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Full Length Article

# Hydrophilization of rice seeds by plasma treatments – Super-hydrophilic surface finish and hydrophobic recovery

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ABSTRACT

The hydrophobic character of rice seeds protects them from quick water adsorption and, thus, premature germination. This property is, however, a drawback in modern agriculture, where rapid and uniform germination represents a high-quality trait. A method for rapid hydrophilization of the Lomello variety of rice is presented. The rice seeds were treated with low-pressure gaseous plasma to tailor the wettability. The treatment of seeds with hulls with oxygen plasma afterglow enabled the super-hydrophilic surface finish within 10 ms. Such extremely fast hydrophilization was attributed to irreversible surface oxidation by neutral oxygen atoms whose flux onto the seeds was approximately $3 \times 10^{23}$ $m^{-2}s^{-1}$. Dehulled seeds were made super-hydrophilic by subsequent treatments with hydrogen and oxygen plasma, and the required dose of O atoms was between $2 \times 10^{23}$ and $6 \times 10^{24}$ $m^{-2}$. Larger doses caused a loss of the super-hydrophilicity. Hydrophilization kinetics is proposed and supported by measuring surface wettability, morphology, and composition using various techniques. The hydrophobic recovery of seeds with hulls is marginal within the first few days after plasma treatments, but dehulled seeds lose the super-hydrophilic surface finish within a few minutes after the plasma treatment when stored at ambient conditions.

## 1. Introduction

Rice (*Oryza sativa*) is one of the most produced crops in the world and feeds billions of people daily [1]. It provides 20 % of the global caloric supply, representing more than the contribution of wheat and maize [2]. Rice is primarily used for food, whereas a large portion of wheat and maize are used for feed [3]. The relevance of rice in the agri-food system can derived from its power to shape economies, diets, culture, and food security, especially in countries from Asia, Sub-Saharan Africa, and South American regions [4]. In this context, seed quality is highly important because it safeguards rice yields. High seed quality can be responsible for a 5–20 % production increase due to improved germinability, germination speed, uniformity, and growth vigor. Additionally, high-quality seeds are recognized for better tolerance to pests and diseases and can aid in weed management [5].

Numerous rice varieties are grown in different world regions, depending on the soil, climate, and water supply. The major European rice region is Lombardy, and one of the locally cultivated varieties is Lomello. This variety is characterized by a long, semi-tapered, and pearly grain. The caryopsis measures 6.8 mm in length, and the plant vegetative cycle is about 160 days. The variety is characterized by good germinability, fair tolerance to lodging, and low tolerance to fungal infections [6]. Recent studies reported Lomello as a variety resistant to drought stress at germination [7] as well as to other abiotic stress during

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plant growth due to better functioning of the PSII photosystem [8].

Rice is hydrophobic and will float when placed in water. The hydrophobic character of the rice protects the seeds from unwanted water adsorption. This trait is important during storage when low moisture levels (10–12 %) are indicated to preserve rice seed quality [9]. During germination, water uptake proceeds slowly, which may be a drawback in modern agriculture. Furthermore, due to climate changes and thus increasingly longer periods of drought, slow water imbibition inhibits germination in case of occasional rare rainfall.

The hydrophobic character of the rice seeds could be disadvantageous when priming the seeds, i.e., stimulating factors that would lead to rapid and uniform germination after sowing. Seed priming is a versatile strategy to provide alternative and sustainable solutions to enhance seed germination. It is defined as a pre-germination treatment used to allow controlled hydration for the seeds to reach the early stages of germination without radicle protrusion [10,11]. Multiple seed priming techniques are used (i.e., hydropriming, osmopriming, halopriming, biopriming, chemical or physical priming). Most of them are based on soaking seeds in liquid solutions while coating them with nutrients and bacteria is also encountered; additionally, other methods include the use of physical agents like low doses of microwaves, sonication, or irradiation [12,13]. The effectiveness of each method depends on treatment duration, water potential, and physiological state of the seed [14,15].

An alternative to classical methods for rice seed priming is the application of non-equilibrium gaseous plasma. Such plasma is characterized by a rather low gas temperature (often close to room temperature) and high chemical reactivity. The high reactivity is due to the presence of reactive species with high potential energy, such as neutral atoms in the ground and metastable excited states, molecules in metastable states, and positively charged molecular and atomic ions. The type of reactive plasma species depends on the type of gas or gas mixture, and the concentration of plasma species depends on the plasma parameters, which in turn depend on the type of electric discharge used for sustaining gaseous plasma and peculiarities of the plasma reactors including the dimensions and materials facing the plasma. The plasma species interact chemically with the surfaces of any organic material, causing irreversible chemical modification of the surfaces of organic materials. The plasma treatment induces a biological response in the seeds too, but the exact mechanisms are still not well understood [16].

Several reports on the treatment of rice seeds with non-equilibrium plasma have appeared in scientific literature. Srisonphan et al. [17] treated rice seeds with atmospheric pressure plasma sustained in a mixture of argon and air and reported a super-hydrophilic surface finish after half a minute of plasma treatment. To the best of our knowledge, this is the only scientific document that reports the hydrophilicity of the plasma-treated rice seeds. The water imbibition time was approximately 17 min for untreated seeds and gradually decreased with increasing plasma treatment time. After treating the seeds with plasma for 15 s, the imbibition time was 5 min and approached approximately 1.5 min for prolonged plasma treatments. In another paper, the same authors reported an increased germination rate for plasma-treated rice seeds [18]. The plasma treatment was also beneficial for suppressing the proliferation of fungi [19]. Penado et al. [20], on the other hand, found that plasma treatment of rice seeds significantly affected germ growth but not germination rate, but they used a powerful discharge to sustain the plasma in the air, so the conditions are not comparable. Mekarun et al. [21] treated rice seeds with a plasma sustained in bubbles inside water and found significant improvement in the germination rate. A 100 % germination was reported a day after the sowing of seeds treated for an hour with plasma inside the water, as compared to a 68 % germination rate for untreated seeds. However, such plasma treatment times are too long for application in modern agriculture.

Some authors sowed plasma-treated seeds in fields and reported various results. For example, Recek et al. [22] sowed different hybrid maize. In the harvest year 2020, the yield from plasma-treated seeds of hybrids P9537 and P9757 was three times larger than for untreated seeds, but the differences in the yield of other hybrids were statistically insignificant. They repeated the field experiments in 2021 and found statistically insignificant differences. Ruzic et al. [23] treated one hybrid only (the yellow dent corn hybrid) but the seeds were treated with plasma sustained by three completely different discharges. The seeds were sowed at six locations across central Illinois. They reported statistically insignificant results. The discrepancy is attributed to different conditions, such as soil, weather, and pests. Unlike laboratory, field experiments are time-consuming (only one harvest annually), and it is difficult to consider all the variables, so plasma agriculture is still in its infancy.

The brief literature survey indicates that plasma treatment could represent a means for rice priming, but there is a lack of systematic measurements of the wettability evolution of rice seeds and its correlation with the surface composition. Furthermore, the reported experimental configurations may not be scalable because of the peculiarities of the atmospheric pressure plasma sources and rather long treatment times [24]. In order to pave the way for possible application, we performed a detailed study on the wettability of a European variety of rice seeds (Lomello) using low-pressure gaseous plasma, which is scalable enough to meet agricultural demands. A simple treatment with oxygen atoms from oxygen plasma flowing afterglow and a two-step procedure that involved a pre-treatment with glowing hydrogen plasma, followed by oxygen atoms treatment, were elaborated.

## 2. Experimental details

### 2.1. Rice seeds

The rice seeds were obtained from the Plant Germplasm Bank at the University of Pavia (Italy), part of the Lombardy Seed Bank (Labecove Seed Bank, Laboratorio di Ecologia Vegetale, Italy). Seeds were maintained under standard seed bank conditions. Hulled (paddy rice) and dehulled (brown rice) seeds were used in these experiments. The seeds were dehulled manually by eliminating the external hull layer.

### 2.2. Experimental plasma reactor

The experimental plasma reactor enabled the treatment of seeds both in glowing plasma and plasma flowing afterglow. A set of experiments was performed using an oxygen plasma afterglow, and more systematic experiments were performed by the two-step plasma treatment: in the first step, the seeds were briefly treated with hydrogen plasma, and in the second step, the oxygen plasma afterglow was used, without breaking vacuum conditions. Such a treatment was adopted since it enables hydrophilization of all polymers, including a highly chemically resistant polymer polytetrafluoroethylene (PTFE) [25].

