The fate of plasma-generated oxygen atoms in aqueous solutions: non-equilibrium atmospheric pressure plasmas as an efficient source of atomic O\textsubscript{(aq)}

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Non-equilibrium radio-frequency driven atmospheric-pressure plasma in He/0.6%O\textsubscript{2} gas mixture has been used to study the reaction mechanism of plasma-generated oxygen atoms in aqueous solutions. The effluent from the plasma source operated with standard and \textsuperscript{18}O-labeled O\textsubscript{2} gas was used to treat water in the presence of phenol as a chemical probe. Comparing the mass spectrometry and gas chromatography-mass spectrometry data of the solutions treated with plasma under normal and labeled oxygen provides clear evidence that O\textsubscript{(aq)} originating from the gas phase enters the liquid and reacts directly with phenol, without any intermediate reactions. Additionally, the atmospheric-pressure plasma source demonstrates great potential to be an effective source of O\textsubscript{(aq)} atoms without the requirement for any precursors in the liquid phase.

This lack of data is due to several reasons; it is difficult to generate O atoms in water or aqueous solutions. For example, O\textsubscript{(aq)} atoms are believed not to be produced in electron-initiated processes in radiation chemistry,\textsuperscript{7} where the dominant channel of electron recombination with water clusters such as H\textsubscript{2}O\textsuperscript{−} or H\textsuperscript{+}(H\textsubscript{2}O\textsubscript{2}) are H atoms and water molecules. Still, they have been detected in water radiolysis studies,\textsuperscript{8,9} but without knowing their origin at that time. The triplet \textsuperscript{3}OH + \textsuperscript{3}OH recombination has been proposed recently\textsuperscript{10} as the possible source of reactions for O\textsubscript{(aq)} atoms, where high concentrations of \textsuperscript{3}OH radicals are generated. Still it is not clear whether O\textsubscript{(aq)} can be generated by direct dissociation or in reactions involving water. For the quantitative studies of reactivity, O\textsubscript{(aq)} has been generated by laser flash photolysis of oxoanions (such as ClO\textsuperscript{−}, ClO\textsubscript{2}\textsuperscript{−}, or BrO\textsubscript{3}\textsuperscript{−})\textsuperscript{11} or from irradiated dibenzothiophene-S-oxide (DBTO) derivatives.\textsuperscript{12} O\textsubscript{(aq)} was also suggested to be the precursor of the O\textsubscript{2} generated in \gamma-ray irradiated FeSO\textsubscript{4}–CuSO\textsubscript{4} solutions.\textsuperscript{13} O atoms cannot be easily generated through dissociation of water and mirrors the case for non-equilibrium (cold) atmospheric plasmas (briefly introduced later), where the humid gas mixture generates preferentially OH radicals and hydrogen peroxide and not O atoms.\textsuperscript{14,15} Only dry gas mixtures containing oxygen molecules (He/O\textsubscript{2} or Ar/O\textsubscript{2}) leads to the production of O atoms and, subsequently, ozone.\textsuperscript{16–19} Thus a general method to generate atomic O\textsubscript{(aq)} without the involvement of chemical precursors would be of significant value.

Another reason for the lack of data for atomic O\textsubscript{(aq)} reactivity is probably due to the fact that it was believed to react rapidly

