Dusty Plasma-Assisted Synthesis of Silica Nanoparticles for In Situ Surface Modification of 3D-Printed Polymer Scaffolds

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Dusty Plasma-Assisted Synthesis of Silica Nanoparticles for In Situ Surface Modification of 3D-Printed Polymer Scaffolds

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Abstract: We report a rapid and easy method for the synthesis of silica nanoparticles from a liquid precursor. Specifically, plasma enhanced chemical vapor deposition of a very small amount of a liquid precursor, tetraethoxysilane (300 μL), for a very short exposure time (5 min) resulted in the generation of dusty plasma of silica nanoparticles with a narrow size distribution. The prepared silica nanoparticles were systematically characterized with various analytical techniques. Furthermore, this method was found to modify the surface of the 3D printed polyester scaffold with silica nanoparticles in a very quick and efficient manner.

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Key Words: Silica nanoparticles, Dusty plasma, Chemical vapor deposition, 3D printed polyester, Surface modification.

Introduction

Silica nanoparticles (SiNp) have a wide range of applications such as drug delivery, tissue engineering and photocatalysis.[1-3] The main synthetic route to prepare SiNp is via the hydrolysis of tetraethoxysilane (TEOS) in basic medium known as Stöber method.[4] However, this wet chemistry method of synthesizing SiNp requires several steps, reagents and longer time to produce silica nanoparticles with desired functionality. Alternatively, flame based synthesis of SiNp from TEOS has also been a known method for several years.[5,6] However, the high temperature requirement and polydispersity limits the practical utility of this method.

Hence a more efficient, facile and scalable method of producing stable SiNp will be highly appreciated in the current state of research.

SiNp has a unique capability to control the spread and differentiation of various cell types (Table S1).[S1-S5] It also plays a major role in bone tissue engineering by endowing polyester scaffolds with osteogenic potential (Facilitating natural bone formation).There are different reports on the osteogenic potential endowed by SiNp surface modified polyester scaffolds such as PLGA and PCL.[7-9] The mechanism for this phenomenon was found to correlate with the degradation and release of Si based ions from the SiNp (having appropriate sizes, 200&400 nm) inside the cells.[10] However, the current process of modifying the polyester scaffolds with SiNp are multistep (have to separately prepare SiNp and then modify the scaffolds) and time consuming (can take several hours).[7,8] To best of our knowledge, there are no reports of a one step rapid SiNp modification on polyester scaffolds. In the current study, as part of the on-going plasma-based materials processing, we have designed a new rapid synthesis method based on dusty plasma to prepare SiNp. Also, we have demonstrated the capability of this new process to modify the surface of a 3D printed Polyester Polylacticacid (PLA) scaffold in a robust (5 min) and efficient manner (single step).

Dusty plasma was created via the introduction of TEOS vapors into a low temperature plasma chamber and subsequently this plasma deposited SiNp on the surfaces of the 3D-printed scaffold. We employed a very small quantity of TEOS liquid precursor (300 μL). A very short time period of 5 minutes was used for the plasma enhanced chemical vapor deposition of TEOS monomer to produce dusty plasma of nanoparticles. Air was supplied to the plasma chamber (40 SCCM) to favor the hydrolysis and condensation of TEOS monomer to form

SiNp inside the plasma chamber. We hypothesize that the whole process of nanoparticles production inside the chamber comprises of 3 different phases (Fig 1).