Rice seeds were treated in an experimental plasma reactor, as shown schematically in Fig. 1. The discharge tube was made from borosilicate glass. The tube length was 76 cm, and the internal diameter was 3.6 cm. On one side, the tube was pumped with a two-stage rotary vacuum pump with a nominal pumping speed of 80 $m^3 h^{-1}$ (Edwards, Burgess Hill, UK) and ultimate pressure below 1 Pa. Gases were introduced on the other side of the discharge tube via a mass flow controller. Hydrogen or oxygen were used in these experiments. Due to continuous pumping on one side and the introduction of gas on the other side of the discharge tube, the gas flowed through the discharge tube at high speed, estimated at approximately 7 $m s^{-1}$.

A water-cooled coil was mounted onto the discharge tube, as shown in Fig. 1. Also, the discharge tube was forced air-cooled to keep the temperature close to the room temperature even for the longest treatment times. The coil was connected to a matching network connected to a radio frequency (RF) generator with a standard coaxial cable. The RF generator operated at the standard industrial frequency of 13.56 MHz and adjustable output power of up to 1000 W. The matching network enabled impedance adjustment and, thus, maximization of the power

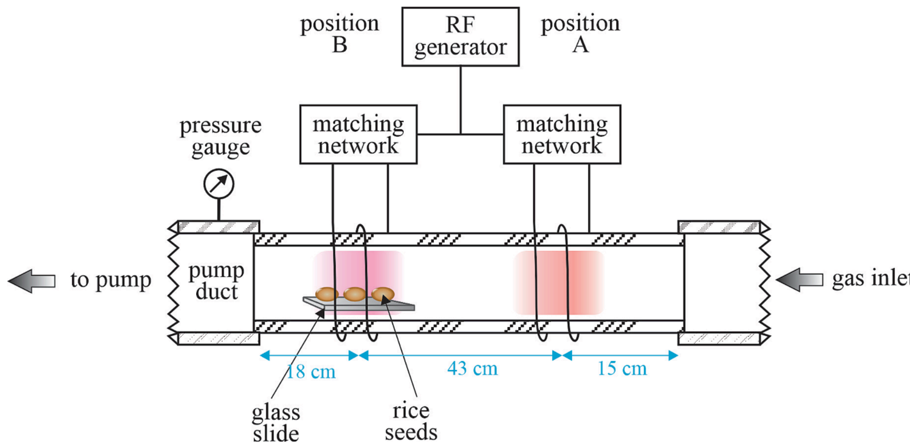


**Fig. 1.** Schematic of the experimental setup for rice seeds treatment in glowing hydrogen plasma (coil position marked as "position B") or oxygen plasma afterglow (coil position marked as "position A").

spent on sustaining plasma. The matching network was movable along the discharge tube, which enabled the positioning of the RF coil at any position along the tube. The rice seeds were always placed in the same position, approximately 18 cm from the pump duct, as shown in Fig. 1. This distance was selected to ensure a rather large flux of O atoms and to prevent the effect of short-leaving plasma species (like charged particles and VUV photons) during the seed treatment in the oxygen plasma afterglow. The coil was positioned either at the position of the rice seeds or 43 cm from the rice seeds in the gas upstream direction. Such a configuration enabled the treatment of rice seeds either directly in the dense plasma sustained within the coil (position "B" in Fig. 1) or approximately 40 cm away from the dense plasma downstream of the gas flow (position "A" in Fig. 1). The gas downstream of the plasma (at the position of rice seeds when the coil is at position "A" in Fig. 1) contains a marginal concentration of charged particles, and the irradiation with plasma-born photons is suppressed as compared to the position of seeds inside the dense plasma (position "A" in Fig. 1). Downstream gas is often referred to as flowing afterglow because it does not glow, but the concentration of relatively stable plasma radicals is almost as high as in the glowing plasma [26]. The seeds treated in plasma (RF coil at position "B") are, on the other hand, exposed to a flux of positively charged ions, electrons, metastables (both molecular and atomic), and neutral atoms in the ground electronic state. On the contrary, seeds placed into the flowing afterglow (RF coil at position "A") are treated practically only with neutral atoms in the ground state. The gas temperature in the afterglow is very close to room temperature, so the atoms only provide chemical interaction with organic matter, and the seeds do not heat up even for prolonged treatments. The seeds were always placed onto glass slides, as shown in Fig. 2. They are hardly visible in Fig. 3 because of the intense glowing plasma. Five seeds were treated simultaneously, but for the surface aging evaluation, 10 seeds were treated simultaneously.

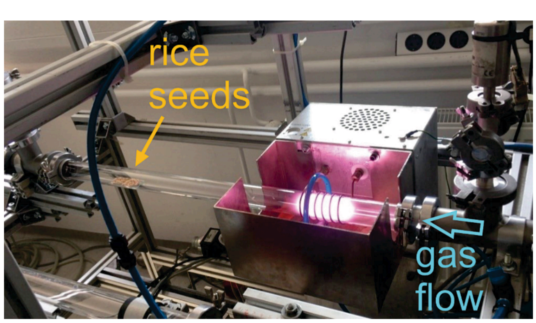


**Fig. 2.** A photo of the discharge tube when the RF coil is positioned away from the seeds so the seeds are treated in the oxygen plasma flowing afterglow.

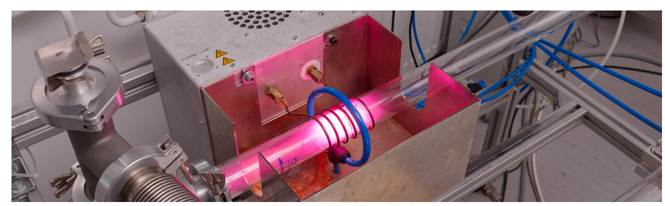

**Fig. 3.** Rice seeds in the glowing hydrogen plasma.

A photo of the discharge tube when the RF coil is in position "A" in Fig. 1 is shown in Fig. 2. The gas flow is indicated with an arrow in Fig. 2. The glowing plasma (oxygen is used in the case of the coil position "A") is limited to the volume within the RF coil since the plasma is sustained in the H-mode. Any capacitive coupling is to the flange upstream of the gas flow, so there is no plasma at the position where rice seeds are placed. Rice seeds in the afterglow are thus treated practically only with O atoms in the ground electronic state. The density of O atoms at the position of the rice seeds was determined with a catalytic probe (not shown in Fig. 2). Catalytic probes enable spatially resolved measurements of oxygen atom density in flowing afterglows [27]. Some materials exhibit catalytic activity for heterogeneous surface recombination of O atoms, so the material heats well above the ambient temperature. The heat dissipated on the surface is measured, and the O-atom density is calculated, taking into account that surface recombination is the predominant exothermic reaction. The recombination coefficient depends enormously on the type of material [28]. We used a probe made from oxidized cobalt, which exhibits optimal sensitivity at low pressures [29].

Dehulled rice seeds were also treated in the glowing plasma sustained in hydrogen. The position of the RF coil for such treatments is marked as "B" in Fig. 1. A photo of hydrogen plasma is shown in Fig. 3. The glowing plasma in the H mode is limited to the volume within the RF coil, and a capacitive component of discharge coupling towards the flange is visible as weakly luminous plasma between the coil and the pump duct. Rice seeds are not visible in Fig. 3 because of the high luminosity of hydrogen plasma. Only a segment of the glass slide stretching approximately 1 cm from the dense plasma within the RF coil is visible in Fig. 3. The pink color arises from the predominant radiation of $H_\alpha$ of the Balmer series (transitions of neutral hydrogen atoms from the second to the first electronically excited states). The radiation in the ultraviolet (UV) and vacuum ultraviolet (VUV) range of the spectrum is much stronger (approximately 100 times). It arises from the transition from Lyman atomic series (the most intensive is $LH_\alpha$ at 121.6 nm) as well as from Werner and Lyman molecular bands, which appear within the wavelengths between approximately 130 and 190 nm. Detailed investigation of radiation arising from hydrogen plasma in the H-mode was reported by Fantz et al. [30]. They used almost identical discharge configurations, as shown in Fig. 3, and reported over 20 % of total RF power spent on radiation in the VUV range. Seeds were treated with hydrogen plasma in pulses, and the duty cycle was small to prevent seed heating. The discharge parameters used for sustaining oxygen and hydrogen plasmas are shown in Table 1. Such parameters prevented any visible modification of the seeds or hulls. If continuous treatment is used, the edges of the hulls start darkening after approximately 1 s of treatment in hydrogen plasma. Darkening is explained by exothermic surface reactions. The most significant are weak bombardment with positive ions and surface neutralization of charged particles, but the heterogeneous surface recombination of H-atoms is marginal on polymers [31].

