Application of low-temperature plasma treatment for rapid and efficient polydopamine coating on 3D-printed polymer scaffolds

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Abstract
Polydopamine-based bioinspired surface coating can augment improved adhesive nature and functional performance to materials. Here in, we report for the first time the capability of low-temperature hydrogen plasma treatment to enhance the polydopamine coating on 3D-Printed Polymer Scaffolds. The hydrogen plasma-treated scaffolds were systematically characterized with different analytical techniques. It was seen that hydrogen plasma treatment can significantly enhance the polydopamine coating on scaffolds. This observed finding of the utility of plasma to enhance the polydopamine coating on 3D-printed polymer scaffolds could significantly reduce the current processing time of polydopamine coating on material surfaces.

Introduction
Surface properties of biomaterials are very important as they can control the biocompatibility and functional performance.[1] Different advanced regenerative engineering strategies such as microfluid manipulation devices and bioactive micro/nanomotors are currently being explored for biomedical applications.[2–5] The surface properties of these advanced biomaterial devices need to be carefully tuned to augment favorable properties or biological responses. 3D-printed polymer scaffolds are another important class of biomaterials widely employed for tissue engineering applications, like bone tissue engineering.[6] However, the hydrophobicity and low cellular attachment make it important to tailor the surface properties of 3D-printed scaffolds. Low-temperature plasma treatment (LTPT) is regarded as a green method to modify the surface properties of biomaterials.[7] LTPT can modify/deposit the surface of biomaterials with reactive coatings and nanoparticles.[8–10] These modifications can significantly impact the biocompatibility and functional performance of biomaterials. Recently, LTPT has been explored to modify the surface of 3D-printed scaffolds to impart multiple properties which includes but not limited to improved hydrophilicity and antimicrobial capability.[10] This makes the LTPT of 3D-printed biomaterials important in medicine.

Polydopamine is a naturally inspired sea mussel-based surface coating which can be deposited on different material surfaces.[11] This material independent coating potential of polydopamine makes it an attractive candidate to modify the surface of different biomaterials, including the surface of 3D-printed polymer scaffolds.[12] The process of polymerization of dopamine in to polydopamine occurs in alkaline environment via an oxidative self-polymerization process without the usage of additional chemicals and reagents.[13] The polydopamine modification can augment important surface functional groups, such as catechol, amine, and imine. These groups can be further modified with bioactive peptides or ligands which can improve the functional performance of the biomaterial.[13] These attractive properties of polydopamine coating make it highly important for use as a coating material on different polymeric biomaterials. Apart from coating polymers, polydopamine coatings have currently been applied to many different materials, such as metals,[14] ceramic,[15] and composite materials.[16] The coating of these different materials with polydopamine provides/augments some important properties which includes but not limited to corrosion inhibiting coating,[17] enhanced thermal conductivity,[18] and enhanced adhesion strength.[19] This shows the high relevance of polydopamine surface coating in material science research. This makes the development of innovative polydopamine coating process highly important for many applied fields of material science, such as biomedicine, energy, and development of advanced composite materials.

Even though the polymerization and subsequent deposition of polydopamine is a straightforward process, it is a relatively slow process which generally requires 10 h or even several days.[20] This can significantly impact the large-scale production of polydopamine-coated biomaterials. Different parameters such as dopamine concentration, pH, temperature, and oxidation are optimized to get rapid and efficient polydopamine coating on biomaterial surface.[21] However, optimizing these parameters and scaling it up for large-scale production of the coating is very challenging. There were many studies which reported the development of rapid polydopamine coating using different oxidizing agents, such as iron (III) chloride/hydrogen peroxide,[22] copper sulfate/hydrogen peroxide,[23] and sodium periodate.[15] Even though this reported process can increase the polydopamine deposition rate, it still required multiple chemical reagents which have potential toxicity concerns and are not easily scalable for the large-scale production of rapid polydopamine coating. This necessitates the development of a scalable and green/safer process which can enhance the effectiveness of polydopamine coating on biomaterial surfaces. Inspired by this unexplored challenge, we have explored the potential of low-temperature plasma to enhance the polydopamine coating on biomaterial surface. As plasma is a highly scalable and industrially viable method, development of plasma-based process for polydopamine coating will be of high importance in engineering polydopamine modified biomaterials. To the best of our knowledge, this is the first report regarding the utility of low-temperature plasma to enhance the polydopamine coating on 3D-printed polymers scaffolds.