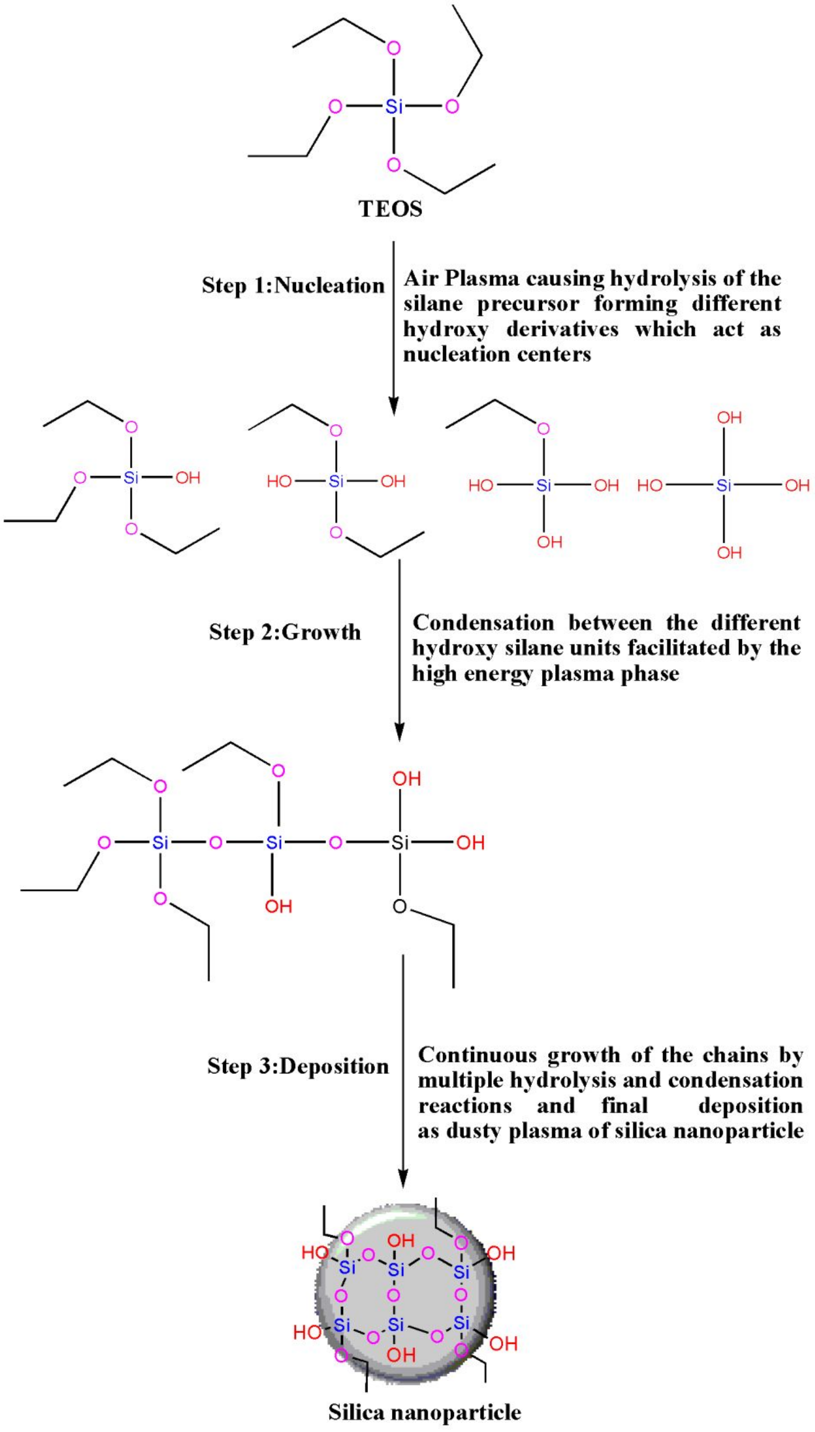

Fig 1: Schematic representation of the dusty plasma assisted synthesis of SiNp

The first phase is the nucleation phase where the water vapor component present in the air plasma causes the hydrolysis of the different ethoxy groups present in TEOS forming different hydroxyl derivatives. These hydroxyl derivatives act as nucleation centers which initiates the process of the nanoparticles formation. More specifically, in the growth phase these hydroxyl derivatives of TEOS condense together under the assistance of high energy plasma phase in to bigger chains. Finally, in the deposition phase, these chain grows in to nanoparticles and deposit inside the chamber. The beauty of this process is that these three different steps are taking place in a very rapid phase (5 min). This greatly facilitates the quicker and cost-effective production of SiNp. After this process, the plasma chamber was found to have white particles deposited which was found to be highly dispersible in water (Fig S1a&b). This white powder was collected and was analyzed for its morphological and size distribution. The SEM imaging of the white powders formed inside the plasma chamber have revealed the presence of spherical clusters of uniform SiNp with average particle size around 200±20 