### 2.3. Determination of the seeds' wettability

The wettability of the seeds was evaluated by measuring the contact angles of water droplets deposited on the seeds' surfaces. We used a drop shape analyzer DSA100 (Krüss GmbH, Hamburg, Germany). Because the rice grains are small, one droplet of Milli-Q water with a volume of 1 μL was applied to every grain of rice. A static contact angle was measured using a sessile drop method. For the measurements of the contact angles, a manually applied curved baseline was drawn to designate the base of the droplets in the Advance software (version 1.10). As the grains were of various shapes, the top of the grain could shade the base of the droplet. An additional strong LED lamp was used to illuminate the bases of the droplets. For better statistics, a static water contact angle was measured on five rice grains for each treatment condition. The water contact angles were measured within a few minutes after the plasma treatment of the rice seeds.

### 2.4. XPS characterization

Changes in the surface composition of plasma-treated rice were characterized by X-ray photoelectron spectroscopy (XPS). XPS characterization was performed using a TFA-XPS spectrometer (Physical Electronics, Munich, Germany). The samples were irradiated with monochromatic Al $K_\alpha$ radiation at the photon energy of 1486.6 eV. The diameter of the analyzed area was approximately 400 μm. Spectra were acquired at a photoelectron take-off angle of 45°. XPS-survey spectra were acquired at a pass-energy of 187 eV using an energy step of 0.4 eV, whereas high-resolution C 1 s spectra were measured at a pass-energy of 23.5 eV using an energy step of 0.1 eV. An additional electron gun was used to avoid charging the samples. Spectra were calibrated by setting the C–C peak of C1s to 284.8 eV. The MultiPak version 8.1c software (Ulvac-Phi Inc., Physical Electronics) was used to analyze the spectra. Shirley-type background subtraction was used. The samples were installed into the XPS instrument within several minutes after the plasma treatment, so there may have been only minor changes in the surface composition after treatment.

**Table 1**
Experimental conditions of the plasma system for rice seed treatment.

| Treatment conditions | Sample position | pressure | flow | Real RF power | Treatment time |
|---|---|---|---|---|---|
| $H_2$ plasma – glow | As shown in Figs. 1 and 3 | 18 Pa | 100 sccm | 370 W | – 2 × 0.5 s with a pause of 30 s for dehulled rice – 5 × 0.2 s with a pause of 10 s for rice with hulls |
| $O_2$ plasma – afterglow | As shown in Figs. 1 and 2 | 27 Pa | 84 sccm | 340 W | 0.01, 0.05, 0.1, 0.5, 5, 3, 20, 100, 200, 1000 s |

### 2.5. SEM characterization

SEM micrographs were recorded with a scanning electron microscope (SEM) Quanta 650 ESEM (Thermo Fisher, USA) with a tungsten filament. This particular SEM operates in the so-called 'low-vacuum' mode, in which the main sample chamber is evacuated and then filled with water vapor, maintaining pressure at 70 Pa. Such pressure enables analyzing samples with higher water vapor content and without the need to coat them with a conductive material. All micrographs are, therefore, recorded on the actual surface without additional coatings. Micrographs were recorded with a Large Field Detector (LFD) measuring secondary electrons upon scanning the samples with the primary electron beam. The acceleration voltage for the primary beam was 10 kV, the spot size was 2.5, and the beam current was around 33 pA.

### 2.6. Determination of the sinking speed

The untreated seeds float on the water, but those treated with plasma rapidly sink when placed onto the water's surface, and the sinking speed may represent additional information about the influence of plasma treatment on seed wettability. A 5-mL measuring glass cylinder was used to evaluate the sinking speed. A photo is shown in Fig. 4. The height of the measuring cylinder was approximately 100 mm, and the diameter was 10 mm. The sinking speed of the seeds was determined from the sinking time during the sinking seed's travel downward past the 5 mL and 1 mL marks on the measuring cylinder. The marks are visible in Fig. 4. The sinking time of the travel of the seeds through 4 mL volume within the cylinder was determined. The distance between the 5-mL and 1-mL mark was 50 mm. For each plasma treatment, four seeds were sunk, and their sinking times were averaged. The water level in the measuring cylinder for the sinking of rice grains was 2 to 3 mm below the top of the cylinder, as shown in Fig. 4. Treated seeds were gently laid onto the water surface in the cylinder with tweezers. Because the height of the water was approximately 2 cm above the 5 mL mark, the seeds already gained relatively constant sinking speed before they traveled past the 5-mL mark and further downward past the 1-mL mark.

The sinking of the seeds was captured on video by a Nikon D 5600 camera with Sigma EX DG Macro HSM 105 mm f/2.8 lens (shaded by extended APS-C-lens hood). Video resolution was set to full HD (1920 × 1080 px), video compression was set to high quality, the frame rate was 59.94 images per second, and the footage was recorded in sRGB color space. The camera was set to aperture priority mode. The aperture was set to f9, ISO was set to auto mode, and the low shutter speed limit was set to 1/200 s. Due to the changes in ambient light conditions, the shutter speed varied between 1/200 s and 1/400 s (and ISO between 800 and approximately 2500). The light metering mode was set to matrix mode, and the exposure compensation was set to −7/3 of apertures to compensate for the black background (for the background, a curved black rubber with a matte surface finish was used). The composition was set so that the entire cylinder fit into an image when the camera was oriented upright. Focusing of the lens to the measuring cylinder was performed manually in the live view. The videos were analyzed in DaVinci Resolve software, which enabled easy scrolling through individual frames of the videos and showed the exact timestamps of every individual frame. For each rice grain, the frames at which the rice grain was closest to the 5-mL and 1-mL volume designation marks were identified, and their timestamps were then subtracted to calculate the grain's sinking time. The sinking speed was obtained by dividing the distance between 5-mL and 1-mL volume marks with the measured sinking time.

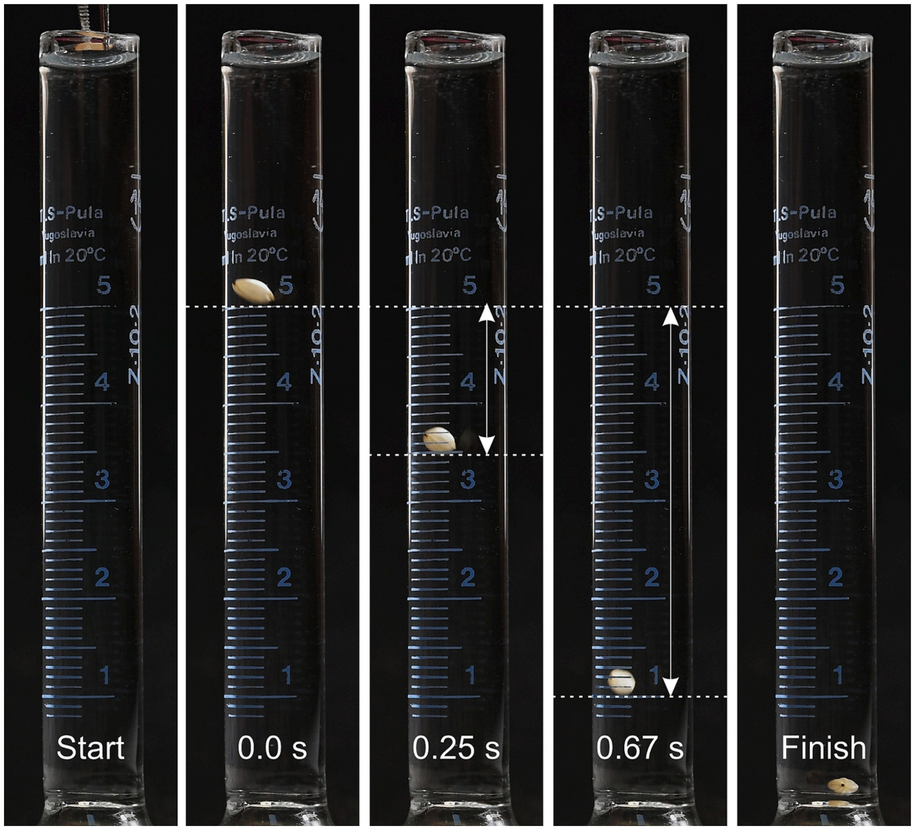


**Fig. 4.** A photo of the experiment for determination of the sinking speed.

## 3. Results and discussion

### 3.1. *Treatment of seeds with hulls*

The as-received seeds with hulls were mounted in the discharge tube, as shown in Fig. 1. The RF coil was placed in position "A", as shown in Fig. 1, so that the seeds were exposed to oxygen plasma afterglow. Any attempt to treat the seeds with hulls in the glowing oxygen plasma resulted in overheating because of extensive oxidation of the hulls.