Experimental section

Materials

Dopamine Hydrochloride and Copper Sulfate Pentahydrate ($CUSO_4.5\ H_2O$) were purchased from Fisher Scientific. 3D-printed polylactic acid (PLA) scaffold printed using PLA filaments was purchased from FLASHFORGE USA, (Flashforge 1.75-mm PLA 3D Printer Filament, 1 kg Spool). Harrick Plasma chamber (PDC-001-HP) used for the in situ surface reduction process was purchased from Harrick Plasma, New York, USA. Hydrogen gas used for the in-surface reduction process was purchased from Air Gas Company (Ultra High-Purity Grade Hydrogen, Size 300 High Pressure Steel Cylinder, CGA-350).

Methods

3D printing process of PLA scaffold wafers

3D Polylactic Acid (PLA) scaffold wafers, having a dimension of 5.85 mm diameter and 1 mm height, that fit exactly inside the well of a 96-well plate were designed using SolidWorks as per a previously reported method.[24] 3D printing was done using 1.75-mm Poly (lactic acid) (PLA) filaments. The temperature for printing was set to 200°C and the printing bed was set at 50°C. A printing speed of 60 mm/s was used for the printing process.

LTPT process on 3D-printed PLA scaffold wafers

3D PLA Scaffold wafers were initially activated with air plasma treatment for 10 min prior to soaking in different solutions; the objective of this step of air plasma treatment was to improve the hydrophilicity of the 3D PLA scaffold wafers. The scaffolds were then soaked in 10-ml solutions of 250-µm $CuSO_4.5H2O$ and 10 mg/ml of Dopamine Hydrochloride. Both these solutions were prepared in 0.1-M Tris–HCL with pH 8.0.

The 3D-printed PLA scaffolds were soaked in 3 different solutions, (a) Dopamine Hydrochloride, (b) Copper Sulfate, and (c) A mixture of Dopamine Hydrochloride and Copper Sulfate for 5 min. After the soaking process, the scaffolds were dried by placing the scaffolds on Kim wipes and gently wiped to remove any moisture/residual solvent present on the surface of the scaffolds after solution soakings. This removed the possibility of the presence of residual water/any other volatile components from the surface of the scaffolds before placing them inside the plasma machine. The base pressure of the plasma chamber before the hydrogen plasma treatment was 760 Torr. Subsequently, the scaffolds soaked in solutions and dried using Kim Wip were transferred to the plasma chamber and subjected to hydrogen plasma treatment for 10 min to deposit the polydopamine coating. We used 4 samples ($n = 4$) from each group (Dopamine Hydrochloride, Copper Sulfate, A mixture of Dopamine Hydrochloride and Copper Sulfate) for the hydrogen plasma treatment. The base pressure of the plasma chamber was continuing to reduce to upon switching the vacuum pump (Edward RV8 Rotatory Vane Vacuum Pump) connected to the plasma chamber, for ensuring consistency between batch-to-batch treatments, and the plasma was ignited upon reaching a low base pressure of 0.9 torr. The base pressure dropped from 760 to 0.9 torr in 120 s and plasma was ignited. The characteristic purple glow of the hydrogen plasma was seen from the plasma chamber once plasma was ignited. This shows the presence of Hydrogen plasma formed inside the chamber. We have used a Harrick Plasma chamber (PDC-001-HP) with the following reaction conditions: 13.56-MHz radiofrequency and plasma power of 45 W and a flow rate of 40 sccm was used to generate hydrogen plasma inside the chamber.

Characterizations

XPS spectra of plasma-treated samples were obtained using a Phi 5000 Versaprobe made by Phi Electronics, Inc. (Chanhassen, WI USA). The X-ray source of this instrument is a monochromatic, focused, Al K-alpha source ($E = 1486.6$ eV) at 25 W with a 100 -m spot size. The high-resolution XPS scans (average 8 scans per analysis) were obtained with pass energy of 23.5 eV and a step size of 0.1 eV.

The surface features and the coating of the 3D-printed PLA scaffolds were systematically studied using 3D Laser Scanning Confocal Microscope VK-X1000 (developed by Keyence Corporation of America). The Scanning Electron Microscopy Images of the scaffolds were taken as follows. Briefly, Samples were sputter-coated with Au−Pd and observed using a field emission SEM (Quanta FEG 650 from FEI, Hillsboro, OR) microscope.