nm (Fig 2a&b, Fig S1c&d). The TEM analysis was also found to have good agreement with the SEM analysis of having a uniform cluster of SiNp (Fig 2c). To assess the effect of time on the nanoparticles formulation, we have employed an additional time point of 20 min for the preparation of SiNp. The SEM and TEM analysis of 20 min nanoparticles sample has clearly shown more fusion which has resulted in the loose of uniformity in the nanoparticles (Fig 2d,e&f). The observed process of more fusion and lack of uniformity observed in 20 min can be attributed to the availability of additional nucleation centers offered by the residual TEOS which was not completely reacted during a short time of 5 minutes. The continuous supply of air in the plasma chamber can thus initiates more hydrolysis and condensation reactions of TEOS this causes higher nucleation and growth process which may cause higher deposition that eventually lead towards the fusion and loss of uniformity in the formed nanoparticles.

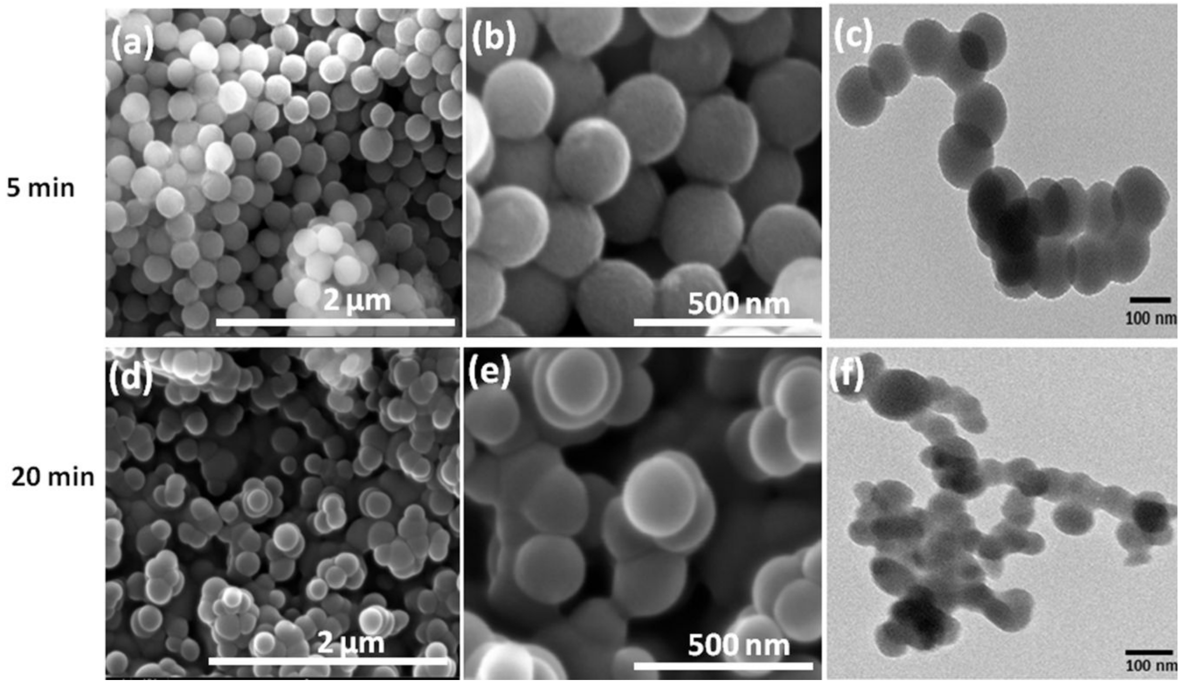

Fig 2: Scanning electron microscopy (SEM) imaging of the SiNp prepared at 5 min (a,b), Transmission electron microscopy (TEM) imaging of the SiNp prepared at 5 min (c). SEM imaging of the SiNp prepared at 20 min (d,e), TEM imaging of the SiNp prepared at 20 min (f).