Rice seeds with hulls were laid onto the objective glass, as shown in Fig. 2. The flux of neutral oxygen atoms was measured at the position of the sample with a cobalt catalytic probe [29] and was determined to be $3 \times 10^{23}$ $m^{-2}s^{-1}$. The fluence (dose) of atoms is a product of the flux and the treatment time. The wettability was measured within a few minutes after the treatment of seeds with hulls in oxygen plasma afterglow. Fig. 5 shows a water contact angle on an untreated seed and a seed treated in the afterglow of oxygen plasma for the shortest available time, i.e., 10 ms. The water contact angle on an untreated seed is approximately 105° (Fig. 5a). The contact angle on the seed treated in the afterglow for 10 ms is immeasurably low, as shown in Fig. 5b. Even a brief exposure of the seeds with hulls to atomic oxygen thus causes a super-hydrophilic surface finish. The seeds with hulls were treated in oxygen plasma afterglow for various times up to 1000 s (Table 1), and the super-hydrophilic surface finish was always observed. Such treatment times corresponded to the doses (fluences) of oxygen atoms between approximately $3 \times 10^{21}$ and $3 \times 10^{26}$ $m^{-2}$. Obviously, practically any dose of O atoms does the job.

Systematic research involving rice seeds with hulls was also performed by using the two-step method, i.e., a brief treatment with hydrogen plasma followed by a treatment with the oxygen plasma afterglow. The hydrogen plasma treatment was performed in the configuration marked as "B" in Fig. 1. A photo of this configuration is presented in Fig. 3. The treatment with hydrogen plasma was performed in five pulses with a duration of 0.2 s and with a 10-s off-time between subsequent treatments to avoid serious heating of the seeds. The total treatment time in hydrogen plasma was thus 1 s. After hydrogen plasma

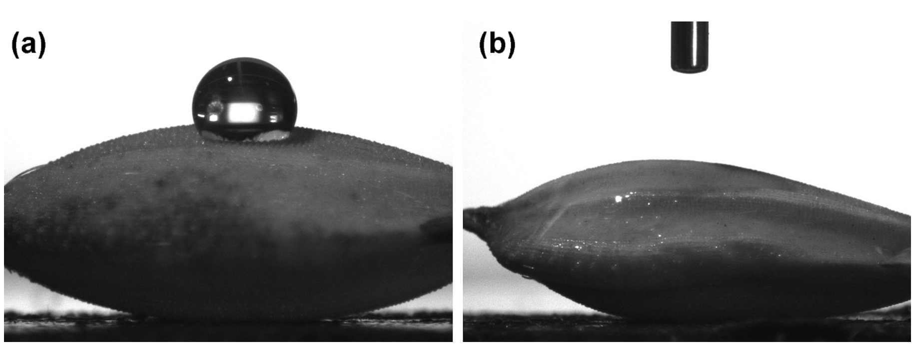


**Fig. 5.** A water droplet deposited on the surface of seeds with hulls: (a) as-received seed, and (b) seed after treatment with oxygen plasma afterglow for 10 ms.

treatment in configuration “B”, the RF coil with the matching network was moved to position “A” (Fig. 1, Fig. 2), oxygen was introduced into the system, and the seeds were further treated in the oxygen plasma afterglow. The water contact angle was measured, and we observed the super-hydrophilic surface finish for all probed durations of the treatment with oxygen plasma afterglow, i.e., from 10 ms to 1000 s.

The water contact angle was also measured for seeds treated with hydrogen plasma only, and the wettability was practically the same as for untreated samples. This is explained by an insignificant modification of the surface composition because the hydrogen plasma treatment of polymers causes the formation of an extremely thin polyolefin-like surface film, and all polyolefins are hydrophobic [32].

The as-received seeds with hulls floated on the water, as shown in Fig. 6a. The treated seeds, on the other hand, almost immediately sank to the bottom, as shown in Fig. 6b. The rapid sinking of seeds after treatment in oxygen plasma afterglow is explained by surface hydrophilization, which is, in turn, explained by the formation of polar functional groups. The evolution of the surface composition of seeds with hulls was studied by XPS. Table 2 presents the composition of the surface layer of hulls (of thickness as probed by XPS, i.e., several nm) treated at various conditions. As expected, carbon and oxygen prevail, but there are various concentrations of silicon and some other elements. Silicon is, of course, in the form of $SiO_2$ [33]. The Si concentration varies significantly between the samples, which cannot be explained by the effects of plasma radicals because none of the available radicals interacts chemically with silicon dioxide at low temperatures. The variation of Si concentration is instead attributed to uneven distribution in the surface film of the rice hulls. Since Si is oxidized, the oxygen concentration in Table 2 cannot be attributed only to oxygen bonded in/on organic matter but also to silicon.

The same applies to calcium. Examining Table 1, one cannot attribute the changes in the Ca concentration to plasma treatment because there is no correlation with the treatment time.

Fig. 7 represents a plot of oxygen concentration in the surface film of hulls versus the silicon concentration, as determined by XPS. The measured points are scattered, but the correlation is obvious: the oxygen concentration increases with increasing silicon concentration. To deduce the effect of oxygen afterglow treatment on the surface functionalization of organic matter with polar oxygen-containing functional groups, the oxygen bonded to silicon was subtracted ($O–O_{Si}$) from the values in Table 2. The oxygen concentration bonded to silicon in $SiO_2$ ($O_{Si}$) was estimated to be twice the silicon concentration. The O/C ratio after subtracting oxygen bonded to silicon, i.e., $(O–O_{Si})/C$ is shown in Fig. 8. The $(O–O_{Si})/C$ ratio is roughly doubled during treatment in the oxygen plasma afterglow, indicating significant oxidation of the organic matter on the surface of rice hulls (Fig. 8). Again, the results are scattered because of the spatially non-homogeneous composition, but taking into account this fact, the oxygen concentration does not depend much on the treatment time, same as the wettability.

The rapid hydrophilization of the hulls on the rice seeds is thus explained by surface functionalization with oxygen-containing functional groups. The hulls exhibit a rich morphology, as shown in Fig. 9. The untreated seeds with hulls are hydrophobic (Fig. 5a), so they float on the water (Fig. 6a). The hydrophobicity of untreated seeds with hulls prevents water from entering the volume between the morphological features (Fig. 9), so air remains trapped in that space. Once the water imbibition is rather complete, the seeds sink into the water, but this can take hours.

**Table 2**
XPS surface composition of plasma-treated seeds with hulls.

| Time (s) | C | O | Si | N | K | Ca | O/C | $(O–O_{Si})/C$ |
|---|---|---|---|---|---|---|---|---|
| Untreated | 62.8 | 27.0 | 6.4 | 3.5 | | 0.3 | 0.43 | 0.23 |
| $H_2 + O_2$: 0.1 | 35.3 | 46.5 | 17.0 | 0.4 | 0.5 | 0.2 | 1.32 | 0.35 |
| $H_2 + O_2$: 0.3 | 50.7 | 38.6 | 8.2 | 1.1 | | 1.5 | 0.76 | 0.44 |
| $H_2 + O_2$: 1 | 54.2 | 36.3 | 8.1 | 1.0 | | 0.4 | 0.67 | 0.37 |
| $H_2 + O_2$: 3 | 46.6 | 40.5 | 10.1 | 1.3 | | 1.5 | 0.87 | 0.44 |
| $H_2 + O_2$: 10 | 58.6 | 31.9 | 5.9 | 1.1 | 1.9 | 0.7 | 0.54 | 0.34 |
| $H_2 + O_2$: 30 | 50.5 | 35.9 | 13.0 | | | 0.6 | 0.71 | 0.20 |

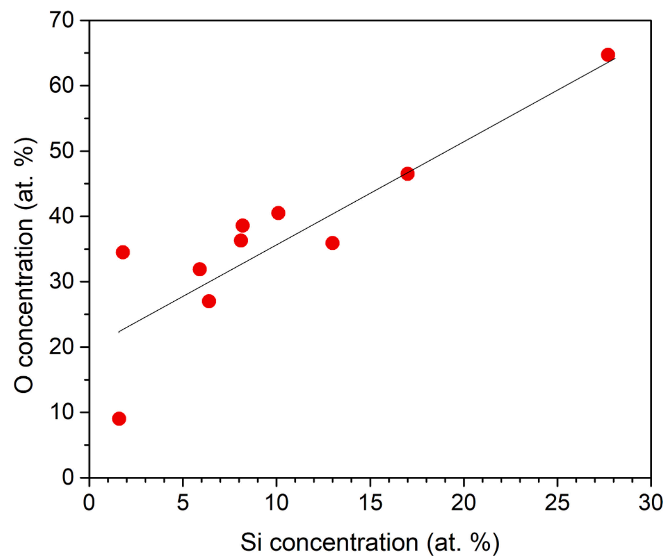


**Fig. 7.** XPS oxygen concentration versus silicon concentration for seeds with hulls treated first in hydrogen plasma and then in oxygen plasma afterglow.

