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rsc.li/rscsusHydrogen production *via* water splitting using noble gas plasma-collisional splitting (NgPCS)[†]Souma Yoshida, Yoshiyuki Takatsuji and Tetsuya Haruyama ^{*}

Noble gas plasma-collisional splitting (NgPCS) is an emerging hydrogen production technology. Conventional methods, such as fossil fuel-based decomposition and water electrolysis (the latter requiring large amounts of electrolytes), have been widely used, but NgPCS eliminates the need for electrolytes, offering an eco-friendly and cost-effective alternative for producing hydrogen.

Hydrogen, when used as a combustion fuel, does not emit carbon dioxide; therefore, hydrogen can be utilized in fuel cells.^{1–3} Hydrogen fuel cell-based vehicles are already on the market, gaining attention as a clean energy source. As the demand for hydrogen is expected to rise rapidly, expanding the production capacity of hydrogen within the supply chain is essential. Currently, hydrogen is primarily produced through two main methods: (i) the decomposition of fossil fuels^{4,5} and (ii) the electrolysis of water, a process that requires significant energy input and substantial quantities of electrolytes.^{6,7} Both methods have limitations regarding efficiency and environmental impact. Additionally, bioprocesses can also produce hydrogen; however, bioprocesses result in small production volumes of hydrogen per fermenter, limiting the production scalability.⁸

Typically, hydrogen from fossil fuels is produced using coal or methane gas. Hydrogen production from coal is well established and involves two processes as follows: (i) the first process involves gasifying coal with steam heat to generate synthesis gas (a mixture of carbon monoxide and hydrogen), followed by a shift reaction to convert carbon monoxide into additional hydrogen; (ii) the second process involves extraction of hydrogen from coke oven gas (COG), a byproduct of coke production. Subsequently, the obtained COG is cooled to remove impurities, such as tar, ammonia, naphthalene,

Sustainability spotlight

The demand for hydrogen (H₂) is expected to increase in the future. Thus, extensive research is needed to overcome the limitations of the existing H₂ production methods. The method involving steam reforming of fossil fuels generates substantial CO₂. The electrolysis of water requires large quantities of electrolytes, and H₂ production *via* water electrolysis strongly depends on the surface area of the electrodes. We demonstrate a novel approach for synthesizing H₂ using noble gases and water. The proposed method shows the potential to advance several sustainable development goals, including clean energy (SDG 7), industry, innovation, infrastructure (SDG 9), and climate action (SDG 13).

hydrogen sulfide, and BTX (a mixture of benzene, toluene, and xylene). In the next step, high-purity hydrogen is obtained by further removing impurities, such as carbon monoxide, carbon dioxide, methane, and nitrogen *via* the pressure swing adsorption (PSA) process from the purified COG.

Although fossil fuel-based hydrogen production processes are well established and have been extensively improved over the past few decades, they are accompanied by considerable limitations that make them unsustainable. Although hydrogen production from fossil fuels is efficient, the associated high carbon dioxide emissions render it incompatible with clean energy goals. Consequently, reliance on fossil fuels for hydrogen production fundamentally conflicts with the vision of a sustainable future.

In contrast to fossil fuel-based hydrogen production processes, water electrolysis provides a cleaner alternative; however, water electrolysis also has inherent limitations that challenge its environmental sustainability and scalability. Conventional electrolysis requires the dissolution of large amounts of supporting electrolytes (*e.g.*, salts) in water, introducing serious environmental concerns and generating problematic waste that must be carefully managed. Conventional electrolysis is a surface-dependent process in which the hydrogen yield relies heavily on the size and surface area of electrodes (typically made from precious metals), creating further scalability issues.^{9,10} In conventional electrolysis, as the

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electrode size must be increased to upscale the hydrogen production, the associated costs increase and necessary electrolytes gradually degrade; thus, the system efficiency degrades over time, necessitating extensive waste treatment. Moreover, contamination of the electrode surface during electrolysis further reduces the process efficiency. Since the electrochemical reactions are confined to the surface region near the electrodes (approximately 10 angstroms within the Helmholtz layer) during electrolysis, increasing the hydrogen production requires costly expansion in the surface area of the electrodes, imposing significant commercial and technical challenges.