Statistical analysis

Statistical Analysis was performed using GraphPad prism software. Student T test (unpaired, 2 tailed) and Ordinary One-Way ANOVA (was performed to determine the significance of difference in the percentage of nitrogen between plasma-treated and non-plasma-treated 3D PLA scaffolds.

Results and discussion

We have hypothesized that the application of low-temperature plasma can enhance the oxidative polymerization process of dopamine which could lead toward a more rapid and effective polydopamine coating on biomaterial surface. To test this hypothesis, we have used 3D-printed Polylactic Acid (PLA) as a model biomaterial to deposit the polydopamine coating. Low-temperature hydrogen plasma was applied during the oxidative polymerization process of dopamine in the presence and absence of copper sulfate. As the first step, we have 3D-printed 96-well plate-sized Polylactic acid (PLA) scaffold wafers as per our previous printing protocol.[24] The objective behind printing such smaller and consistent 3D scaffold wafers was to ensure more reliable and efficient comparison of the polydopamine coating formed on the surface of the 3D scaffolds.

The 3D-printed PLA scaffolds were subsequently soaked in 3 different solutions of dopamine hydrochloride, copper sulfate, and a combination of dopamine hydrochloride and copper sulfate [Fig. 1(a)].

All these solutions were prepared using Tris Buffer with a pH value of 8. The rationale behind preparing these solutions using an alkaline environment Tris Buffer was to facilitate the oxidative polymerization process of dopamine.[25] After soaking the scaffolds in these 3 different solutions for 5 min, they were subjected to hydrogen plasma treatment for 10 min [Fig. 1(b)]. As a control experiment, we used 3D PLA scaffolds which were only soaked in these 3 solutions without any plasma treatment. Interestingly, it was seen that the plasma treatment has changed the color of the scaffolds to be more intense [Fig. 1(c)]. This gave a good preliminary indication that