Introduction

Reactive oxygen species (ROS) such as \textsuperscript{1}OH radical, superoxide (O\textsubscript{2}\textsuperscript{−}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), ozone (O\textsubscript{3}), or singlet oxygen (\textsuperscript{3}O\textsubscript{2}) play a crucial role in various areas such as regulation of other ROS, but only 8 records for O\textsubscript{(aq)}\textsuperscript{1–6} have been recorded in the Solution Kinetics Database, which contains over 2500 records can be illustrated by the number of records in the NDRL/NIST database. Moreover, very little is known about the reactivity of atomic oxygen, which has been detected in water radiolysis studies,\textsuperscript{8,9} but without knowing their origin at that time. The triplet \textsuperscript{3}OH + \textsuperscript{3}OH recombination has been proposed recently\textsuperscript{10} as the possible source of reactions for O\textsubscript{(aq)} atoms, where high concentrations of \textsuperscript{3}OH radicals are generated. Still it is not clear whether O\textsubscript{(aq)} can be generated by direct dissociation or in reactions involving water. For the quantitative studies of reactivity, O\textsubscript{(aq)} has been generated by laser flash photolysis of oxoanions (such as ClO\textsuperscript{−}, ClO\textsubscript{2}\textsuperscript{−}, or BrO\textsubscript{3}\textsuperscript{−})\textsuperscript{11} or from irradiated dibenzothiophene-S-oxide (DBTO) derivatives.\textsuperscript{12} O\textsubscript{(aq)} was also suggested to be the precursor of the O\textsubscript{2} generated in \gamma-ray irradiated FeSO\textsubscript{4}–CuSO\textsubscript{4} solutions.\textsuperscript{13} O atoms cannot be easily generated through dissociation of water and mirrors the case for non-equilibrium (cold) atmospheric plasmas (briefly introduced later), where the humid gas mixture generates preferentially OH radicals and hydrogen peroxide and not O atoms.\textsuperscript{14,15} Only dry gas mixtures containing oxygen molecules (He/O\textsubscript{2} or Ar/O\textsubscript{2}) leads to the production of O atoms and, subsequently, ozone.\textsuperscript{16–19} Thus a general method to generate atomic O\textsubscript{(aq)} without the involvement of chemical precursors would be of significant value.

Another reason for the lack of data for atomic O\textsubscript{(aq)} reactivity is probably due to the fact that it was believed to react rapidly
with water to form two *OH radicals, even if this process is
thermodynamically unfavorable. This reaction was also
observed in classical force-field molecular dynamics (MD)
simulations of O radicals in liquid water.20 Using more accurate
density-functional based tightbinding (DFTB) force potential to
evaluate the interactions of O atoms in bulk water, it was found
that the O atoms form oxywater for singlet configuration or they
remain stable in solution throughout the simulated time scale
of 10 ps for triplet configuration.21 Car-Parrinello MD simulations
have demonstrated that O (aq) is stable in liquid with an
energy barrier of 10 kcal mole−1 and can even be generated in a
triplet *OH + *OH recombination reaction.10 Other researchers
have also suggested O atoms as reaction partners in aqueous
solutions. Korang et al. have concluded that photo-induced
strand cleavage of pUC19 plasmid DNA (monitored by gel
electrophoresis) was at least partially caused by atomic O.12
The plasma generated O atoms and their subsequent reactions
in the aqueous environment have been proposed by authors
using non-equilibrium atmospheric plasma jets22,23 including
our initial work with phenol as a chemical probe.16,24

Non-equilibrium (cold) atmospheric plasmas (CAPs) have
attracted much attention from researchers in recent years
because of their ability to generate high densities of reactive
species at room temperature without the need for expensive
vacuum systems.25 This reactivity is achieved by selective heat-
ing of electrons by electric fields, leaving the heavy particles
(ions, neutral species) cold. The energetic electrons generate
high densities of internally excited species (metastables) or
radicals in inelastic electron-impact excitation and dissociation
collisions, respectively. These reactive species can be used in
many applications such as water treatment, generation of
nanoparticles, material syntheses, or plasma medicine.26–35

The CAPs exist in many variants, with the most abundant being
dielectric barrier discharges (DBD), DBD jets, radio-frequency
operated jets or even microwave plasma sources.36–41 Most
of these sources are operated in a noble gas with a small
admixture of a molecular precursor, but some of them, espe-
cially the DBD’s can be operated in ambient air without any
need for a gas supply.