## 3.2. Treatment of dehulled seeds

The rice hulls are quickly hydrophilized, but they cover the rice seed, so the plasma treatment of the seeds with hulls may not influence the seeds’ hydrophilicity. The next set of experiments was thus performed with dehulled seeds. The treatment in oxygen plasma afterglow was performed using the system configuration shown in Fig. 2 and marked as “A” in Fig. 1. The evolution of the wettability versus the treatment time during the treatment of dehulled seeds in oxygen plasma flowing afterglow is shown in Fig. 10. The wettability of the seeds with hulls treated at the same conditions is added for comparison.

The water contact angle (WCA) of as-received dehulled seeds is approximately 100°, indicating their hydrophobic character. Even a short treatment in oxygen plasma afterglow for 0.1 s causes a drop in the

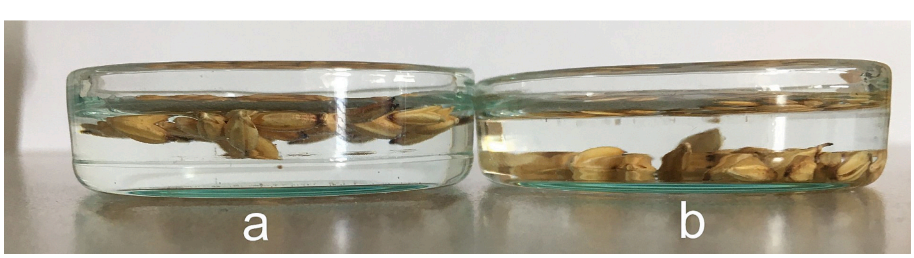


**Fig. 6.** Photo of: (a) as-received seeds with hulls that floated on the water and (b) seeds that sank in the water after treatment with oxygen plasma afterglow for 0.5 s.

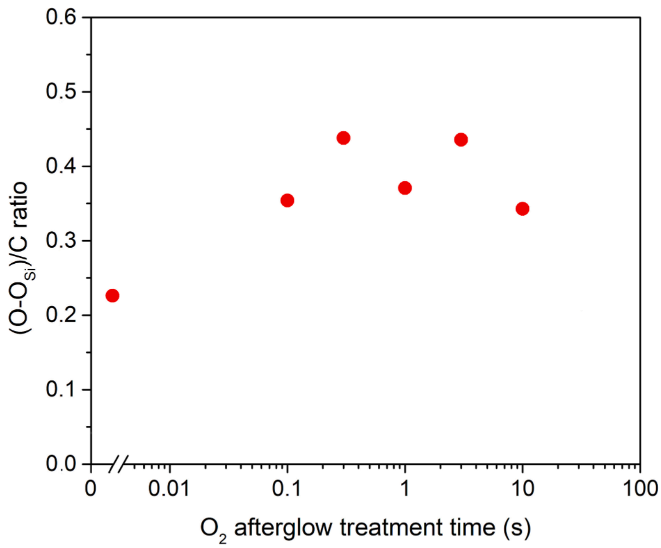


**Fig. 8.** XPS O/C ratio for organically bound oxygen in the surface layer of rice hulls versus treatment time in oxygen plasma afterglow. Oxygen content in $SiO_2$ ($O_{Si}$) was subtracted from the overall oxygen concentration ($O_{Si}$ = 2 × Si concentration).

WCA to half the original value. The WCA remains around 50° for the first few seconds and then decreases with prolonged treatment in oxygen plasma afterglow. The super-hydrophilic surface finish is only obtained after a very long treatment. Fig. 10 reveals that the super-hydrophilization of dehulled seeds occurs after treatment for approximately 15 min. Such a slow increase in wettability is not applicable in agriculture praxis, so a two-step processing was adopted to speed up the hydrophilization.

Systematic measurements of the evolution of surface wettability of dehulled rice were performed on seeds subjected to a two-step treatment. Dehulled seeds were first treated with hydrogen plasma (Fig. 3) using the configuration "B", as marked in Fig. 1. The treatment in hydrogen plasma was in two pulses, each of duration 0.5 s. The time between two pulses was 30 s. Such a short treatment time prevents significant heating of the dehulled seeds. After completing the hydrogen plasma treatment, the RF coil with the matching network was moved to position "A" in Fig. 1 without breaking the vacuum conditions; the hydrogen valve was closed, and the oxygen valve was opened. The seeds pre-treated with hydrogen plasma were then treated in oxygen plasma afterglow. After this two-step treatment, the system was vented, and the seeds were probed for wettability. The total treatment time in hydrogen plasma was 1 s, and the treatment time in oxygen plasma afterglow was varied between 10 ms and 200 s. The evolution of the water contact angle of dehulled rice seeds is shown in Fig. 11. The wettability of seeds with hulls treated by the same two-step procedure is added for comparison.

A comparison of Figs. 10 and 11 reveals the beneficial effect of hydrogen plasma pre-treatment. The WCA of dehulled seeds pre-treated with hydrogen plasma dropped to approximately 30° after just 10 ms of treatment in oxygen plasma afterglow, gradually decreased with further treatment, and the super-hydrophilic surface finish appeared after approximately half a second of treatment in oxygen plasma afterglow. The super-hydrophilic surface finish is also observed for somewhat longer treatment times, but after treating the hydrogen-plasma pre-treated dehulled rice longer than 10 s in oxygen plasma afterglow, the WCA becomes easily measurable. Further treatment (from 15 to 200 s) caused WCA to slowly increase with increasing treatment time in oxygen plasma afterglow, but the surface was highly hydrophilic (WCA below 25°) for all samples probed.

The interesting behavior of dehulled 'seeds' wettability could be explained by considering the results of the surface layer composition as probed by XPS and the surface morphology as probed by SEM. The surface composition deduced from XPS survey spectra is shown in

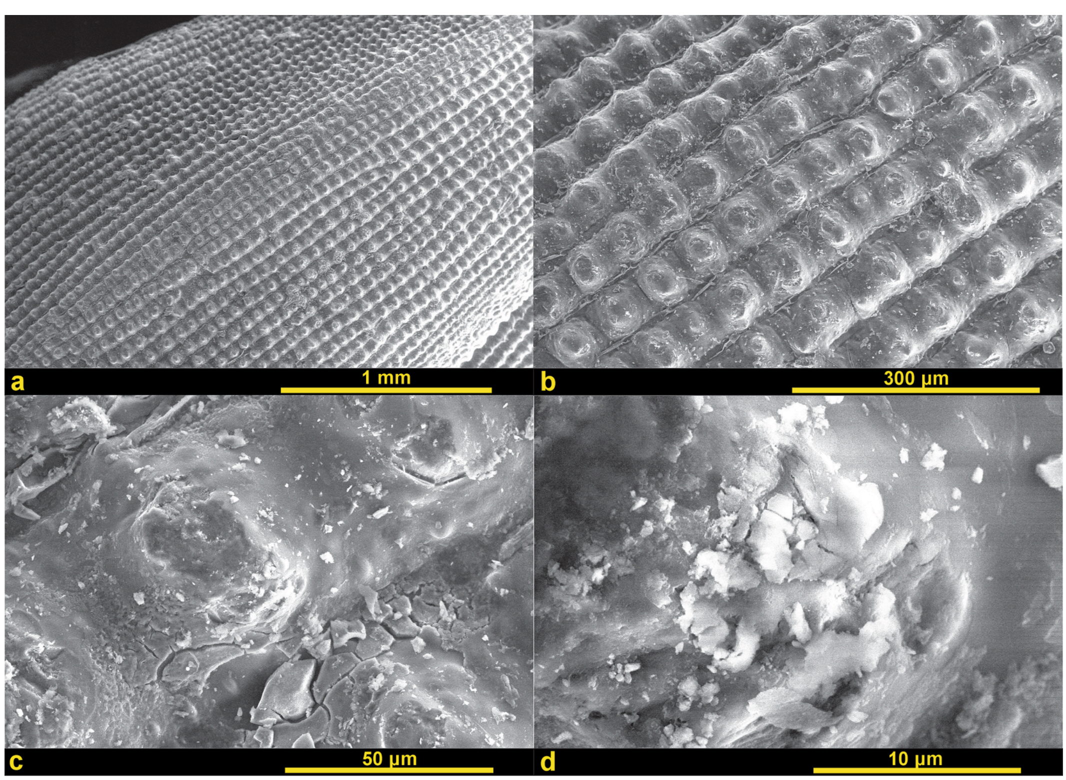


**Fig. 9.** Representative SEM images of the rice hulls at three different magnifications. Scale bars are 1 mm, 300 µm, 50 µm, and 10 µm in (a), (b), (c), and (d), respectively.