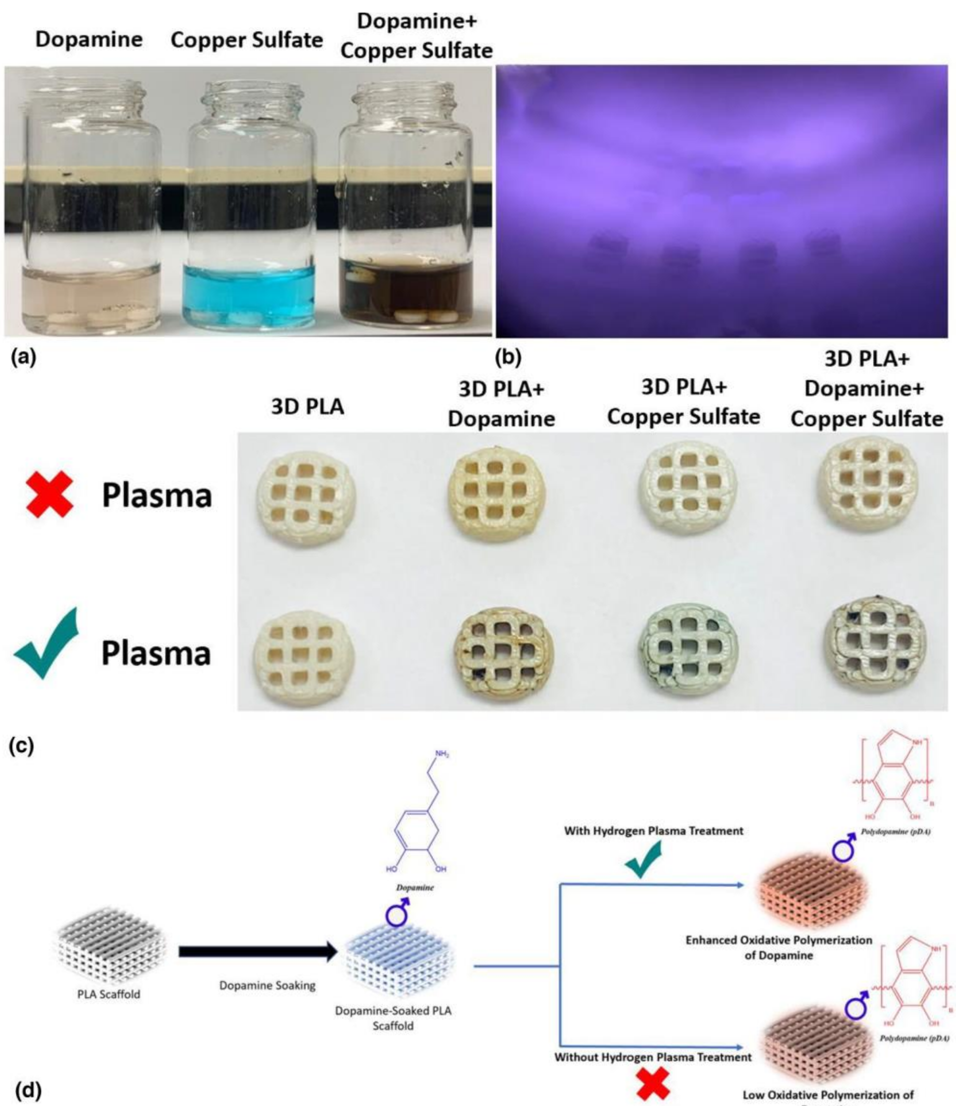

Figure 1. Image of the PLA scaffolds soaked in different solutions (a), Image of the scaffolds undergoing hydrogen plasma treatment (b), Photograph of the scaffolds with and without plasma treatment (c), Schematic Representation of the Enhanced Polydopamine coating on the 3D PLA scaffolds under the application of Hydrogen Plasma Treatment (d).

the plasma treatment was enhancing the polydopamine coating on the scaffolds. We believe the potential mechanism behind the capability of plasma to enhance polydopamine can be attributed to its capability to enhance the oxidative polymerization process of dopamine in tris solution [Fig. 1(d)].

To systematically confirm this observation, initially we have imaged these scaffolds with and without hydrogen plasma treatment using 3D Laser Scanning Microscopy (Fig. 2 and Figure S1). The low- and high-magnification 3D images of the scaffolds have clearly shown that the hydrogen plasma treatment was found to enhance the polydopamine coating on the scaffolds in comparison with non-plasma-treated scaffolds. This was consistent for scaffolds soaked in dopamine and a combination of dopamine and copper sulfate. More specifically, there was a clear formation of polydopamine layer coating on the surface of hydrogen plasma-treated scaffolds. Whereas with the scaffolds with no plasma treatment, the formation of coating was not evident. This observation of increased polydopamine coating in the presence of plasma treatment corroborated well with our experimental hypothesis of rapid and enhanced polydopamine coating in the presence of hydrogen plasma treatment.

Further, we have employed Scanning electron microscopy to get more detailed insights on the properties of the polydopamine coating formed on the scaffold surface. It was seen that for the scaffolds soaked in dopamine solution without hydrogen plasma treatment, there was formation of dense aggregates of dopamine layer formed over the surface of the scaffold [Fig. 3(a)]. This observed self-assembly of dopamine is the indication of the early phase oxidative polymerization process of dopamine in tris buffer.[25] The images of the scaffold soaked in dopamine and treated with hydrogen plasma have shown a more fused and uniform surface layer coating on the scaffold surface [Fig. 3(b)]. This observation clearly supported our hypothesis that plasma treatment can significantly enhance the efficiency of polydopamine coating on the surface of the 3D scaffolds. Similar to the dopamine-soaked batch, in the copper sulfate and dopamine-soaked scaffold also the plasma-treated scaffolds have shown a more uniform surface coating on the scaffold surface in comparison with the non-plasma-treated scaffolds [Fig. 3(c) and (d)]. We believe the potential mechanism behind the capability of plasma to enhance polydopamine can be attributed to its capability to enhance the oxidative polymerization process of dopamine in tris solution. It was already known that plasma is a highly energetic mixture of ionized gas composed of ions, radicals, and electrons.[26] These highly energetic components of hydrogen plasma may influence the rate of the oxidative polymerization process of dopamine in Tris which makes the polydopamine deposition more rapid and efficient.

