Direct synthesis of hydrogen peroxide from plasma-water interactions

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Hydrogen peroxide (H2O2) is usually considered to be an important reagent in green chemistry since water is the only by-product in H2O2 involved oxidation reactions. Early studies show that direct synthesis of H2O2 by plasma-water interactions is possible, while the factors affecting the H2O2 production in this method remain unclear. Herein, we present a study on the H2O2 synthesis by atmospheric pressure plasma-water interactions. The results indicate that the most important factors for the H2O2 production are the processes taking place at the plasma-water interface, including sputtering, electric field induced hydrated ion emission, and evaporation. The H2O2 production rate reaches ~1200 μmol/h when the liquid cathode is purified water or an aqueous solution of NaCl with an initial conductivity of 10500 μS cm⁻¹.

It has been proven that H2O2 can be formed by the reaction of H2 + O2 → H2O2 in plasma containing H2 and O2 gases9-19. When plasma is in contact with water, the plasma-water interactions can entail many direct reactions at the plasma-water interface and indirect cascade reactions in the bulk water20-25. One important species at the plasma-water interface is hydroxyl radical (OH) produced by plasma-induced water reactions with electrons and ions. The exact OH formation pathways by plasma-water interactions are very complicated, and one can refer to a review paper26 for details. As the building blocks, the generated OH radicals combination contributes to the main process of H2O2 formation in plasma-water interactions. In addition, other less probable pathways such as OH + H2O* → H2O2 + H27,28 are also possible. In fact, there exist many reports on the H2O2 formation by discharge plasma operated over and inside aqueous solutions27-35. However, the determining factors which influence the H2O2 production from the plasma-water interactions remain unclear. To optimize the H2O2 production from plasma-water interactions, a better understanding of the H2O2 production process is desired. Herein, we present an insight into

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the understanding of H$_2$O$_2$ production by the plasma-water interactions. The results indicate that the sputtering, the electric field induced ion emission, and the evaporation at the water surface strongly influences the H$_2$O$_2$ production.

**Results**

**Experimental approach and the H$_2$O$_2$ production.** H$_2$O$_2$ was produced by the device schematically shown in Fig. 1 [see Supplementary Information (SI) for details]. A direct current Ar atmospheric pressure plasma was generated between a tungsten steel tube (1.02 mm and 6.35 mm in inner and outside diameters, respectively) and a liquid surface. The liquid acts as cathode or anode (positive or negative voltage applied to the tungsten steel electrode), and NaCl was used to adjust the initial conductivity of the liquid. The Ar flow rate, the discharge current, and the gap between the tungsten steel tube and the liquid surface were set to be 20 sccm, 30 mA, and 3 mm, respectively. To refresh the surface liquid, the total 400 ml liquid was circulated by a peristaltic pump at a flow rate of 200 ml/min. During the plasma-solution interactions, the H$_2$O$_2$ yield was measured at a given interval of 10 min, and the temperature, pH value, and the conductivity of the solution were also investigated.

Figure 2 presents the H$_2$O$_2$ yields at different experimental conditions. For liquids with low initial conductivities (1.60 $\mu$S cm$^{-1}$ and 1440 $\mu$S cm$^{-1}$), the H$_2$O$_2$ production rate (the slope of the yield curve) decreases with increasing time, while they are constants for the liquids with high initial conductivities (4800 $\mu$S cm$^{-1}$ and 10500 $\mu$S cm$^{-1}$) [Fig. 1(a)]. Even with an initial conductivity of 4800 $\mu$S cm$^{-1}$, the H$_2$O$_2$ yield for NaOH solution is almost zero after 60 min plasma treatment [Fig. 1(b)]. As the discharge current increases, the H$_2$O$_2$ production rate is enhanced [Fig. 1(c)]. When the liquid acts as anode (negative voltage applied to the tungsten steel electrode), there is almost no H$_2$O$_2$ production [Fig. 1(d)]. These results guide us to a question: What is the underlying mechanism for these differences? To answer this question, we must carefully analyse the processes taking place at the plasma-liquid interfaces from which the H$_2$O$_2$ is formed during the plasma-liquid interactions.

**Water molecule transfer processes at the plasma-liquid interface.** When the liquid acts as cathode, a cathode voltage fall ($V_C$) will be built between the plasma and the liquid surface due to the space charge accumulation$^{36-40}$. The $V_C$ will be located at a limited distance called cathode sheath, and for an atmospheric pressure discharge plasma, the thickness of the cathode sheath is smaller than 100 $\mu$m when the discharge current is more than 5 mA$^{36}$. In our case, the discharge current is 30 mA, it is reasonable to take the sheath thickness as 100 $\mu$m. Table 1 presents the $V_C$ for liquids with different initial conductivities (see SI for the details of the $V_C$ estimation). The following analysis will demonstrate that this cathode region near the liquid surface is very important to the water molecules transfer at the plasma-liquid interface.