This study introduces a novel hydrogen production technology fundamentally different from traditional methods. We discovered that when noble gas plasma collides with water molecules, the resulting collision energy can split the water molecules and generate hydrogen; this process, known as Noble gas Plasma-Collisional Splitting (NgPCS), offers a promising alternative to traditional hydrogen production methods.¹¹ The process of NgPCS does not require fossil fuels or supporting electrolytes, making NgPCS compatible with various water sources, such as river water, rainwater, well water, and seawater. Notably, 97.5% of water on earth is seawater, with only 2.5% being freshwater.

We believe that NgPCS holds potential as a low-cost and eco-friendly hydrogen production technology. In this study, we used argon as the noble gas to perform NgPCS for hydrogen production. This study demonstrates that when argon plasma generated *via* dielectric barrier discharge interacts with water at the gas/liquid interface, the argon plasma decomposes the water molecules, producing hydrogen (H_2) in the gas phase and leaving hydrogen peroxide (H_2O_2) in the liquid phase. This study also includes an analysis of the reaction mechanism behind NgPCS. When examining just the four keywords—argon gas, water, discharge, and hydrogen—a number of previously reported studies seem to be similar. The previously explored hydrogen production processes involve either a water surface discharge in an argon gas atmosphere¹² or a method of simultaneously discharging water and noble gases.^{13,14} The NgPCS process proposed and studied in this work is completely different from the previously reported processes for hydrogen production. In the NgPCS process, the discharge locus, *i.e.*, the plasma generation locus, and reaction locus, *i.e.*, water, are physically separated, and the water splitting reaction is driven by the energy transferred from the argon plasma to water molecules through collisions. In other words, the reaction mechanism and products of the NgPCS are fundamentally different from those of the processes reported previously.

Fig. 1 presents a schematic showing the mechanism of NgPCS. The reaction involved in NgPCS was discovered during the study of the plasma/liquid (P/L) reaction,^{15–21} which was initially developed to reduce nitrogen with water and synthesize ammonia. Notably, the NgPCS acts as a negative control experiment, utilizing a noble gas that does not chemically react. Although both NgPCS and P/L reactions supply the reaction energies through gas discharge, they differ significantly in terms of the underlying chemical and physical processes.

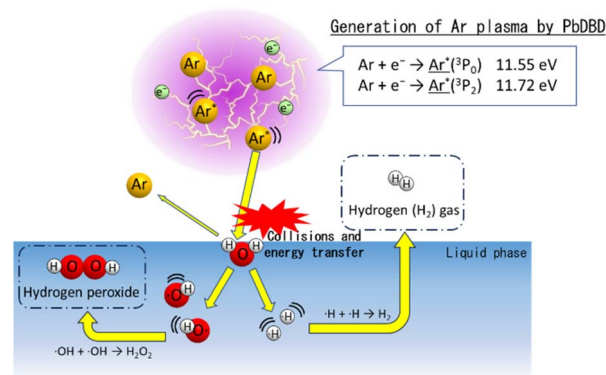


Fig. 1 Schematic diagram illustrating the mechanism of water decomposition *via* NgPCS, resulting in hydrogen (gas phase), and hydrogen peroxide (liquid phase) production. Water molecules are dissociated by the collision energy of noble gas plasma (argon: Ar).

For the NgPCS experiments, argon was introduced at a flow rate of 3 L min^{-1} . Argon gas was activated by a dielectric barrier discharge within a packed bed of dielectric beads that filled the discharge locus.¹⁶ When activated argon atoms collide with water molecules at the gas/liquid interface, they dissociate the water, resulting in the production of gaseous H_2 and liquid H_2O_2 . A schematic of the experimental setup is shown in Fig. 2. Ultrapure water (10 ml; specific resistance: $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was dissociated through collisions with the activated argon in the reaction vessel, and the reaction mechanisms based on plasma diagnostics were explored and analyzed. The produced H_2 gas was quantified using a gas chromatography system (GC3210, GL Science), which was equipped with a thermal conductivity detector (TCD) and molecular sieve 5 A column. H_2O_2 was measured using a digital water analyzer (DP M2- H_2O_2 and DPM2- H_2O_2 -C, Kyoritsu Chemical-Check Lab., Corp). Calibration curves for both analytes are presented in Fig. S1 and S2.[†]