To show the active components of hydrogen plasma, we have conducted optical emission spectroscopy studies (OES) of the hydrogen plasma (Figure S2). The OES spectrum has displayed major peaks at 434 nm (Balmer series atomic hydrogen H_γ line), peaks from 510 to 530 nm (H_2 peaks) and 650 nm (Balmer series atomic hydrogen H_α line). The peak assignment from the OES spectra was found to correlate well with the previously reported OES spectrums of the different low-pressure

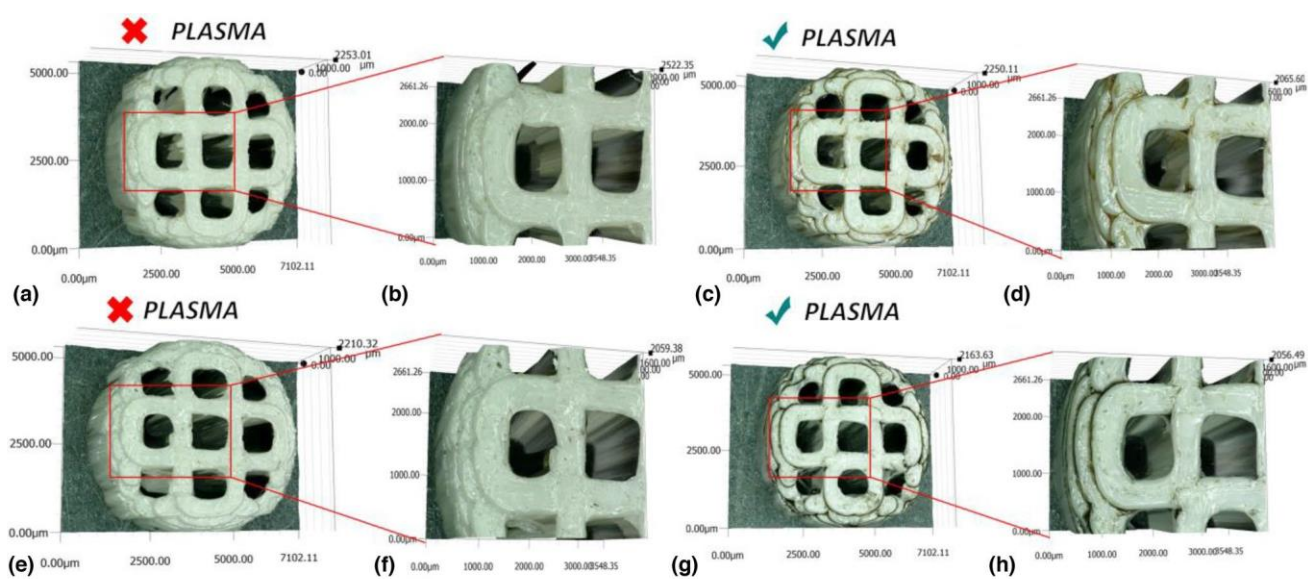

Figure 2. 3D images of the PLA scaffolds soaked in Dopamine without plasma treatment (a), High Magnification-enlarged 3D images of the PLA scaffolds soaked in Dopamine without plasma treatment (b), 3D images of the PLA scaffolds soaked in Dopamine with plasma treatment (c), High Magnification-enlarged 3D images of the PLA scaffolds soaked in Dopamine with plasma treatment (d), 3D images of the PLA scaffolds soaked in Dopamine and Copper Sulfate without plasma treatment (e), High Magnification-enlarged 3D images of the PLA scaffolds soaked in Dopamine and Copper Sulfate without plasma treatment (f), 3D images of the PLA scaffolds soaked in Dopamine and Copper Sulfate with plasma treatment (g), and High Magnification-enlarged 3D images of the PLA scaffolds soaked in Dopamine and Copper Sulfate with plasma treatment (h).