Figure 3 depicts three processes contributing to the water transfer from the liquid phase to the gaseous plasma, and the qualitative characteristics of the voltage potential ($V$) and the electric field ($E$) in the plasma-liquid system (ref. 41). Firstly, positive ions in the plasma passing the cathode sheath will be accelerated by the $V_C$, and the constituents of liquid will be sputtered into the gaseous phase by the accelerated energetic ions. This sputtering process has been widely used in low pressure plasma for material fabrication$^{41}$. Secondly, the $V_C$ measured in our
case is in the magnitude of ~500 V (see Table 1) which forms an electric field in the order of 100 kV cm$^{-1}$ near the liquid surface (see latter analysis for the electric field estimation). This electric field is high enough to pull out the hydrated negative ions (carrying water molecules) from the liquid surface and transfer them to the gaseous plasma$^{36,42-44}$, which is similar to the field emission at a solid surface. Thirdly, there is evaporation at the liquid surface caused by plasma and Joule heating. Obviously, all these three processes can transfer water molecules from the liquid phase into the gaseous plasma, and then the number of water molecules entering the plasma phase is influenced by the above three processes. Water molecules in the gaseous plasma can react with plasma species to form OH, and then H$_2$O$_2$ is formed by the combination of OH. Finally, H$_2$O$_2$ dissolves into the liquid to form an aqueous solution. Therefore, H$_2$O$_2$ production will increase with the number of water molecules entering the plasma phase which is strongly dependent on the above mentioned processes.

The number density of water molecules ($n$) entering the plasma phase can be expressed as

$$n = n_{\text{spu}} + n_{\text{eva}}$$  \hspace{1cm} (1)

where

- $n_{\text{spu}}$: the number density of water molecules entering the plasma phase due to the sputtering. $n_{\text{spu}}$ is related to the cathode voltage fall ($V_C$), discharge current ($I_d$), liquid surface tension etc. and it can be described as $n_{\text{spu}} = k_{\text{spu}} I_d (E_i)^{1/2}$, $k_{\text{spu}}$ is the sputtering coefficient, and $E_i$ is the energy of incident ion. The positive ion in the plasma obtains its energy by passing the plasma cathode sheath, and therefore the obtained energy is proportional to the $V_C$. Thus, $n_{\text{spu}}$ can be expressed as $n_{\text{spu}} = k_{\text{spu}} I_d (V_C)^{1/2}$.

**Figure 2.** H$_2$O$_2$ yields at different experimental conditions. Plasma-liquid interactions were performed with liquids of (a) initial conductivities of 1.60, 1440, 4800 and 10500 μS cm$^{-1}$, (b) NaCl and NaOH with the same initial conductivity of 4800 μS cm$^{-1}$, (c) NaCl with the initial conductivity of 4800 μS cm$^{-1}$ at discharge currents of 30 mA, 40 mA and 50 mA, and (d) NaCl with an initial conductivity of 4800 μS cm$^{-1}$ (The liquid acts as cathode or anode).

| Time (min) | $1.60 \mu$S cm$^{-1}$ | $1440 \mu$S cm$^{-1}$ | $4800 \mu$S cm$^{-1}$ | $10500 \mu$S cm$^{-1}$ |
|-----------|---------------------|----------------------|---------------------|----------------------|
| 0         | N/A$^{[a]}$         | 581                  | 504                 | 512                  |
| 20        | 663                 | 559                  | 494                 | 505                  |
| 40        | 590                 | 560                  | 507                 | 510                  |
| 60        | 558                 | 526                  | 493                 | 506                  |

**Table 1.** Cathode voltage falls ($V_C$) for liquids with different initial conductivities. NaCl was used to adjust the solution conductivity. [a] Data are unavailable because the discharge is unstable in the very beginning for the liquid with an initial conductivity of 1.60 μS cm$^{-1}$.
n_{Ele} : the number density of water molecules entering the plasma phase due to the electric field induced hydrated ion emission, and $n_{Ele}$ is an increasing function of the ion concentration in the liquid phase ($C_{Ion}$) and the electric field near the liquid surface ($E_C$) but depends on these parameters in a complicated way. We can express it as $n_{Ele} = f(V_C, C_{Ion})$. In addition, the electric field near the liquid surface ($E_C$) can be estimated as follows. In the cathode sheath, $E = E_c(1 - z/d_C)$, and $V = V_c(z/d_C)(2 - z/d_C)$, where $E$ is the electric field in the cathode sheath, $z$ is the distance away from the liquid surface, $d_C$ is the thickness of the cathode sheath, $V_c$ is the voltage potential near the liquid surface, and $E_c$ is the electric field at the liquid surface.