To analyze the plasma-activated argon, we employed a packed-bed dielectric barrier discharge reactor to activate the gas and measured the plasma emission with a UV-visible spectrophotometer (UV-2600, Shimadzu Corporation) using a quartz optical fiber. By examining the emission spectrum of

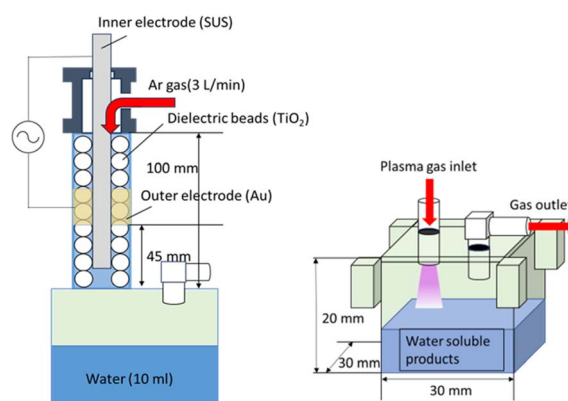


Fig. 2 Schematic diagram showing the experimental setup used for performing the NgPCS.



the plasma, we determined the activated state of argon. The electron temperature, a key parameter influencing the formation of activated species *via* inelastic collisions, was assessed using the Boltzmann plot method that analyzes the Ar–I spectral line intensity. The Boltzmann plot uses intensities of several lines with varying threshold energies, assuming that the population of emission levels follows a Boltzmann distribution. The electron temperature can be derived from the slope of the Boltzmann plot using the following equation:^{22,23}

$$\ln\left(\frac{\lambda_{ji} I_{ji}}{hc A_{ji} g_j}\right) = -\frac{E_j}{k_B T} + C \quad (1)$$

$$T_e = k_B T \quad (2)$$

where λ_{ji} is the wavelength, I_{ji} is the measured intensity, A_{ji} is the transition probability, g_j is the statistical weight of the upper level, h is the Planck's constant, c is the speed of light, E_j is the upper energy of the excited state (eV), k_B is the Boltzmann constant, T is the electron temperature (K), and C is a constant. The spectral line data required for deriving the Boltzmann plot are shown in Table S1.† The electron temperature was calculated using eqn (2) and converted to electron volts, denoted as T_e . Except for the measured values, the other spectroscopic data were obtained from the National Institute of Standards and Technology (NIST) atomic spectra database.²⁴

For experiments, plasma was generated using eight different electrical power inputs. Fig. 3 presents the results of quantitative analysis showing the amounts of H_2 and H_2O_2 produced. The production of both H_2 and H_2O_2 increases with increasing electrical power input. However, as is clear from the results in Fig. 3, the yields of hydrogen and hydrogen peroxide are not balanced. This is because the gas phase product H_2 is quickly discharged outside the NgPCS system and collected and quantified, but the other product, H_2O_2 , remains in the NgPCS reactor inside and is also decomposed by NgPCS. As a result, the analyzed amount of H_2O_2 is lower than the actual amount produced. We believe that in the future it will be possible to improve the NgPCS reactor and extract the generated H_2O_2 before it is decomposed. In any case, we have clarified that the distinctive feature of NgPCS is its ability to simultaneously

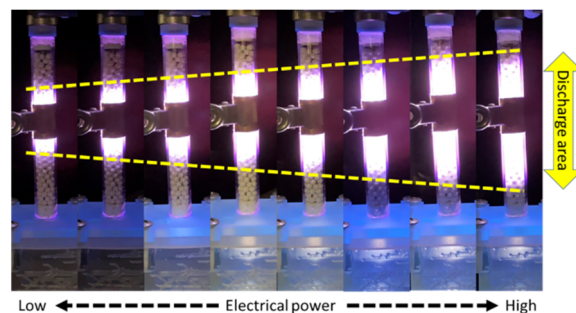


Fig. 4 Pictures showing argon plasma discharge at different electrical power inputs. At higher electrical power levels, the plasma extends to the surface of the water.

produce hydrogen and hydrogen peroxide, whereas only hydrogen and oxygen are produced by electrolysis of water.