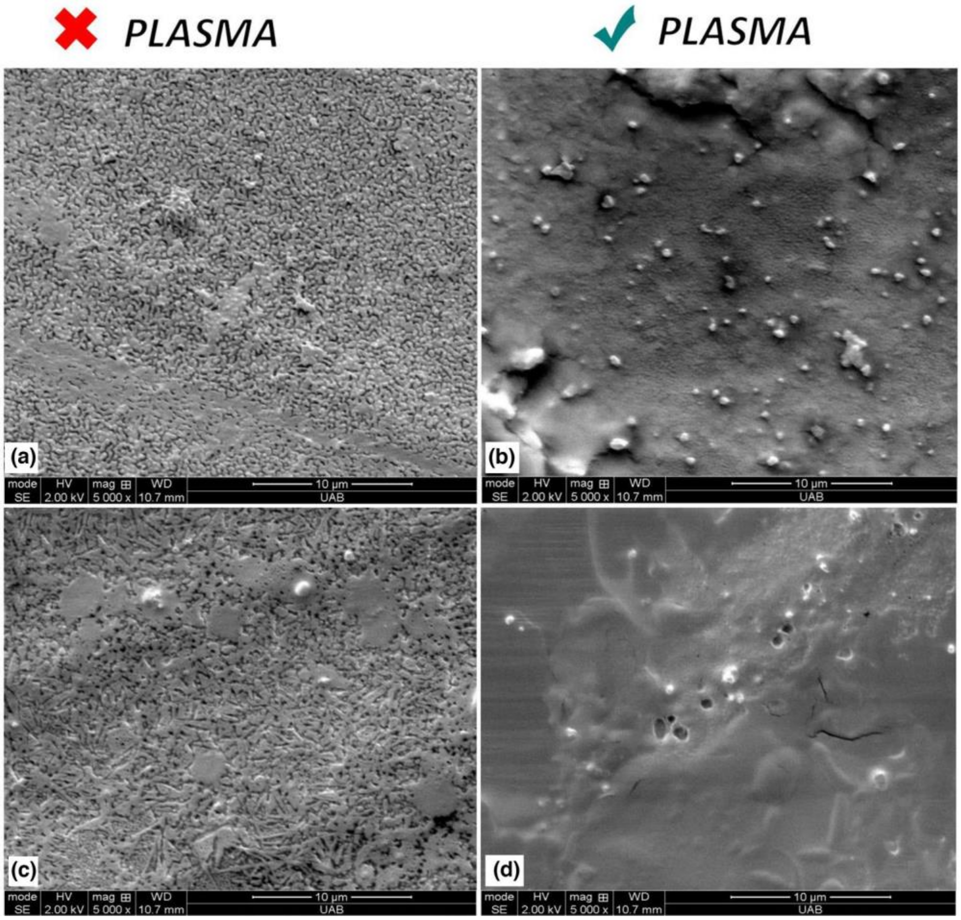

Figure 3. Scanning Electron Microscopy images of the PLA scaffolds soaked in Dopamine without and with plasma treatment (a, b). PLA scaffolds soaked in Dopamine and Copper Sulfate without and with plasma treatment (c, d).

hydrogen plasma.[27,28] This shows that the plasma formed inside the chamber composed of different active hydrogen species. The interaction of these energetic hydrogen species may be the responsible factor for accelerating the dopamine coating. However, more detailed studies are warranted to fully elucidate the mechanistic aspect of the plasma's interaction with the dopamine coated scaffolds, which is beyond the scope of the current study.

The rationale behind using a combination system of copper sulfate and dopamine was to explore the oxidative potential of copper sulfate in dopamine polymerization; it is already known that copper sulfate is a oxidizing agent which can facilitate the oxidative polymerization and formation of polydopamine.[29] Our previous studies has also shown the high reducing environment provided by hydrogen plasma treatment on 3D scaffolds.[24] Hence, we believe that this reducing nature of the hydrogen plasma may cause reduction of the copper sulfate deposited on the scaffold surface. During this reduction process, the reduced copper sulfate can simultaneously facilitate the oxidative polymerization of dopamine. We believe that there is a possibility for a redox reaction (reduction of copper sulfate by hydrogen plasma and oxidative polymerization of dopamine by copper sulfate) which takes place on the surface of the 3D scaffolds.

We have used X-ray Photoelectron Spectroscopy (XPS) as a tool for obtaining detailed insights on the surface properties of the scaffolds (Fig. 4). XPS is one of the important surface quantitative methods used to quantify the surface elemental composition. The XPS spectrum of the control PLA scaffolds only shows carbon and oxygen as the major elements [Fig. 4(a)]. The major goal of using XPS was to see the effect of plasma treatment on increased polydopamine formation on surface. As it is known that polydopamine is a mussel-inspired catecholamine-based polymer.[11] It was seen that for the scaffolds soaked in dopamine and dopamine + copper sulfate undergoing hydrogen plasma treatment was showing higher percentage of surface nitrogen in comparison with non-treated scaffolds [Fig. 4(b) and (c)]. This supported our hypothesis that plasma treatment is enhancing the oxidative polymerization of dopamine which significantly increases the surface nitrogen percentage.