Herein we report on the fate of oxygen atoms after their
generation using plasma in the gas phase and after their
transfer into aqueous solution with phenol as chemical probe.42
The main question is whether O atoms can exist as a
stable species in water and diffuse towards dissolved (organic
or other) molecules to react directly, or whether the O atoms are
reacting with water first:

\[
O_{(aq)} + H_2O_{(aq)} \rightarrow 2*OH_{(aq)} \quad (1)
\]

In the latter scenario the subsequent reactions, such as the
hydroxylation of phenol, will involve the newly formed *OH
radicals. Employing the 18O2 isotope, we can distinguish
between these two cases. In the first case, stable O(aq) atoms
will have a longer lifetime, will be able to diffuse into the
solution and will be available to interact directly with phenol
without any intermediate reactions. The subsequent oxidation
reaction should result in the incorporation of predominantly
18O atoms when a He/18O2 plasma is used. The latter case
would result in equal amounts of 16O and 18O among the newly
formed hydroxylated products because half of the reacting *OH,
in this case, would be derived from water molecules involved in
the reaction (1) and therefore will contribute 16O atoms.

### Results and discussion

The plasma source used in this work is an earlier version of the
COST reference jet41 (see Fig. 1 and ESI† for more details). It is a
capacitively coupled plasma source with two stainless steel
electrodes at 1 mm distance in between two quartz glass plates.
One of the two electrodes is powered by a 13.56 MHz sinusoidal
voltage. As feed gas, helium with the flow of 1.4 standard liters per
minute (slm) is used and admixed with 0.6% of molecular oxygen
(18O2) or molecular oxygen isotope (16O2, 99 atomic percent 18O).

The O2 admixture of 0.6% was previously shown to yield the
maximum O density of 8 × 1014 cm−3 when measured 4 mm away
from the jet nozzle by molecular beam mass spectrometry.43

Simulation of the gas flow, diffusion/convection transport of O
atoms, and the gas phase recombination reactions have shown that
more than 50% of O atoms leaving the plasma source reach the
surface of the liquid and the integrated flux of O atoms to the liquid
surface is around 9 × 1015 s−1.16 It should be noted that the
generated plasma is strongly non-thermal. Only electrons are heated
by electric fields, and the gas temperature stays below 40 °C.41

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**Fig. 1** (a) Plasma jet with He gas in operation. (b) Scheme of the closed
treatment chamber for plasma liquid treatment under atmospheric pressure.
(c) Plasma jet in the chamber during solution treatment.
Plasma treatments of aqueous solutions were performed in a small glass chamber with a closed atmosphere, without contact to the ambient air. The shear forces between the He/O₂ flow and liquid surface result in the movement of the liquid. The short-lived reactive species can react, therefore, with the whole volume of the liquid in a matter of minutes.¹⁶

Two different phenol concentrations, 0.5 mM and 5 mM, were treated for four and eight minutes, respectively, by the plasma feed gas containing ¹⁶O₂ or labeled ¹⁸O₂ (referred to unlabeled and labeled treatments respectively).

When 0.5 mM phenol solution is treated with the exhaust gas of the He/O₂ plasma, it starts to degrade at a rate of around $5 \times 10^{15}$ s⁻¹ into the following reaction products: catechol (CC), resorcinol (RS), hydroquinone (HQ), and hydroxy-1,4-benzoquinone (HBQ).¹⁶ The maximum concentrations of these products are reached after four minutes of treatment. We have argued that the observed chemistry in the liquid phase is due to the plasma-generated oxygen atoms, which enter the liquid and react with phenol.

To distinguish among the oxidized products with different O isotopes, high-resolution mass spectrometry (MS) and gas chromatography-mass spectrometry (GC-MS) were employed to determine the composition of treated solutions. Details of the treatment procedure and both diagnostics are provided in ESI.†

The mass spectra of untreated samples and samples treated with He/¹⁶O₂ plasma are shown in Fig. 2(a) and (b), respectively. The treatment results in appearance of new peaks. The molecular ion peak of $m/z = 109.03$ corresponds to CC, RS, or HQ (diols, all mass 110). Its relative abundance compared to the phenol peak is about 148%. An additional molecular ion peak at $m/z = 123.01$ corresponds to HBQ (mass 124 amu) with 45% abundance. The molecular ion peak of $m/z = 125.02$, which corresponds to phosphogluconol (C₅H₁₀O₄, mass 126 amu), has about 71% abundance. Fig. 2(c) shows the mass spectrum of 0.5 mM phenol solution treated with He/¹⁸O₂ plasma. Depending on whether one or two heavy O atoms were incorporated, the compounds are two or four mass units heavier than those treated with He/¹⁸O₂ plasma in Fig. 2(b).