$n_{Eva} :$ the number density of water molecules entering the plasma phase due to evaporation. Based on the thermodynamics law, $n_{Eva}$ can be expressed as $n_{Eva} = n_0 \exp(-W/kT)$, where $n_0$ is the number density of water molecules in the liquid phase, $W$ is the heat of evaporization, $k$ is the Boltzmann constant and $T$ is the liquid temperature.

Therefore, $n$ can be expressed as

$$n = k_{Spd} I_d(V_C)^{1/2} + f(V_C, C_{Ion}) + n_0(-W/kT).$$

(2)

Besides depending on $I_d$ for $n_{Spd}$ and on $C_{Ion}$ for $n_{Eva}$, both $n_{Spd}$ and $n_{Ele}$ depend on the cathode voltage fall ($V_c$), and $n_{Eva}$ depends on the solution temperature.

H$_2$O$_2$ energy yields. Based on the discharge voltages shown in Fig. S2, we estimated the average power consumed in the plasma-liquid interactions, and then the H$_2$O$_2$ generation energy yields were calculated for liquids with different initial conductivities and the results are summarized in Table 2. The H$_2$O$_2$ energy yields are larger than most of the H$_2$O$_2$ energy yields generated from discharge plasmas which have been summarized in ref. 28. The maximum energy yield appears for liquid with an initial conductivity of 10500 μS cm$^{-1}$, although the liquid with an initial conductivity of 1.60 μS cm$^{-1}$ produces the largest generation rate. The energy yield can be expressed as

$$\text{Energy yield} = \frac{\text{Generation rate}}{\text{Energy Yield}_{Liq} + \text{Energy Yield}_{Plas-Liq}}.$$
where Energy$_{\text{Liq}}$ and Energy$_{\text{Pla-Liq}}$ are energy consumed in the liquid (mostly taking a form of heating the liquid cylinder) and energy consumed in the plasma-liquid interactions, respectively, and only the latter contributes to the H$_2$O$_2$ production. Therefore, Energy$_{\text{Liq}}$ can affect the energy yield of the H$_2$O$_2$ formation. The largest generation rate for the liquid with an initial conductivity of 1.6 $\mu$S cm$^{-1}$ can be attributed to the high resistance of the liquid cylinder between the plasma and the graphite electrode. The Joule heating consumes a large portion of the supplied power in the liquid with the initial conductivity of 1.6 $\mu$S cm$^{-1}$, but in this case, a larger cathode voltage fall is close to the liquid surface as shown in Table 1, and therefore, it produces a large H$_2$O$_2$ generation rate with a lower energy yield if compared with the case using liquid with the initial conductivity of 10500 $\mu$S cm$^{-1}$. In the plasma-induced H$_2$O$_2$ generation, to select the liquid with a high or low initial conductivity is dependent on one’s aim: to obtain high energy yield or high generation rate.

**Discussion**

Based on the expression of $n$, the water molecules transfer from the liquid phase to the gaseous plasma is largely determined by the sputtering and the electric field induced hydrated ion emission in the case of liquid cathode since the evaporation for all cases are estimated to be similar [Fig. S6(a)]. The results in Table 1 indicate that the $V_C$ decreases with increasing time for liquids with initial conductivities of 1.60 $\mu$S cm$^{-1}$ and 1440 $\mu$S cm$^{-1}$, while it almost keeps constant for liquids with low initial conductivities of 4800 $\mu$S cm$^{-1}$ and 10500 $\mu$S cm$^{-1}$. Therefore, from the expression of $n$ and the data in Table 1, one can deduce that $n$ for liquids with initial conductivities of 1.60 $\mu$S cm$^{-1}$ and 1440 $\mu$S cm$^{-1}$ will decrease with increasing time, while it is almost constant for the liquids with initial conductivities of 4800 $\mu$S cm$^{-1}$ and 10500 $\mu$S cm$^{-1}$. Therefore, the H$_2$O$_2$ production rate decreases as time increases for liquids with low initial conductivity, while it is almost constant for liquids with high initial conductivity. Because the evaporation for all cases are estimated to be similar [see Fig. S6(a)], $n$ is determined by \( I_d, V_C \) and \( C_{\text{ion}} \). For the case with a constant \( I_d \), $n$ is related to $V_C$ and \( C_{\text{ion}} \). Although $C_{\text{ion}}$ is low in case of the liquid with low conductivity (1.6 $\mu$S cm$^{-1}$), $n$ can be still large since the high $V_C$ (see Table 1) in this case. Therefore, there is a high H$_2$O$_2$ production rate for the liquid with a low conductivity (1.6 $\mu$S cm$^{-1}$). In addition, the estimated $V_C$ are almost the same for discharge currents of 30 mA, 40 mA and 50 mA (~500 V, not shown). When the discharge current increases, the ion flux (related to \( I_d \)) near the liquid surface is enhanced and thus water transfer from the liquid phase to the gaseous plasma is increased. Consequently, the H$_2$O$_2$ yield increases with increasing discharge current as shown in Fig. 2(c). The estimated $V_C$ for NaOH solution with an initial conductivity of 4800 $\mu$S cm$^{-1}$ is ~30 V higher than that for the NaCl solution with the same conductivity. Based on the above analysis, one must expect that the NaOH solution should produce more H$_2$O$_2$. However, the H$_2$O$_2$ yield for NaOH solution is almost zero as shown in Fig. 2(b). The reason might be as follows. H$_2$O$_2$ is a weak acid and it can react with OH$^-$ to form HO$_2$ in concentrated NaOH solution (H$_2$O$_2$ + OH$^-$ → HO$_2$ + H$_2$O$^-$). Therefore, the produced H$_2$O$_2$ was consumed by reacting with NaOH, resulting in a very low H$_2$O$_2$ yield.