Fig. 4 illustrates the plasma emissions at different levels of electrical power input. As the electrical power input increases, the expansion of the discharge area indicates that a large volume of argon gas is introduced into the plasma. Additionally, when the electrical power input exceeds a certain threshold, the plasma emissions extend above the water surface within the reaction vessel.

Optical emission spectroscopy is an *in situ* analytical method that enables the measurement of plasma without direct contact with the detector, thereby providing detailed and valuable insights into plasma characteristics. The plasma emission spectrum was obtained in the range of 650–900 nm, and the results are shown in Fig. 5. The electron temperatures for each electrical power input used in this experiment are shown in Fig. 6 (blue legend). The results reveal that the electron temperatures determined at both the discharge locus and within the reaction vessel at different electrical power inputs are relatively stable at approximately 0.6 eV across all power levels. Fig. 4 demonstrates that the reaction vessel emitted a glow when the electrical power exceeded a certain threshold, suggesting that the plasma extended above the water surface. Consequently, the electron temperature calculated from the emission spectrum of the plasma within the reaction vessel was recorded, as shown in Fig. 6 (orange legend). The results indicate that the electron temperature within the reaction vessel

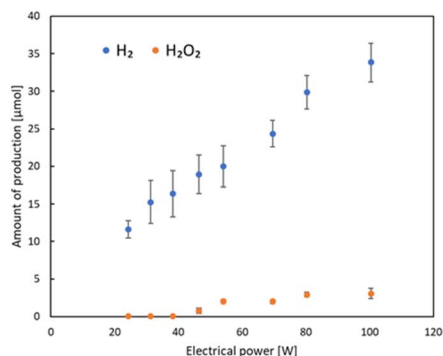


Fig. 3 Relationship between electrical power input and the amount of H_2 and H_2O_2 generated *via* NgPCS.

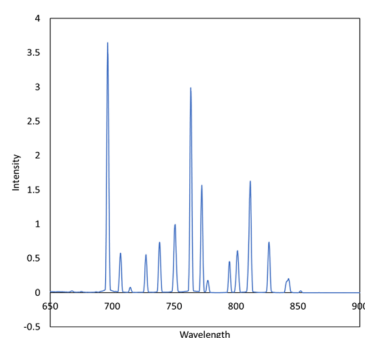


Fig. 5 Measurement of Ar plasma emission at the 650–900 nm range using optical emission spectroscopy.



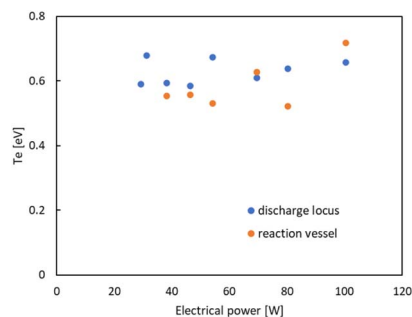
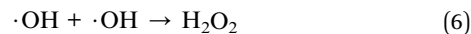
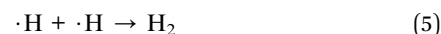
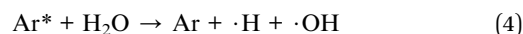


Fig. 6 Electron temperatures at the discharge locus (blue legend) and within the reaction vessel (orange legend) at different electrical power inputs.

also remained relatively stable at around 0.6 eV (when the input power is low, the plasma glow does not reach the water phase surface, so the plasma emission cannot be measured and the electron temperature cannot be calculated. Therefore, the results for the two conditions with low input power do not show the electron temperature). As shown in Fig. 7(a) and (b), the plasma emission spectra contain two peaks at wavelength ranges of 645–655 nm and 300–320 nm, which can be attributed to emissions from H α and OH, respectively. The emission intensities increase with increasing electrical power inputs. Given the negligible variation in electron temperatures concerning electrical power inputs, it was not feasible to compare electron collision-induced water splitting. Therefore, the observed differences in emission intensities can be attributed to the enhanced water splitting, resulting from collisions between activated argon and water molecules. The production of H $_2$ and H $_2$ O $_2$ can be described by the following equations.



where Ar activated by the discharge is denoted as Ar*.