Apart from Nitrogen, other important elements present in polydopamine structure such as carbon and oxygen were also

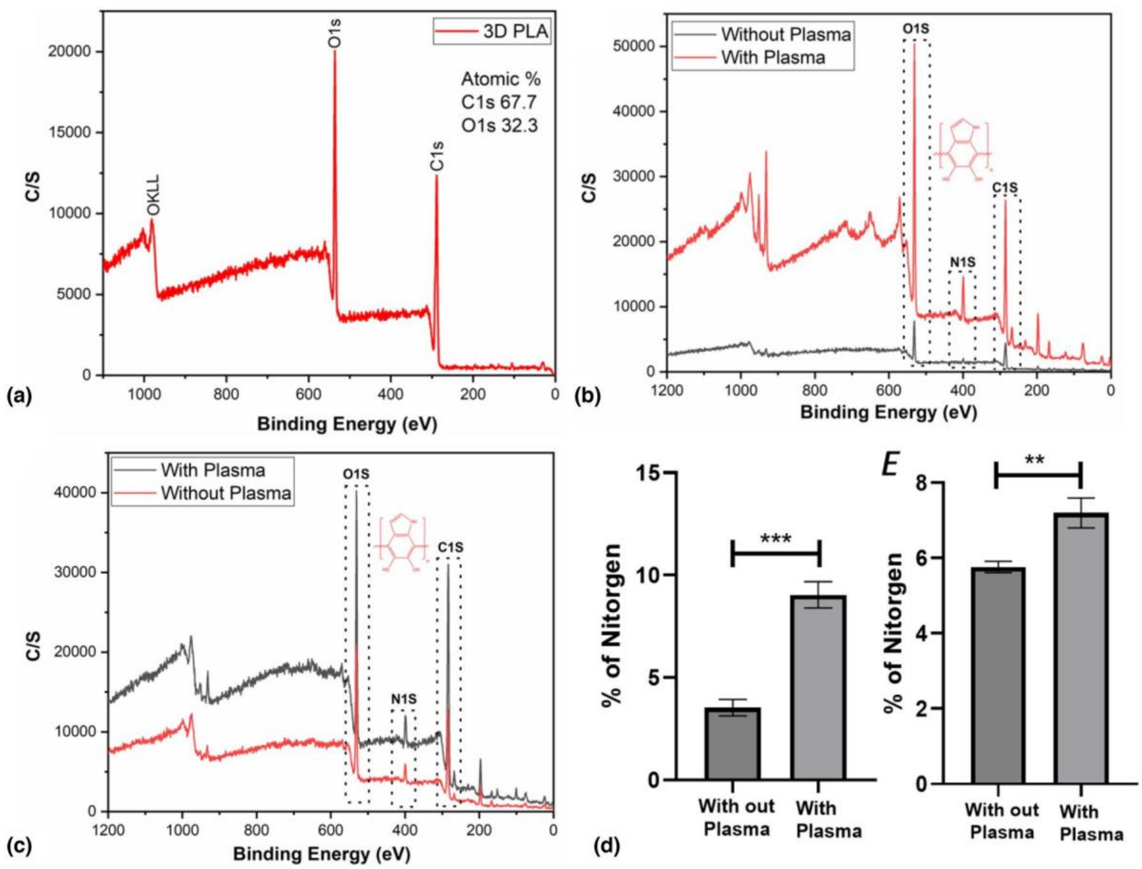

Figure 4. XPS spectra of the control 3D PLA scaffold (a), XPS spectra of the PLA scaffolds soaked in Dopamine without and with plasma treatment (b), XPS spectra of the plasma-treated 3D PLA scaffold soaked in Dopamine and Copper Sulfate without and with plasma treatment (c), XPS-based Quantitative comparison of the atomic percentage of nitrogen in PLA scaffolds soaked in Dopamine without and with plasma treatment (d), and plasma-treated 3D PLA scaffold soaked in Dopamine and Copper Sulfate without and with plasma treatment (e).

found to be significantly higher for hydrogen plasma-treated scaffolds. Thus, XPS analysis has clearly validated our claim of increased polydopamine coating on 3D scaffold surface in the presence of hydrogen plasma treatment.

