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Time-resolved in situ UV absorption spectroscopic studies for detection of reactive oxygen and nitrogen species (RONS) in plasma activated water

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Abstract: Plasma activated water (PAW) is receiving a lot of attention in biomedical applications since its high bactericidal properties. In this work, we used a conventional UV-VIS spectrometer associated with a custom-built-sample chamber which enables in-situ measurement. UV absorption according to reactive oxygen and nitrogen species (RONS) in PAW generated was successfully measured during an atmospheric-pressure helium plasma jet irradiation.

Keywords: in-situ UV absorption, plasma activated water, plasma jet, reactive species

1. Introduction

Plasma activated water (PAW) also referred to as plasma treated water (PTW) are rapidly gaining importance in biomedical applications, particularly for the inactivation of microorganisms [1-3]. Atmospheric-pressure plasma jets (APPJs) are a candidate to induce reactive oxygen and nitrogen species (RONS) in water. APPJ is well-known that can generate various reactive species by an interaction between emerging plasma and ambient air, and its gas flow can deliver the generated species on a target surface.

Many RONS in PAW are open discussed e.g. hydroxyl radical (OH•), nitric oxide radical (NO•), singlet oxygen ($^1O_2$), ozone (O_3), superoxide anion radical (O_2^-•), hydroperoxyl radical (HOO•), nitric dioxide radical (N_2O•), hydrogen peroxide (H_2O_2), nitrate (NO_3^-) and nitrite (NO_2^-). For the detection of the plasma-generated RONS in liquid solution, electron spin resonance (ESR) [4], ion chromatography [2], free radical scavenging [2, 5], Fourier transform infrared spectroscopy (FTIR) [6] and UV-VIS absorption spectroscopy [6, 7] are often used.

A similar work of PAW using helium APPJ has been reported by Ikawa *et al.* [2] who observed O_2^-•, HOO•, H_2O_2 and NO_x^- in the PAW. Among them O_2^-• and HOO• have short half-life (< several seconds) and H_2O_2 and/or NO_x^- have relatively long lifetimes (< min). In our report, we measured UV absorption according to RONS in PAW mentioned above and investigated the temporal behaviour.

2. Experimental procedure

An APPJ generated by a cylindrical dielectric barrier discharge (DBD) system was used in this work. The plasma jet apparatus consisted of a 150 mm long glass tube with a 2.4 mm inner diameter. Helium gas was fed into the glass tube with a fixed gas flow rate of 2 slm through a digital flowmeter. High-voltage bipolar square pulse of 7 kV (peak-to-peak) at a frequency of 10 kHz was applied to a metallic external electrode.

A commercially available double-beam UV-VIS-NIR spectrometer (Hitachi, U-3900) and a custom-built-sample chamber were used. These enable to measure the optical property of the PAW temporally and in situ. The spectrometer used in this study could detect to down to a wavelength of 190 nm with fixed spectral resolution of 0.2 nm and scan speed of 120 nm/min. An optical path of the light is fixed distance of 10 mm. A 600 µm thick quartz plate (VIOSIL-SX, Shinetsu Chem. Ltd.) was used as a barrier of the gas flow. The quartz has a high transmittance over 90% in the broadband wavelength between 190 and 900 nm (Fig. 1).

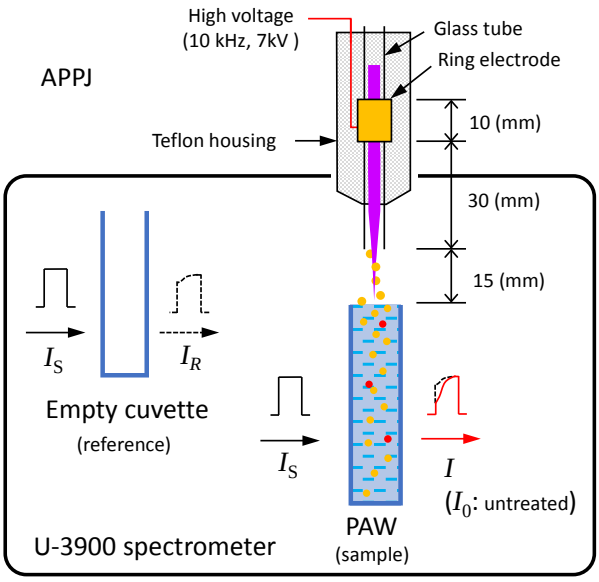

Fig. 1. In-situ UV absorption spectroscopy for detection of reactive oxygen and nitrogen species (RONS) in plasma activated water.

3. Results and discussion

The transmitted spectra of untreated DI water I_0 and PAW I were measured between 190 and 340 nm. The transmitted spectra were converted into absorbance (*Abs*) using an equation (1) below,

$$Abs = -log\left(I/I_0\right). \quad (1)$$

The transmittance of PAW decreased across a specific UV range between 190 nm and 250 nm; no other intensity changes in the visible and near-infrared range between 400 and 900 nm were measured.

Fig. 2a shows a schematic of plasma jet irradiation for DI water (4 mL). Transmittance is decreased as a function of time as shown in Fig. 2b. Using eq. (1) transmittance was converted into absorbance, we observed absorption spectra having a broad width of ~30 nm and the peak at around 206 nm. A close inspection of Fig. 2c shows there is a peak shift: the absorption peak wavelength became shorter from 207.4 nm to 205.8 nm as function of time and eventually, it became stable at the peak wavelength of 205.8 nm after 20 min exposure to the plasma jet irradiation. The absorbance is also increased as function of time. It should note that the negative absorbance of the case of the direct APPJ exposure (10 min) at short wavelength range below 200 nm was caused by helium gas flow reduced O_2 (aq.) concentration in the liquid [8].