The Dynamic light scattering experiments have revealed that the average hydrodynamic size of the SiNp 5 and 20 min were 210±20nm and 230±30nm respectively (Fig S2a&b). The zeta potential measurements of the SiNp 5 and 20 min have revealed negative values of -12 and -17 mV respectively (Fig S3a&b). The surface chemistry of the prepared SiNp was further evaluated with the help of X ray photoelectron spectroscopy (XPS). The XPS analysis of SiNp collected on the top of the aluminum substrate has clearly shown the presence of silica and oxygen as major elements (Fig 3a). The high resolution $Si2_P$ XPS spectrum has shown mainly two different bonding environments, SiO_2 and SiO (Fig 3b). Thus XPS analysis has suggested the formation of SiNp. FTIR spectra of the SiNp have revealed characteristic peaks of silica at 450 cm^{-1} (Si-O rocking vibrations), 793 cm^{-1} (Si-O symmetric stretching vibrations), 950 cm^{-1} (Si-OH stretching vibrations), 1020 cm^{-1} (Si-O asymmetric stretching vibrations) and 3420 cm^{-1} (OH stretching vibration in Si-OH and bound water groups) (Fig 3c). Apart from these peaks, there were presence of other peaks at 1392 cm^{-1} &1444 cm^{-1} (symmetric CH bending and asymmetric CH bending) and 2891&2973 cm^{-1} (asymmetric and asymmetric CH stretching vibrations).[11-12] These peaks may be originated from some of the unhydrolysed ethoxy groups of TEOS.