The treatment of 0.5 mM phenol solutions with two different types of plasmas, He/¹⁶O₂ plasma and He/¹⁸O₂ plasma and study of the products of the treatment using MS led to the following observations (see also Table S2 in the ESI†):

(a) The ratio of labeled diols (HQ, CC, or RS, $m/z = 111$) to unlabeled diols ($m/z = 109$) changes from 0.005 for He/¹⁶O₂ treatment to 11.2 for He/¹⁸O₂. The former ratio is close to the natural concentration of the ¹⁸O isotope (0.002), and the latter one shows that 92% of diols are formed with ¹⁸O isotope in the He/¹⁸O₂ treatment. Considering the fact that the purity of the oxygen isotope was around 99% and that any oxygen-containing impurity in the gas phase (O₂, H₂O vapor) will lead to the formation of the unlabeled O or OH groups and also unlabeled diols, we can conclude that O atoms are stable in the pure water and can be, therefore, directly involved in the formation of diols in the aqueous phenol solutions.

(b) The ratio HBQ labeled with two ¹⁸O atoms ($m/z = 127$) to normal HBQ ($m/z = 123$) is around 0.01 for He/¹⁶O₂ treatment and increases to 10.86 for He/¹⁸O₂ treatment. These ratios are very close to the ratios for diols and fully corroborate the conclusion about the stability of the O atoms in an aqueous environment.

(c) The ratio of triols labeled with two isotopes to normal triols changes from 0.01 to 3 when normal treatment changes to the treatment with ¹⁸O₂. Again, a clear trend is observed. The ratio 3 is lower than in the case of diols or HBQ because $m/z = 125$ mass used to estimate the number of unlabeled triols can also contain HBQ molecules labeled just with one ¹⁸O (again due to finite 99% purity of the gas and due to impurities), reducing the ratio compared to the diol case. Considering this effect, the measurement of triols corroborates our conclusion as well.

These MS results provide clear evidence that atomic O can survive in the aqueous solution and directly react with the phenol, without reaction (1) being involved.

Ozone is another plasma chemistry product generated in large quantities in the gas phase by the used He/O₂ plasma. However, as we have discussed previously,¹⁶ its contribution to the aqueous chemistry is negligible due to its very low Henry constant resulting in concentrations in the solution below 0.6 μM. The absence of ozone was corroborated in this work by the absence of cis,cis-muconic acid, a known product of the reaction of ozone with phenol, in the high precision liquid chromatography (HPLC) measurements (detection limit <0.25 μM).

The samples with 5.0 mM phenol concentration treated for 8 minutes were analyzed by GC-MS. The higher phenol concentration and longer treatment is necessary because the sensitivity of the GC-MS is lower than that of the MS. Fig. 3(a) shows the

![Fig. 2](image-url) Abundance relative to the phenol peak as measured by mass spectrometry in negative ionization mode for (a) untreated sample of 0.5 mM phenol solution, (b) 0.5 mM phenol solution treated with He/¹⁶O₂ plasma, and (c) 0.5 mM phenol solution treated with He/¹⁸O₂ plasma. The spectra represents an average of two or three individual spectra recorded for the repetitions.
only CC and HQ were detectable. It should be, however, noted that RS had been identified in our previous work as one of the products after treatment of 0.5 mM phenol solution. Its absence here is very probably due to higher phenol concentration (5 mM) and treatment time that have not been optimized to reach maximum concentration of the products. The RS concentration stays, therefore, very probably under the detection limit of this diagnostics.