When liquid acts as anode, the cathode voltage fall is formed on the tungsten steel electrode, and therefore there is no sputtering and electric field induced ion emission at the liquid surface, and evaporation is the only way to transfer water molecules from liquid phase into the gaseous plasma. Compared with the case of liquid cathode, $n$ is insignificantly small in the case of liquid anode, resulting in a low H$_2$O$_2$ yield as shown in Fig. 2(b). Comparison of OH optical emission intensity in cases of liquid cathode and anode also confirms this conclusion (Fig. S9).

In summary, using water as the only consumed material, H$_2$O$_2$ is directly synthesized by plasma-water interactions and the H$_2$O$_2$ production rate can reach 1200 mol/h when the liquid cathode is purified water or NaCl solution with an initial conductivity of 10500 $\mu$S cm$^{-1}$. The H$_2$O$_2$ production rate strongly depends on the plasma-liquid interactions at the liquid surface: sputtering, high electric field induced hydrated ion emission, and evaporation. Liquid cathode performs much better than liquid anode in producing H$_2$O$_2$ by plasma-water interactions. In addition, the synthesized H$_2$O$_2$ can be consumed if the liquid contains some constituent able to react with H$_2$O$_2$ such as NaOH.

**Methods**

**Measurement of the H$_2$O$_2$ yield.** Because H$_2$O$_2$ can react with titanium sulfate, in strong acid to form H$_2$TiO$_4$ (Ti$^{IV}$ + H$_2$O$_2$ + 2H$_2$O → H$_2$TiO$_4$ + 4H$^+$) and the absorption intensity of the yellow-coloured H$_2$TiO$_4$ in 410 nm is proportional to the reacted H$_2$TiO$_4$ concentration$^{1,54-56}$. We can use it to determine the synthesized H$_2$O$_2$ concentration. 7.5 ml [Ti(SO$_4$)$_2$, 120 g/l] was added to 250 ml H$_2$SO$_4$ (1.5 M) to obtain the test solution of titanium sulfate. We used H$_2$O$_2$ with standard concentrations to obtain the proportionality between the absorption intensity of H$_2$O$_2$ at 410 nm, and the results are presented in Fig. S8(a). Once the proportionality is obtained, the H$_2$O$_2$ yield is estimated by the following equation:

\[
C_{\text{H}_2\text{O}_2} = kIV
\]  

(4)

where $k$ is the proportionality obtained by linearly fitting Fig. S8(b), \( I \) is the absorption intensity of synthesized H$_2$O$_2$ at 410 nm, and \( V \) is the solution volume (in our case, 400 ml).

**Measurement of the pH value, conductivity, and temperature of the liquid.** The pH value and temperature of the solution were measured by a pH detector with a temperature sensor (Yesmylab SX620), and the solution conductivity was measured by a conductivity detector (Yesmylab SX650).
Electrical characterization of the discharge plasma. The voltage between the tungsten steel and the graphite electrodes was measured by a high voltage (H.V.) probe (Tektronix P6015A) and the current was achieved from dividing the voltage across a 10-Ω resistor which was in series connected with the graphite electrode.

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Author Contributions
Q.C. designed the experiments and supervised the project. J.L. and B.H. conducted the experiments, all the data analysis and interpretation guided by Q.C. and H.L. J.L., Q.X., G.Y., X.Z., S.Y. and Q.H.L. provided valuable discussions on the purpose and focus of the study. All authors discussed the results and Q.C. wrote the manuscript.

Additional Information
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