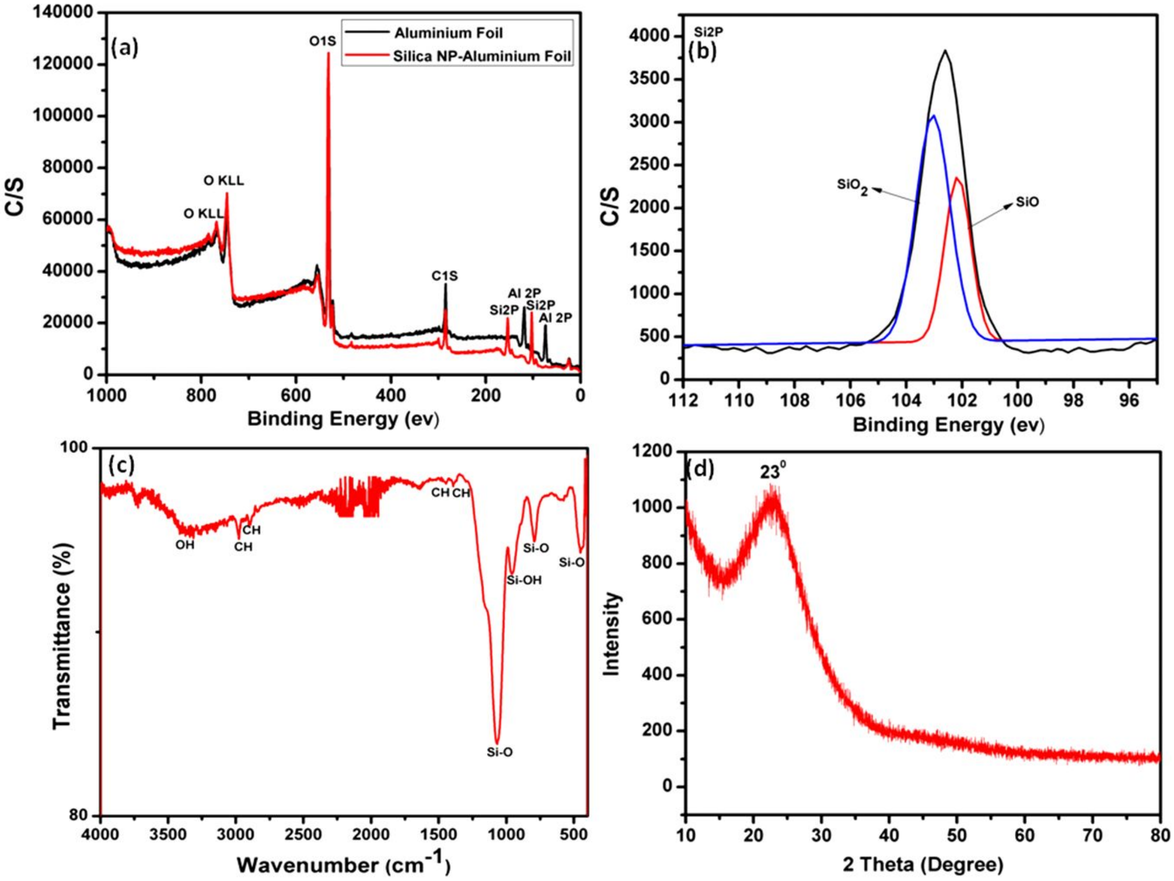

Fig 3: XPS spectra of the Si Np grown on aluminum substrate (a), High resolution Si2$_P$ XPS spectra of SiNp (b), FTIR spectra of the SiNp (c), XRD spectra of the SiNp (d).

The observed FTIR spectrum was in well agreement with the standard FTIR spectrum reported for SiNp produced by modified Stöber process.[13] X ray diffraction analysis (XRD) was further performed on the SiNp (Fig 3d); XRD spectrum has shown peak at 2θ of 23°, the observed broad XRD spectrum was suggesting the possible amorphous characteristics of the prepared SiNp. The observed XRD spectrum of SiNp was comparable to the standard spectrum reported for SiNp.[13] Hence, taken together the XPS, FTIR and XRD analysis has clearly suggested the formation of SiNp. Further, we have tested the capability of this new method to modify the surface of 3D PLA scaffolds. We have designed and 3D printed a porous polyester scaffold based on PLA (Fig S4a). Recently it was reported that the substrate geometry has a greater impact on the collection of duty plasma nanoparticles produced from plasma enhanced chemical vapor deposition.[14] More specifically, a 3 dimensional collection well (Polystyrene plates) was found to enable higher deposition of nanoparticles in comparison with a flat scaffold which leads to a coating (without any significant amount of nanoparticles). Hence, usage of 3D scaffolds is beneficial to enhance the dusty plasma nanoparticle modification compared to thin films. It was found that our method was found to uniformly deposit/modify the surface of the polyester scaffolds with SiNp in a very quicker time (5 min) (Fig S4b&c). SEM imaging of the top, front and left side of the scaffolds were evaluated to get more insight regarding the modification of the scaffolds from different directions (Fig 4).