(b) The ratio of labeled CC (mass 112) compared to unlabeled (mass 110) changes from 0.01 for normal treatment to 16.7 for treatment with He/18O2 plasma. Again, most of the CC (~95%) is formed labeled in the latter treatment in agreement with MS measurements. The higher observed ratio here, compared to MS results, after the labeled treatment can be very probably attributed to the uncertainty in the subtraction of the signal component due to the ion fragment at the mass 110. Additionally, the small change of the impurity concentration in the feed gas can result in the observed higher ratio.

(c) The ratio of labeled HQ (mass 112) compared to unlabeled (mass 110) changes from 0.01 for normal treatment to 19.4 for treatment with He/18O2 plasma. Again, most of HQ (96%) is formed labeled in the latter treatment, in agreement with other results. The uncertainties in the subtraction of the baseline and signal due to fragment ion and the possible change of the impurity level are probably responsible for the higher ratio of the labeled products.

The analysis of the aqueous phenol solutions by using two different diagnostics shows clearly that the mass spectra of the solution treated with He/18O2 plasma regarding phenol byproducts is dominant for products attached with 18O atoms. This result imply that the plasma-generated O atoms are transferred from the gas phase into the phenol solutions and react directly with phenol generating CC, RS & HQ products. These observations are fully consistent with our conclusion from the previous work, which has been drawn based on indirect evidence16 and agrees with theoretical predictions,16 where the authors concluded that the equilibrium clearly favors the left-hand side of reaction (1), implying a slow isotope exchange. We should note here that the hydrogen atom on the new OH group can either originate from the aromatic ring or from water and that our methods were not able to distinguish between these two pathways.

We expect that oxidizing reactions of O(aq) atoms are at least as fast as reactions of *OH radicals due to its increased reactivity as a diradical.44 For example, the reactions of *OH with phenol, CC, and HQ have reaction rate constants of 6.6 × 10^8 M^{-1} s^{-1}, 1.1 × 10^8 M^{-1} s^{-1}, and 1.0 × 10^9 M^{-1} s^{-1}, respectively.

Assuming the same reaction rate constants for O(aq) atoms as for *OH radicals the reaction lifetime of O in phenol solution with 0.5 mM phenol concentration will be around 53 ns. This time is much shorter than the reaction lifetime due to recombination reaction:

\[ O_{(aq)} + O_{2(aq)} \rightarrow O_3(aq), \]  

which is 32 μs when calculated with reported reaction rate constant5 of 4.0 × 10^9 M^{-1} s^{-1} and with 8 μM O2 concentration,
Conclusions

