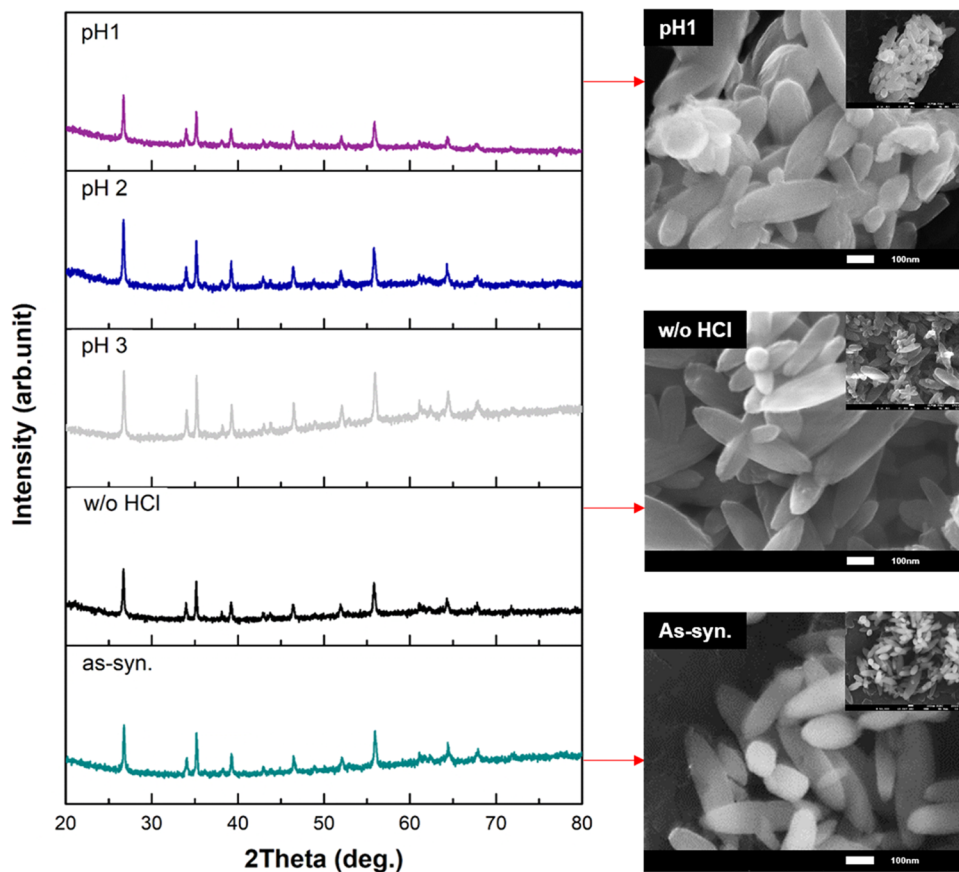

Figure 3. Changes in structural properties of akaganeite (β-FeOOH) according to the pH.

experiment, no size change was observed due to the pH, as shown in Figure 4.[12]
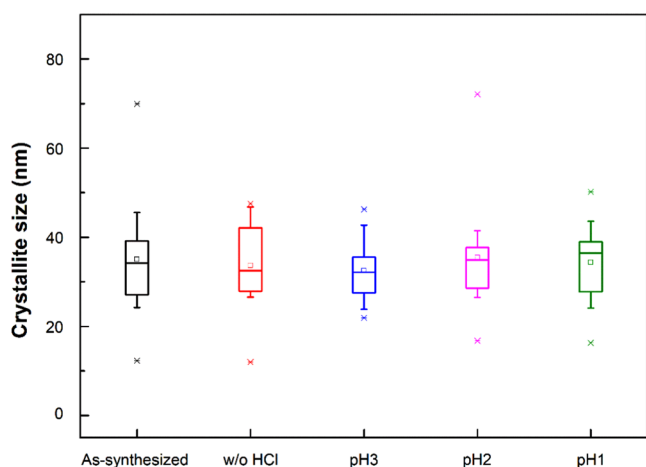

Figure 4. Crystallite size in samples as a function of solution pH measured by XRD patterns.

SEM images of the samples were compared with those of as-synthesized β-FeOOH, which revealed rod-like structures before and after UV irradiation, and the particle size distribution of the samples was measured in Figure 5.
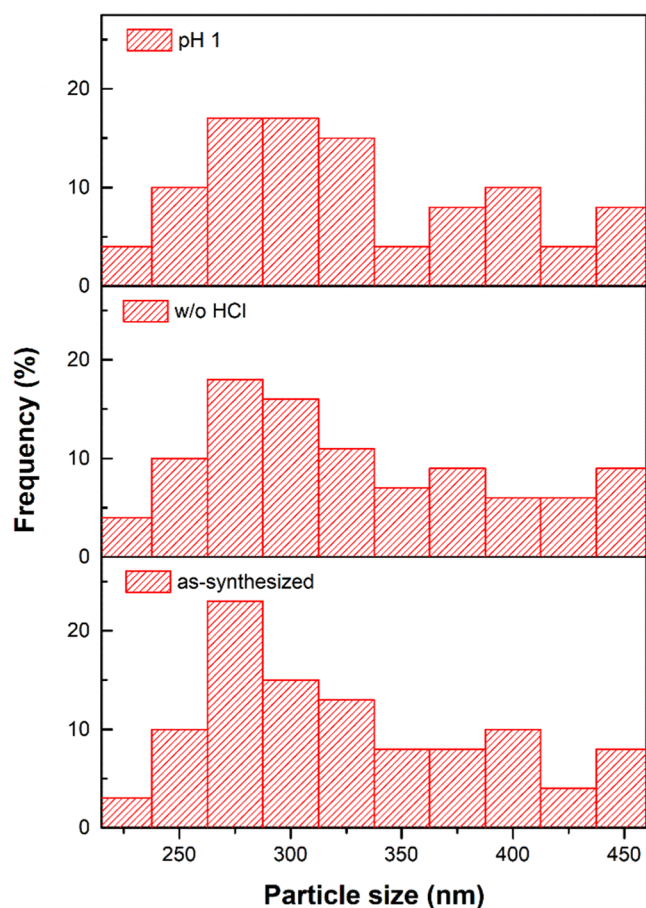

Figure 5. Particle size distribution of samples after hydrogen production experiment with different solution pH values measured by SEM images.

Although the samples showing the highest difference in hydrogen production (pH 1 and initial pH) were compared, no difference was found in the shape or size of the particles (Figures 3 and 5). Table 3 shows the results of EDX analysis to confirm the composition of β-FeOOH before and after hydrogen production.

Table 3. Elemental Composition of β-FeOOH before and after Hydrogen Production

	as-synthesized	pH 1
element	weight %	weight %
C K	11.49	8.54
O K	31.99	25.67
Fe K	56.51	65.79
totals	100.00	100.00

■ CONCLUSIONS

Hydrogen production experiments were conducted using FeOOH under UV irradiation. Various studies have attempted to increase the efficiency of hydrogen production, and accordingly, an experiment was conducted in this study to determine the optimal pH that could accelerate the photo-Fenton reaction. The lower the pH, the larger the amount of hydrogen produced, and the higher the consumption of oxygen, which is essential for the photo-Fenton reaction. As the acid concentration increased, the circulation efficiency of FeOOH increased. Analyzing the structural change of the particles by XRD and SEM revealed that no significant change in FeOOH had occurred even after being used in the hydrogen production experiment. Therefore, this confirmed that FeOOH could be recovered regardless of the pH, and it could be used semipermanently for hydrogen production.

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Notes

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