Qualitative analysis of active species derived from water and quantitative analysis of gaseous H $_2$ and liquid H $_2$ O $_2$ confirmed that stoichiometric water-splitting can be promoted by NgPCS. Increasing the electrical power input to the plasma for water decomposition *via* NgPCS enhances the production of H $_2$ and H $_2$ O $_2$ by increasing the electron density in plasma, which in turn increases the collision probability between activated argon and water molecules. The overall efficiency of NgPCS is limited by two factors: (i) discharge efficiency and (ii) plasma–water collisions. Future work is needed for analyzing the limiting factors of NgPCS and optimizing those factors for developing a highly efficient stoichiometric water-splitting technique.

When producing hydrogen through processes like water electrolysis, oxygen is simultaneously produced. If oxygen were produced in our experiment, we would have observed an emission corresponding O $_2^+$ along with hydrogen in Fig. 7(a). In conclusion, oxygen production is minimal in the proposed NgPCS system, and the main products are H $_2$ and H $_2$ O $_2$. However, since the discussion at this stage is based solely on the emission characteristics, future studies using quantitative techniques, such as electron spin resonance spectroscopy, are needed to advance the discussion.

The production of H $_2$ and H $_2$ O $_2$ utilizing the proposed NgPCS system, which uses argon gas, argon plasma, and water, clearly demonstrates the effectiveness of the system in decomposing water. Typically, when non-noble gases are used in a PCS system, different chemical reactions are observed. For example, when the nitrogen plasma interacts with water, ammonia is synthesized.¹⁶ When the oxygen plasma interacts with water, hydroxyl radicals are produced.²⁵ When air plasma interacts with water, both ammonia and nitric acid are synthesized.¹⁵ The reactions involving gas reduction (oxidation) where gas molecules react with water are known as P/L reactions; these reactions do not occur in an NgPCS system.

Our study showcases the ability of NgPCS to split water into H $_2$ and H $_2$ O $_2$ under ambient temperature and atmospheric pressure without the need for electrolytes. The proposed NgPCS method shows the potential for widespread application in purification of lake water, well water, and seawater. Additionally, the controllable on–off operations of the NgPCS system make it compatible with renewable energy sources, such as solar and wind power. Since NgPCS is a newly discovered and developing technology, optimization of the hydrogen production efficiency of NgPCS systems is still under investigation. However, the ability of the proposed NgPCS system to produce two valuable substances, hydrogen gas and hydrogen peroxide, is a significant advantage. Since noble gases are stable and return to their ground state after collisional reactions, they can

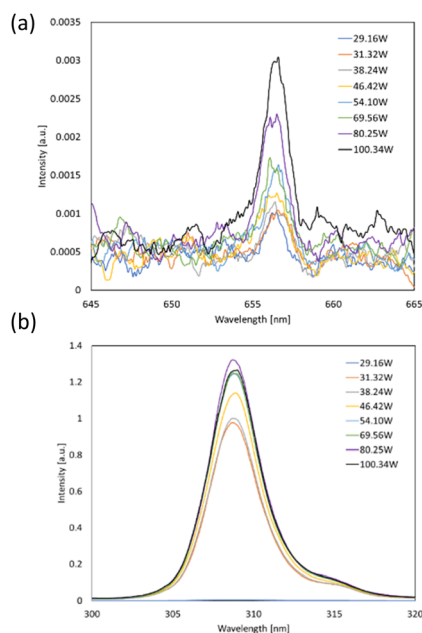


Fig. 7 Plasma emission spectra recorded at different electrical power inputs. Emission spectra corresponding to (a) H α and (b) OH, resulting from water decomposition *via* NgPCS.



be reused, making them highly advantageous for use in NgPCS systems. To enhance the sustainability of H₂ and H₂O₂ production, integrating the NgPCS system with other systems that separate and concentrate gases using PSA can be beneficial.

Data availability

Experimental data related to the discussion in this paper can be disclosed or provided upon request to the corresponding author. Related information will also be made publicly available when possible in the Academic Repository “Kyutacar” (<https://kyutech.repo.nii.ac.jp/>) operated by the institutions to which the authors belong.

Conflicts of interest

There are no conflicts to declare.

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