In summary, we have employed non-equilibrium radio-frequency driven atmospheric-pressure plasma in He/0.6%O₂ gas mixture to study the reaction mechanism of plasma-generated oxygen atoms in aqueous solutions. The gas mixture with O₂ as the only reactive component, without humidity and influence of ambient atmosphere, leads preferentially to the production of O₉(gas) atoms in the plasma. The plasma-generated O₉(gas) atoms enter the aqueous solution and initiate there chemical reactions. The experiments with ¹⁸O₂ isotope demonstrate that the O₉(aq) atoms react with phenol molecules directly, without dissociating water molecules in intermediate reactions. Additionally, the used atmospheric-pressure plasma source demonstrates its potential as an effective source of O₉(aq) atoms without the need for chemical precursors in the liquid phase or photolytic activation. Atmospheric plasma-based sources have, therefore, a very large potential for being used in future studies of O₉(aq) reactivity in solutions and in future applications based on reactions of O₉(aq) radicals for applications such as waste remediation or therapeutic treatments.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1  W. G. Brown and E. J. Hart, J. Phys. Chem., 1978, 82, 2539.
2  E. J. Hart and W. G. Brown, J. Phys. Chem., 1980, 84, 2237.
3  E. J. Hart and W. G. Brown, Radiat. Phys. Chem., 1980, 15, 163.
4  M. C. Sauer, W. G. Brown and E. J. Hart, J. Phys. Chem., 1984, 88, 1398.
5  U. K. Klänning, K. Sehested and T. Wolff, J. Chem. Soc., Faraday Trans. 1, 1984, 80, 2969.
6  NDRL/NIST Solution Kinetics Database, NIST Standard Reference Database 40 (Web Version), A compilation of kinetics data on solution-phase reactions, 2002.
7  B. C. Garrett, D. A. Dixon, D. M. Camaióni, D. M. Chipman, M. A. Johnson, C. D. Jonah, G. A. Kimmel, J. H. Miller, T. N. Rescigno, P. J. Rossky, S. S. Xanthes, S. D. Colson, A. H. Laufer, D. Ray, P. F. Barbara, D. M. Bartels, K. H. Becker, K. H. Bowen, S. E. Bradforth, I. Carmichael, J. V. Coe, L. R. Corrales, J. P. Cowin, M. Dupuis, K. B. Eisenthal, J. A. Franz, M. S. Gutowski, K. D. Jordan, B. D. Kay, J. A. Laverne, S. V. Lymar, T. E. Maday, C. W. McCurdy, D. Meisel, S. Mukamel, A. R. Nilsson, T. M. Orlando, N. G. Petrik, S. M. Pimbllott, J. R. Rustad, G. K. Schenter, S. J. Singer, A. Tokmakoff, L.-S. Wang, C. Wettig and T. S. Zwier, Chem. Rev., 2005, 105, 355.
8  W. G. Brown and E. J. Hart, Radiat. Res., 1972, 51, 249.
9  W. G. Brown, E. J. Hart and M. C. Sauer, Radiat. Res., 1978, 76, 533.
10 E. Codorniu-Hernández, K. W. Hall, A. D. Boese, D. Ziemenianowicz, S. Carpendale and P. G. Kusalik, J. Chem. Theory Comput., 2015, 11, 4740.
11 J. M. Carraher and A. Bakac, Phys. Chem. Chem. Phys., 2014, 16, 19429.
12 J. Korang, I. Emahi, W. R. Grither, S. M. Baumann, C. A. Vasko, D. X. Liu, E. M. van Veldhuizen, F. Iza and J. M. Carraher and A. Bakac, Phys. Chem. Chem. Phys., 2014, 16, 19429.
13 E. Bjergbakke and E. J. Hart, Radiat. Res., 1971, 45, 261.
14 C. A. Vasko, D. X. Liu, E. M. van Veldhuizen, F. Iza and P. J. Bruggeman, Plasma Chem. Plasma Process., 2014, 34, 1081.
15 G. Willems, J. Benedikt and A. v. Keudell, J. Phys. D: Appl. Phys., 2017, 50, 335204.
16 M. M. Hefny, C. Pattyn, P. Lukes and J. Benedikt, J. Phys. D: Appl. Phys., 2016, 49, 404002.