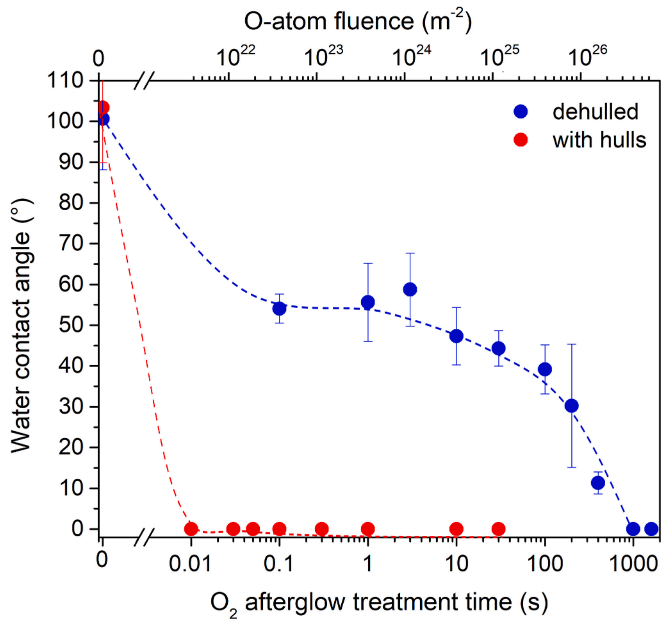


**Fig. 10.** The WCA of rice seeds with and without hulls versus treatment time in oxygen plasma afterglow.

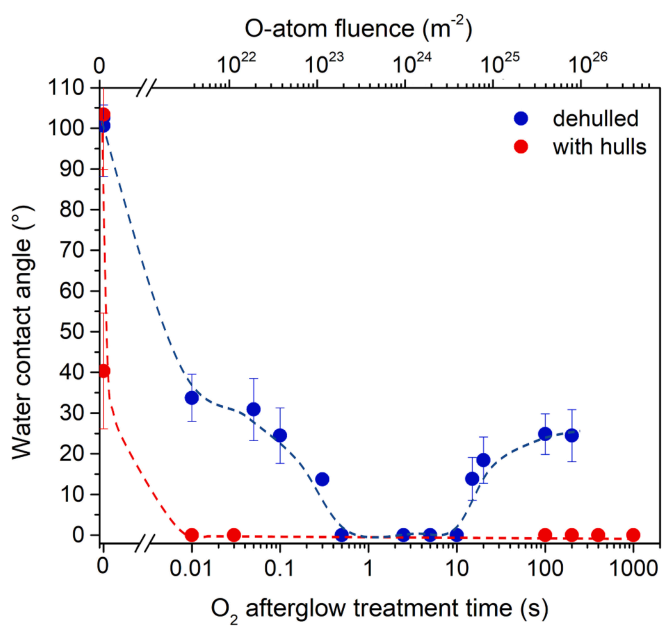


**Fig. 11.** The WCA versus treatment time in oxygen plasma afterglow of rice seeds with and without hulls which were pre-treated with hydrogen plasma.

Table 3. The last column in Table 3 is the oxygen-to-carbon ratio, where oxygen bonded to silicon was subtracted from the total share of oxygen prior to its calculation, i.e. $(O–O_{Si})/C$. The correlation between oxygen and silicon concentrations, presented in Fig. 12, is not as evident as in Fig. 7. The $(O–O_{Si})/C$ ratio of plasma-treated dehulled seeds calculated after subtraction of inorganic oxygen, which is bonded to silicon, is plotted in Fig. 13. The $(O–O_{Si})/C$ ratio is rather low for untreated dehulled seeds (only approximately 0.05), but is at least doubled after treating the seeds by the two-step method, regardless of the treatment time in oxygen plasma afterglow. The results are scattered because of the laterally non-homogeneous surface composition, but the functionalization with oxygen-rich functional groups is an evident consequence of the oxygen-plasma-afterglow treatment of hydrogen-plasma pre-treated dehulled seeds. Still, it is interesting that the super-hydrophilicity is observed only in a limited range of treatment times, between approximately half a second and a few seconds (Fig. 11). The paradox may be explained by the etching of the surface film (formed during hydrogen plasma pre-treatment) upon prolonged treatment with O atoms from the oxygen plasma afterglow.

Fig. 14 shows SEM images of the surface of dehulled rice seeds. Fig. 14a reveals the morphology of an untreated dehulled seed. The surface cells on dehulled rice seeds are coated with a layer of a hydrophobic material (including xylenes, lignin, wax, and phenolic acid [34]), so the cell edges are not visible. The hydrogen plasma treatment causes significant modifications of any polymer structure and composition because of the extensive irradiation with the VUV photons [30]. As a result, the surface morphology of dehulled seeds changes significantly, as shown in Fig. 14b). The rich surface morphology (Fig. 14b) and a high

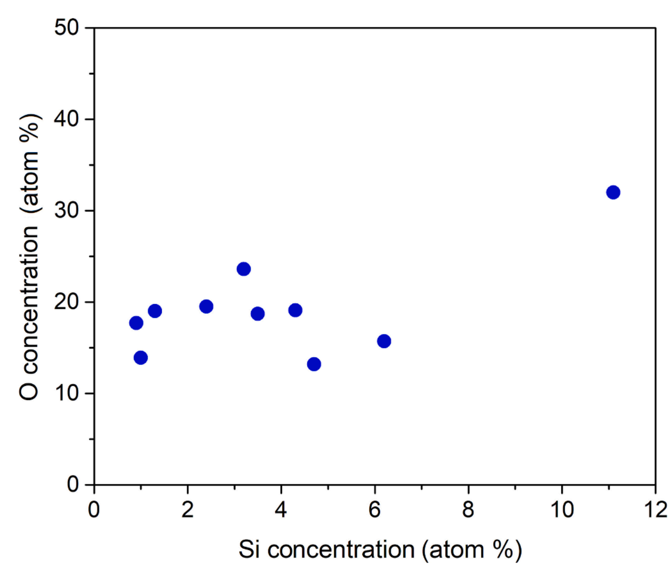


**Fig. 12.** Oxygen concentration determined by XPS versus silicon concentration for dehulled seeds treated first in hydrogen plasma and then in oxygen plasma afterglow.

**Table 3**
XPS surface composition of dehulled rice pre-treated with hydrogen plasma and then treated in oxygen plasma afterglow.

| Time (s) | C | O | Si | N | K | Ca | Na | O/C | $(O–O_{Si})/C$ |
|---|---|---|---|---|---|---|---|---|---|
| untreated | 82.1 | 13.2 | 4.7 | | | | | 0.16 | 0.05 |
| Just $O_2$: 0.1 | 85.1 | 13.9 | 1.0 | | | | | 0.16 | 0.14 |
| $H_2 + O_2$: 0.1 | 81.4 | 17.7 | 0.9 | | | | | 0.22 | 0.20 |
| $H_2 + O_2$: 0.3 | 78.5 | 19.0 | 1.3 | | 1.2 | | | 0.24 | 0.21 |
| $H_2 + O_2$:: 1 | 76.0 | 19.1 | 4.3 | | | 0.2 | 0.4 | 0.25 | 0.14 |
| $H_2 + O_2$: 3 | 77.6 | 18.7 | 3.5 | | | | 0.2 | 0.24 | 0.15 |
| $H_2 + O_2$: 10 | 69.0 | 23.6 | 3.2 | 1.8 | 1.4 | 0.5 | 0.4 | 0.34 | 0.25 |
| $H_2 + O_2$: 30 | 78.1 | 15.7 | 6.2 | | | | | 0.20 | 0.04 |
| $H_2 + O_2$: 100 | 76.1 | 19.5 | 2.4 | 1.6 | 0.3 | | | 0.26 | 0.19 |

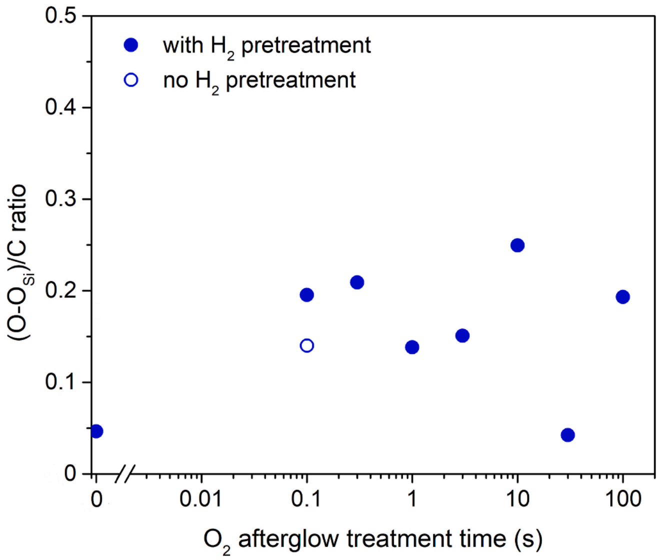


**Fig. 13.** $(O–O_{Si})/C$ ratio in the surface layer of dehulled rice versus treatment time in oxygen plasma afterglow as determined by XPS. Oxygen content in $SiO_2$ ($O_{Si}$) was subtracted from the total oxygen concentration ($O_{Si} = 2 \times$ Si concentration) prior to the O/C ratio calculation.

concentration of polar surface functional groups (Fig. 13) cause the super-hydrophilic surface finish (Fig. 11) of dehulled seeds pre-treated with hydrogen plasma and treated in oxygen plasma afterglow for a short time.