To specifically determine the rate of plasma-assisted acceleration of dopamine coating, we have compared the surface atomic percentage of nitrogen formed on the surface of plasma-treated and non-treated PLA scaffolds for the scaffolds soaked in dopamine and dopamine + copper sulfate undergoing hydrogen plasma treatment [Fig. 4(d) and (e)]. The rationale behind using the percentage of nitrogen as a metric for the polydopamine coating was attributed to the fact that nitrogen was the only additional element that was absent on the surface of the control 3D Polylactic Acid (PLA) scaffold. Hence, navigating the atomic percentage of the nitrogen gives the best quantification of the polydopamine coating formed on the scaffold surface. It was seen that the dopamine-soaked scaffolds treated with hydrogen plasma has shown a 2.3-fold increase in the surface atomic nitrogen percentage (which can be correlated with the polydopamine coating) in comparison with non-plasma-treated dopamine-soaked samples. While in the case of dopamine + copper sulfate-soaked scaffolds treated with hydrogen plasma has shown a 1.3-fold increase in the surface atomic nitrogen percentage in comparison with non-plasma-treated dopamine-soaked samples.

Subsequently, to get more detailed insight on the chemical bonding environment change before and after hydrogen plasma treatment on the polydopamine formation, we have collected high-resolution XPS spectrum (Figure S3). It was already reported that during the process of polydopamine formation, the N1S core region undergoes significant changes as the oxidative polymerization of dopamine proceeds.[30] The high-resolution N1S core-level region spectra of the scaffolds soaked in dopamine without plasma treatment has shown two fitted peaks at 401 eV(R-NH-R) and 398 eV(C=N–R).[30] Before the plasma treatment, the peak intensity was higher for the peak at 398 eV suggesting the predominant presence of intermediate imine formation of polydopamine at surface. However, after the plasma treatment, this trend changes and the peak intensity of 401 eV becomes more predominant in comparison with the peak at 398 eV, indicating the predominance of secondary amine structure of polydopamine on surface. This observation was same for the plasma-treated scaffolds soaked in the combination of copper sulfate and dopamine. These observations clearly suggested the capability of plasma to enhance the formation of polydopamine on the surface of the scaffolds.

As we have already seen the acceleration of polydopamine coating under the application of hydrogen plasma, we were interested to study the effect of the concentration of the plasma on dopamine coating. To do that, we have systematically varied the power of the plasma chamber ranging from 15, 30, and 45 W. We have utilized XPS spectroscopy to get a quantitative evaluation of the atomic percentage of nitrogen formed over the surface of the scaffolds (Figure S4). The rationale behind using the percentage of nitrogen as a metric for the polydopamine coating was attributed to the fact that nitrogen was the only additional element that was absent on the surface of the Polylactic Acid (PLA) scaffold. Hence, navigating the atomic percentage of the nitrogen gives the best quantification of the polydopamine coating formed on the scaffold surface at different plasma powers. The XPS results show a more significant increase in the atomic percentage of nitrogen for the 45-W plasma power in comparison with the 15W plasma for both dopamine and dopamine & copper sulfate-soaked scaffolds. This observed linear response shows that the higher plasma concentration can increase the polydopamine coating on scaffold surface. This could be attributed to the fact that at increased plasma power/concentration the active hydrogen species becomes more energetic which can interact more efficiently with the dopamine on the scaffold surface. We have also utilized Scanning Electron Microscopy to study the surface properties of the scaffolds irradiated with different plasma powers (Figure S5). It was seen that at high power (45 W) the surface was showing more dense and smooth coating. This observation corroborated well with the XPS results of increased polydopamine coating with higher plasma powers. However, we still acknowledge the fact that more detailed studies with long range of plasma powers and other settings are needed to fully elucidate the plasma concentration dependence of the polydopamine coating. Our future studies will aim to explore these factors to elucidate more detailed insights on the important factors of plasma which can control the polydopamine coating on surfaces.

Conclusion

In conclusion, we report the capability of low-temperature plasma treatment to enhance the polydopamine coating on 3D-printed polymer scaffolds. The coating of materials with polydopamine provides/augments some important properties which includes but not limited to corrosion inhibiting coating, enhanced thermal conductivity, and enhanced adhesion strength. This makes the application of polydopamine-coated materials highly important for material science research. The reported new strategy of using low-temperature plasma can significantly contribute to the development of a more robust and efficient process of polydopamine coating on material surfaces. It offers multiple benefits such as (i) it is a highly scalable method which can be used in large scale for polydopamine coating on different material surfaces, (ii) it could significantly reduce the current processing time of polydopamine coating on material surfaces, and (iii) application of low-temperature plasma not only increase the polydopamine coating on material surfaces, but it can also clean/sterilize the material surfaces for different applications.

Future studies aim to further optimize the polydopamine coating by adjusting different parameters, such as concentration of dopamine precursor, plasma exposure time, and plasma power.

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Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interest

The authors declare no competing financial interest.

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