17 D. Ellerweg, A. von Keudell and J. Benedikt, Plasma Sources Sci. Technol., 2012, 21, 24005.
18 S. Zhang, W. van Gaens, B. van Gessel, S. Hofmann, E. van Veldhuizen, A. Bogaerts and P. Bruggeman, J. Phys. D: Appl. Phys., 2013, 46, 205202.
19 S. Reuter, J. Winter, A. Schmidt-Bleker, D. Schroeder, H. Lange, N. Knake, V. Schulz-von der Gathen and K.-D. Weltmann, Plasma Sources Sci. Technol., 2012, 21, 24005.
20 M. Yusupov, E. C. Neys, P. Simon, G. Berdiyvorov, R. Snoeckx, A. C. T. van Duin and A. Bogaerts, J. Phys. D: Appl. Phys., 2013, 47, 25205.
21 C. C. W. Verlackt, E. C. Neys and A. Bogaerts, J. Phys. D: Appl. Phys., 2017, 50, 11LT01.
22 Y. Gorbanev, D. O’Connell and V. Chechik, Chemistry, 2016, 22, 3496.
23 K. Wende, P. Williams, J. Dalluge, W. van Gaens, H. Aboubakr, J. Bischof, T. von Woedtke, S. M. Goyal, K.-D. Weltmann, A. Bogaerts, K. Masur and P. J. Bruggeman, Biointerphases, 2015, 10, 29518.
24 S. Bekeschus, K. Wende, M. M. Hefny, K. Rödder, H. Jablonowski, A. Schmidt, T. von Woedtke, K.-D. Weltmann and J. Benedikt, Sci. Rep., 2017, 7, 2791.
25 T. Yokoyama, M. Kogoma, S. Kanazawa, T. Moriwaki and S. Okazaki, J. Phys. D: Appl. Phys., 1990, 23, 374.
26 K. Oehmigen, M. Hähnel, R. Brandenburg, C. Wilke, K.-D. Weltmann and T. von Woedtke, Plasma Processes Polym., 2010, 7, 250.
27 A. M. Hirst, M. S. Simms, V. M. Mann, N. J. Maitland, D. O’Connell and F. M. Frame, Br. J. Cancer, 2015, 112, 1536.
28 V. Arora, V. Nikhil, N. K. Suri and P. Arora, Dentistry, 2014, 4, 189.
29 J. Benedikt, A. Hećimovic, D. Ellerweg and A. von Keudell, J. Phys. D: Appl. Phys., 2012, 45, 403001.
30 H. A. Aboubakr, P. Williams, U. Gangal, M. M. Youssef, S. A. A. El-Sohaimy, P. J. Bruggeman and S. M. Goyal, Appl. Environ. Microbiol., 2015, 81, 3612.
31 J. Pawlat, Eur. Phys. J.: Appl. Phys., 2013, 61, 24323.
32 J. Benedikt, V. Raballand, A. Yanguas-Gil, K. Focke and A. von Keudell, Plasma Phys. Controlled Fusion, 2007, 49, B419.
33 J. Patel, L. Nemcova, P. Maguire, W. G. Graham and D. Mariotti, Nanotechnology, 2013, 24, 245604.
34 G. Fridman, G. Friedman, A. Gutsol, A. B. Shekhter, V. N. Vasilets and A. Fridman, Plasma Processes Polym., 2008, 5, 503.
35 E. Edengeiser, J.-W. Lackmann, E. Bründermann, S. Schneider, J. Benedikt, J. E. Bandow and M. Havenith, J. Biophotonics, 2015, 8, 918.
36 L. Schaper, S. Reuter, J. Waskoenig, K. Niemi, V. S.-v. d. Gathen and T. Gans, J. Phys.: Conf. Ser., 2008, 162, 012013.
37 X. Li, Y. Li, P. Zhang, P. Jia and L. Dong, Sci. Rep., 2016, 6, 35653.
38 R. Brandenburg, Plasma Sources Sci. Technol., 2017, 26, 53001.
39 A. A. Fridman, Plasma medicine, John Wiley et Sons, Chichester, West Sussex, UK, 2013.
40 L. Bárdos and H. Baránková, Thin Solid Films, 2010, 518, 6705.
41 J. Golda, J. Held, B. Redeker, M. Konkowski, P. Beijer, A. Sobota, G. Kroesen, N. S. J. Braithwaite, S. Reuter, M. M. Turner, T. Gans, D. O’Connell and V. Schulz-von der Gathen, J. Phys. D: Appl. Phys., 2016, 49, 84003.
42 P. Lukes, E. Dolezalova, I. Sisrova and M. Clupek, Plasma Sources Sci. Technol., 2014, 23, 15019.
43 D. Ellerweg, J. Benedikt, A. von Keudell, N. Knake and V. Schulz-von der Gathen, New J. Phys., 2010, 12, 13021.
44 E. Codorniu-Hernández, K. W. Hall, D. Ziemenianowicz, S. Carpendale and P. G. Kusalik, Phys. Chem. Chem. Phys., 2014, 16, 26094.