As already mentioned, the oxygen atoms which abound in the flowing afterglow of oxygen plasma cause etching of organic matter, particularly that of rich morphology. The morphological features observed in Fig. 14b) are thus etched after prolonged treatment in the oxygen plasma flowing afterglow and eventually disappear from the dehulled seed surface as shown in Fig. 14c). It is well known that plasma causes etching of polymer materials [35,36]. The etching rate is much lower when polymers are treated in the flowing afterglow (opposite to glowing plasma, where etching rates are high), but it is easily measurable even for fairly oxidation-resistant polymers [37], but large enough to remove the morphological features observed in Fig. 14b) after treating the dehulled seed for 100 s in the oxygen plasma afterglow.

Let us further explain the wettability behavior of the dehulled seeds (blue curve in Fig. 11). The pre-treatment with hydrogen plasma causes bond scission in the surface film of the hydrophobic coating and at least partial occupation of formed dangling bonds with hydrogen atoms. The pre-treatment with hydrogen plasma does not modify the surface wettability, but it enables rapid oxidation during treatment in the oxygen plasma afterglow. Very short treatment with oxygen atoms, i.e., below approximately 0.1 s, causes incomplete functionalization with polar functional groups, so the super-hydrophilic surface finish is not developed. Treatment for approximately a second causes saturation of the surface layer of the dehulled seeds pre-treated with hydrogen plasma with polar functional groups. Further treatment, however, causes gradual etching and removal of the surface layer modified by the hydrogen-plasma pre-treatment. A similar effect was already observed for PTFE and PVC [38,39]. Ultimately, when the entire modified surface layer of the hydrophobic coating is removed by etching with oxygen atoms, the wettability becomes similar to seeds that have not been pre-treated with hydrogen plasma.

The sinking times and sinking speeds of the Lomello dehulled rice seeds, which were subsequently treated in hydrogen plasma (configuration “B” in Fig. 1) and in oxygen plasma afterglow (Configuration “A” in Fig. 1), were determined by sinking the grains in a 5-mL measuring cylinder as explained in subsection 2.6. The treatment time in oxygen plasma afterglow was varied. The seeds were first treated in glowing hydrogen plasma, then turned around, and the treatment was repeated. This was followed by the treatment of seeds in oxygen plasma flowing afterglow, which was performed on both sides of the seeds. The results

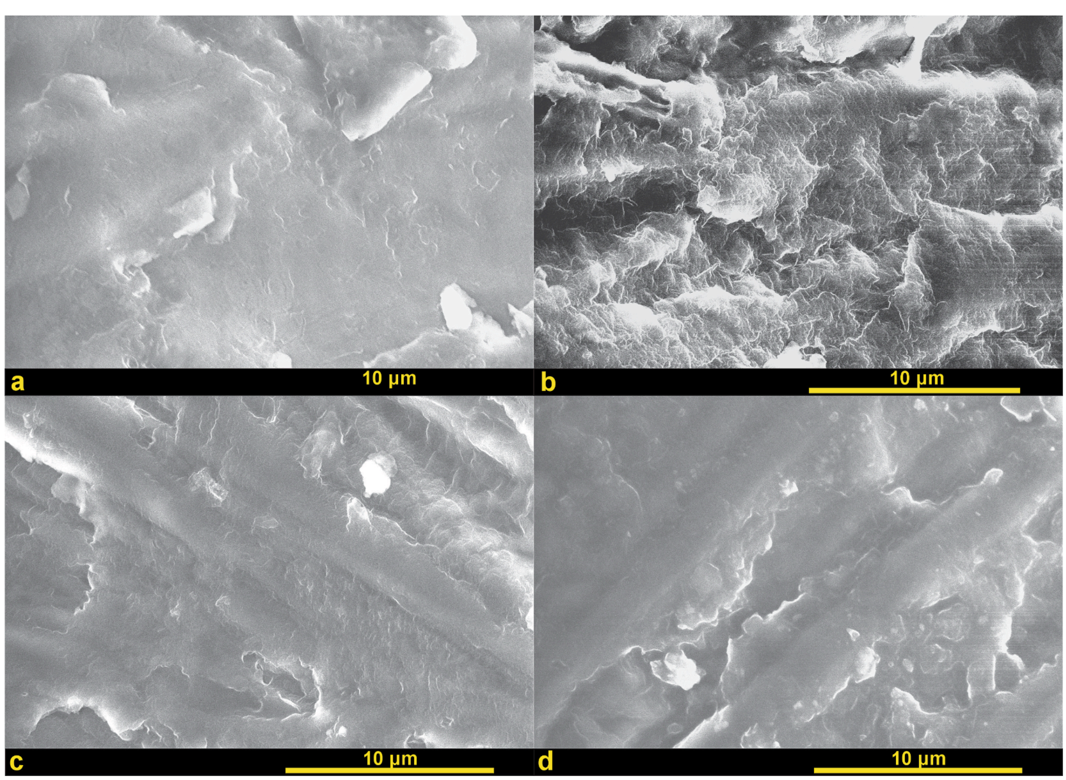


**Fig. 14.** SEM images of: (a) as-received dehulled rice, (b) hydrogen plasma pre-treated and treated for 1 s in oxygen plasma afterglow, (c) hydrogen plasma pre-treated and treated for 10 s in the afterglow, and (d) hydrogen plasma pre-treated and treated for 100 s in oxygen plasma afterglow.

are presented in Fig. 15. It was not possible to determine the sinking speeds of untreated dehulled seeds because the seeds floated on the water. The results for treated seeds are somehow scattered, but it is clear that the sinking speed is quite high. In fact, the time it took to pass the seeds through the water column in the measuring cylinder shown in Fig. 4 was approximately one second for all treated seeds. Measuring the sinking speed, therefore, does not reveal any statistically significant difference between highly hydrophilic and super-hydrophilic seed surfaces.

A super-hydrophilic surface finish is usually not permanent. Hydrophobic recovery was reported for plasma-treated polymers [40–42]. The hydrophobic recovery is a result of numerous effects, including the re-orientation of the surface functional groups, slowly-proceeding modification of the surface chemical structure and/or composition, and adsorption of impurities [41]. The hydrophobic recovery is reflected in a spontaneous increase in the water contact angle with the samples' storage time. The super-hydrophilic dehulled seeds were stored at ambient conditions, and the WCA was measured as a function of the storage time. The hydrophobic recovery of super-hydrophilic dehulled seeds (pre-treated in hydrogen plasma and treated in oxygen plasma afterglow) is shown in Fig. 16. The WCAs for seeds with hulls are added for comparison. The results are scattered, but the logarithmic curve can be easily fitted to measured points (it appears as a straight line in the lin-log scale). Interestingly enough, the super-hydrophilic seeds with hulls treated at the same conditions do not exhibit measurable hydrophobic recovery (at least not for the first 1000 min), so one can conclude that any adsorption of hydrophobic molecules (like organic molecules present in the air at ambient conditions) may not be the reason for the rather rapid hydrophobic recovery of super-hydrophilic dehulled seeds. Regardless of the mechanism, Fig. 16 clearly shows that any application of the two-step method for super-hydrophilization of dehulled seeds in agriculture praxis is limited because of the hydrophobic recovery.