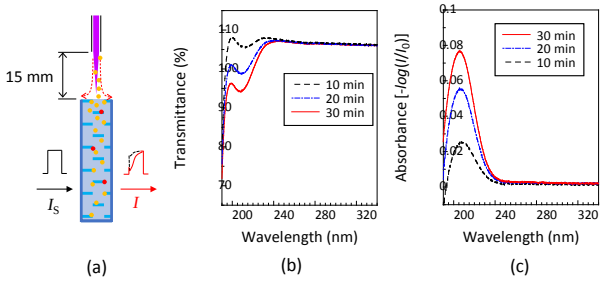

Fig. 2. (a) schematic of in-situ measurement of absorption spectra of DI water by a direct irradiation of APPJ, (b) transmittance of PAW as function of time and (c) converted absorbance from the transmittance.

Here we discuss the chemical composition of the PAW. As mentioned above, it is open reported that the long-living RONS typically H_2O_2 and NO_x are in PAW. However there is no report of UV absorption spectroscopy at the short wavelength range. Thus we measured the absorption spectra for diluted H_2O_2, HNO_3, and $NaNO_2$, respectively, with several different concentrations. Typical absorption spectra of the three reference solutions are shown in Fig. 3. We see the both $NaNO_2$ and HNO_3 have a broad width and absorption peaks between 200 and 210 nm, while H_2O_2 has no peak in the region. The both absorption profiles of $NaNO_2$ and HNO_3 are very similar to the absorbance spectrum of PAW in Fig. 2c. However NO_x cannot clearly explain the absorption tail at longer wavelength over 250 nm, H_2O_2 should be included in PAW. From the measurement of reference solutions, it is believed that the most RONS generated in the plasma-air interaction and transported by the gas flow [9].

Fig. 4a shows a simple experiment with a quartz barrier which placed on the top of DI water filled in the cuvette to block the gas flow but to transmit UV photons mainly related 2nd Positive N_2. Figs. 4b for the transmittance and 4c for absorbance show no significant absorption. The result indicated high energy UV photons play a minor role to generate reactive species in PAW. We also confirmed that there are no significant effect of UV photons using three standard D_2, Xe arc, and mercury lamps.

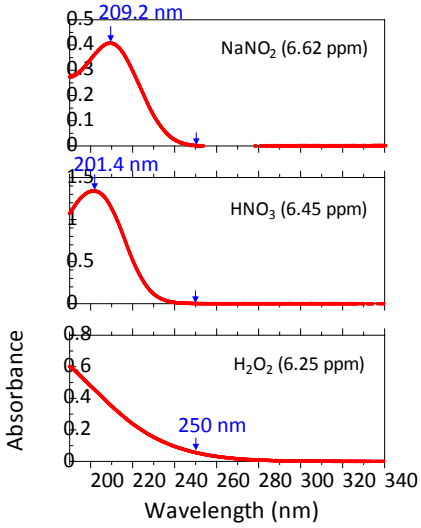

Fig. 3. Absorbance spectra of reference solutions (a) $NaNO_2$ (6.62 ppm), (b) HNO_3 (6.45 ppm), and (c) H_2O_2 (6.25 ppm) diluted in DI water, respectively.

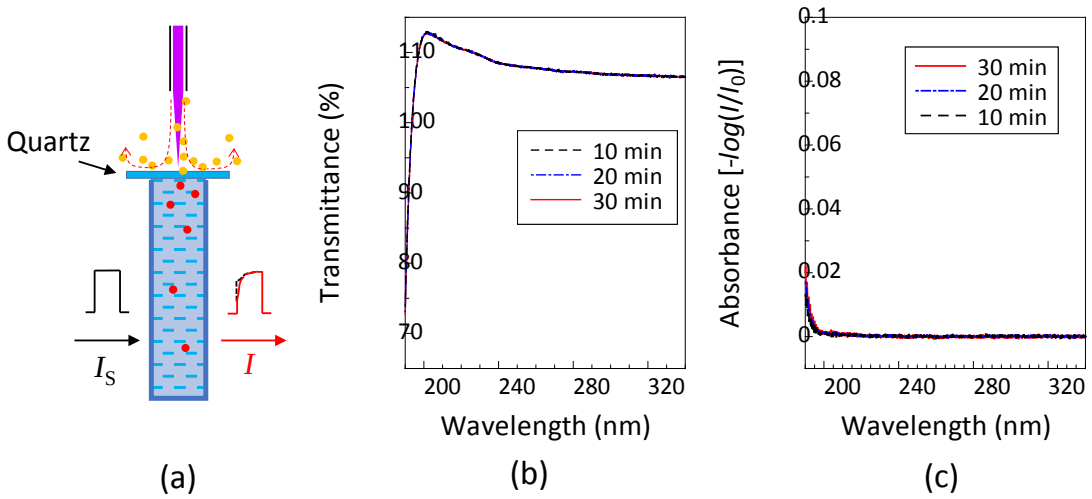

Fig. 4. (a) schematic of in-situ measurement of absorption spectra of DI water by an irradiation of APPJ onto a quartz plate, (b) transmittance of DI water as function of time and (c) converted absorbance from the transmittance.

4. Conclusions

Using an in-situ absorption spectroscopy we successfully measured UV absorption of PAW induced by an APPJ irradiation. The absorption spectrum has a simple spectral profile indicated its simple chemical composition of NO_x and H_2O_2. Using a quartz barrier it remarked the RONS were generated by emerging plasma-ambient air interaction and the He gas flow played a very important role in the transportation of plasma-generated RONS into DI water.

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