## 4. Conclusions and perspectives

Systematic research was performed in order to develop methods for hydrophilization of Lomello variety rice seeds. The seeds with hulls can be hydrophilized rapidly, and the super-hydrophilic surface finish is obtained already after receiving the fluence of neutral oxygen atoms in the ground state as low as approximately $3 \times 10^{21}$ $m^{-2}$. The required O-atom fluence may be even lower, but that was the lowest fluence achievable in our experimental plasma reactor. This fluence was

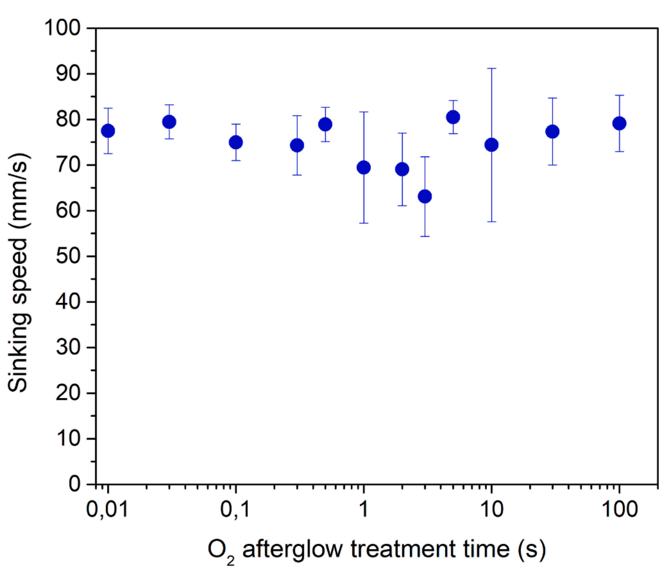


**Fig. 15.** The sinking speeds of dehulled rice seeds versus the treatment time in oxygen plasma afterglow.

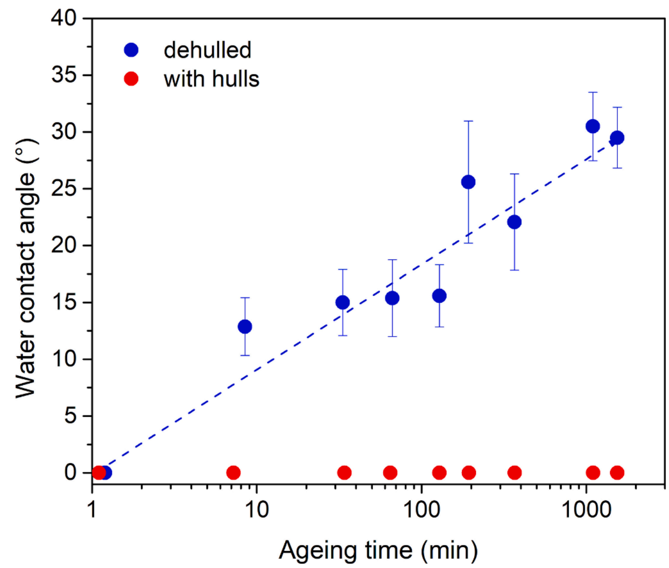


**Fig. 16.** Ageing of the surface of plasma-treated rice seeds with and without hulls evaluated by means of water contact angle variation with storage time.

achieved after 10 ms of treatment in the flowing afterglow of oxygen plasma sustained by an inductively coupled radiofrequency discharge operating in oxygen at the pressure of 26 Pa, oxygen flow rate of 84 sccm, pumping speed of 80 $m^3/h$ and discharge power of 340 W. The flux of O-atoms at these conditions on the seed surface was $3 \times 10^{23}$ $m^{-2}s^{-1}$. Other experimental systems would provide other values of the oxygen atoms fluxes, so the required treatment times may differ at any attempt to repeat the experiments in a different system, including upscaled plasma reactors useful for treating seeds on the industrial scale. The fluence that is required to obtain the super-hydrophilic surface finish, however, should not depend on the peculiarities of the plasma reactor.

The dehulled rice seeds are hydrophilized slowly upon treatment in oxygen plasma afterglow. The fluences of O atoms supplied to the seeds' surfaces in the flowing afterglow of oxygen plasma between approximately $3 \times 10^{22}$ and $1 \times 10^{26}$ $m^{-2}$ enable only moderate hydrophilization of dehulled seeds with the water contact angle of approximately 50°. Higher fluences enable better hydrophilicity since the WCA decreases gradually, but the super-hydrophilic surface finish was only observed for seeds treated at the fluence of approximately $3 \times 10^{26}$ $m^{-2}$. Such a high fluence was obtained in our experimental setup after treating the dehulled seeds for approximately 15 min. Such a long treatment time would not be feasible at any attempt of upscaling and would not meet the requirements of modern agriculture. Such a high fluence was attributed to the requirement for the removal of the hydrophobic layer by etching with O atoms. The fluence might be lower if the seeds are heated during treatment in oxygen plasma afterglow, but this is not advisable in agricultural praxis.

Much quicker hydrophilization of dehulled rice seeds is achievable by the two-step processing. In the first step, the seeds are briefly treated with hydrogen plasma. The seeds were treated in the glowing plasma sustained within the RF coil. Glowing hydrogen plasma is an extensive source of vacuum ultraviolet (VUV) radiation. The photon energy of VUV radiation exceeds the binding energy between any atoms in the organic matter, so these energetic photons are absorbed by breaking bonds in the surface film. The resulting radicals of organic molecules may be involved in various reactions, but one of them is the occupation of the dangling bonds in the surface layer of the organic matter with H atoms. The composition of the surface film thus changes, and the resultant modified surface layer is prone to functionalization with polar functional groups upon exposure to oxygen atoms. The second step is thus the treatment of the seeds in oxygen plasma afterglow. Using this two-step procedure, it was possible to achieve the super-hydrophilic surface finish of dehulled seeds by treating hydrogen plasma pre-treated seeds for a second in oxygen plasma flowing afterglow. The super-hydrophilic surface finish of dehulled seeds pre-treated with hydrogen plasma was observed in the range of fluences of O atoms from approximately $2 \times 10^{23}$ to approximately $6 \times 10^{24}$ $m^{-2}$. These values are achievable in large reactors with the application of seeds' treatment times in the range of a few seconds, so the technology seems to be scalable.

The super-hydrophilic surface finish may not ensure rapid water imbibition into the seeds because the hydrophobic layer on the dehulled seeds still covers the surface, but only the chemical structure in its top sublayer of the thickness of a few nm is enriched with hydrophilic functional groups. Any study of the imbibition kinetics for seeds treated according to the two-step method is beyond the scope of this paper (which is focused on the hydrophilicity kinetics), but the complete removal of the hydrophobic layer may not be necessary for the optimization of the water imbibition.

It should be stressed that the super-hydrophilic surface finish of any solid material is rarely permanent. Instead, the hydrophobic recovery occurs upon storage. Rice seeds with hulls do not exhibit measurable hydrophobic recovery, even after a day, but dehulled seeds were prone to hydrophobic recovery. Nevertheless, the super-hydrophilic surface finish of the dehulled seeds treated according to the two-step method was still preserved approximately 10 min after treatment with oxygen atoms (between immeasurable and 10°). The water contact angle increased roughly logarithmically with increasing storage time of plasma-treated dehulled seeds. The WCA remained unmeasurably low for the first 6 min after the treatment and stayed in a range between 10 and 20° in a time window between 10 min and about two hours. Therefore, any beneficial effect of the super-hydrophilic surface finish of dehulled seeds should be utilized within a few minutes after treatment with oxygen atoms, which may be an obstacle in any attempt to upscale the technology. However, the seeds were still pretty much hydrophilic after 1 day as the WCA remained around 30°. Although this is not a super-hydrophilic surface finish, it could still be hydrophilic enough for various possible applications. The scientific results disclosed in this article should be, therefore, used only as a guide towards implementing the methods of agricultural praxis.

The fast hydrophilization is useful in any attempt to upscale the methods disclosed in this article. Industrial plasma reactors of volume several $m^3$ enable the treatment of large quantities of materials with weakly ionized plasma [43], so the second step, i.e., treatment with oxygen atoms, is scalable. More difficult is treatment with hydrogen plasma because a rather high power density is needed to provide extensive enough VUV radiation. Since the hydrogen plasma treatment time could be even below 1 s, the seed dropping through plasma sustained in a vertical reactor, as disclosed in [44], seems feasible. The application of hydrogen always represents a certain safety risk, so it should be mixed with argon to prevent explosion if leaked into the ambient air."

## CRediT authorship contribution statement

**Alenka Vesel:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation. **Anca Macovei:** Writing – review & editing, Validation, Supervision, Conceptualization. **Alma Balestrazzi:** Writing – review & editing, Validation, Supervision, Conceptualization. **Sri Amarnadh Gupta Tondepu:** Validation, Methodology. **Conrado Dueñas:** Validation, Methodology. **Vittoria Locato:** Resources, Investigation. **Teodora Chiara Tonto:** Resources, Investigation. **Claudia Zoani:** Supervision, Project administration, Funding acquisition. **Dane Lojen:** Methodology, Investigation, Formal analysis, Data curation. **Gregor Primc:** Writing – review & editing, Project administration. **Rok Zaplotnik:** Validation, Methodology, Investigation, Formal analysis, Data curation. **Nives Ogrinc:** Project administration, Funding acquisition. **Marian Lehocky:** Visualization. **Miran Mozetič:** Writing – original draft, Supervision, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

Data will be made available on request.

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