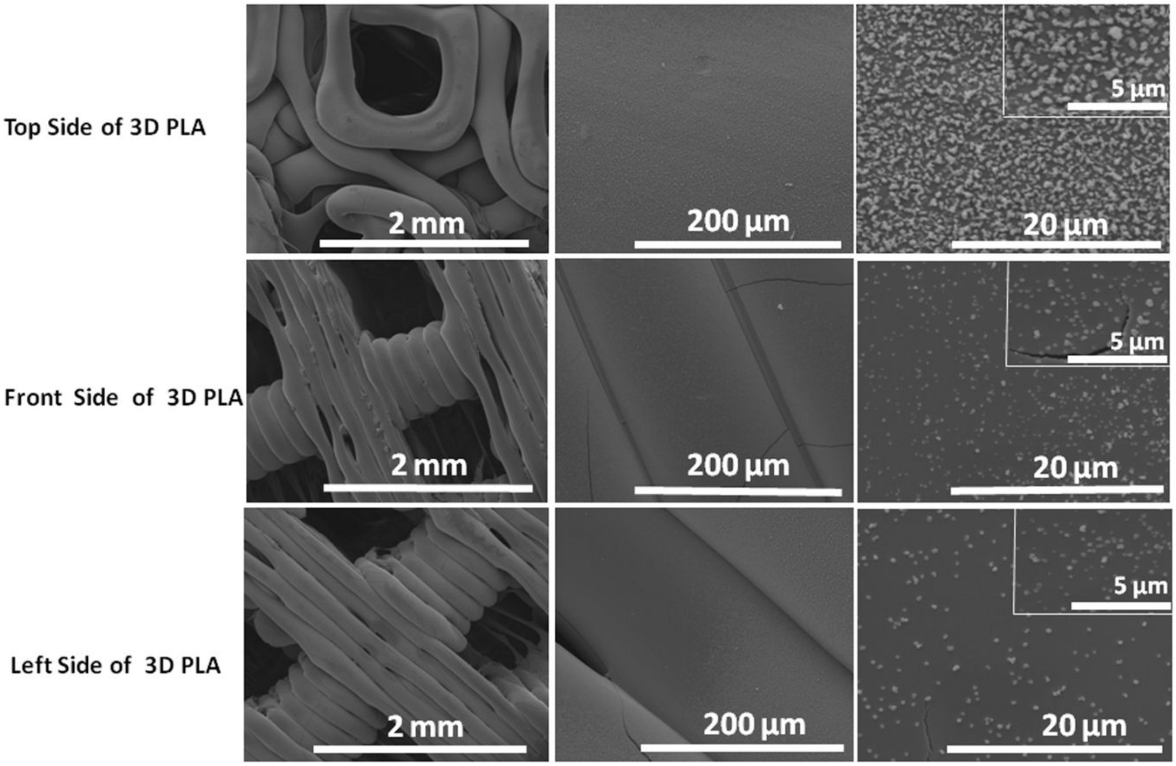

Fig 4: SEM imaging of the 3D PLA scaffolds after 5 min of SiNp dusty plasma treatment from different sides (The inset of the third column of pictures represent high magnification images).

It was seen that top side has the highest deposition compared to front side and left side. This is because top side is the one with high surface area, which get the maximum plasma exposure; SEM imaging also has clearly shown the presence of significant amount of SiNp in front and left side of the scaffolds, suggesting that the modification is happening from all the three sides but not to similar extent due to difference in the surface area available for plasma exposure. Changing the substrate geometry and changing the scaffold position (Instead of placing the scaffold flat inside the chamber it could be hanged in vertical position) inside the plasma chamber could have some potential impact in getting uniform amount of deposition from all the directions. The observed insitu surface modification of 3D PLA scaffolds with silica nanoparticles in single step and quick time are highly efficient compared to the recently reported polydopamine and gold nanoparticles based surface modification on 3D PCL scaffolds which require multistep and longer time.[S5] The longer dusty plasma exposure (20 min) on the 3D PLA scaffold was found to exhibit a very high concentration of SiNp deposition that are highly clustered and lose its uniformity (Fig S5). The XPS spectral analyses have shown that the surface of the PLA scaffolds were found to have the presence of silica and oxygen indicating the formation of silica nanoparticles formation on the surface of PLA (Fig S6a & S6b). The 20 min plasma exposure 3D PLA scaffolds have shown higher amount of silica on its surface which clearly shows the time dependency of this process (Fig S6c). The FTIR spectral analysis of the scaffolds have shown an additional peak at 3420 cm^{-1} (attributed to the OH stretching vibrations) for the 5 and 20 min plasma exposed scaffolds in comparison with the pristine PLA scaffolds (Fig S6d). The emergence of such polar hydrophilic hydroxyl groups may endow favorable biointerface for tissue regeneration applications.

Conclusion: In conclusion, this reported new method has the following appealing attributes (i) it is a single step greener and cost effective process, (ii) the radiofrequency plasma reactor can be an ideal scalable technology for industries to produce and modify the surface of various biomedical scaffolds/devices with SiNp (iii) this method can simultaneously modify the PLA scaffolds with SiNp for biomedical applications like bone tissue engineering and also sterilize the scaffold. The future aspects of this present work will deal with (i) functionalization and attachment of SiNp with biochemical moieties by using volatile amino acids in the plasma phase and (ii) strategies for preparation spiky SiNp and mesoporous SiNp *via* plasma process.

Supporting Information: All the experimental details, some of the nanoparticles characterizations such as DLS, Zeta potential, XPS and SEM are provided in the supporting information of the manuscript

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Author Contributions: VT and VMV conceptualized the idea and experimental plan, VMV and BT carried out the experiments and data analyses. PD has designed the 3D scaffolds used for the experiments. All authors including YK contributed in discussion and writing/editing and all approved the final version of the manuscript.

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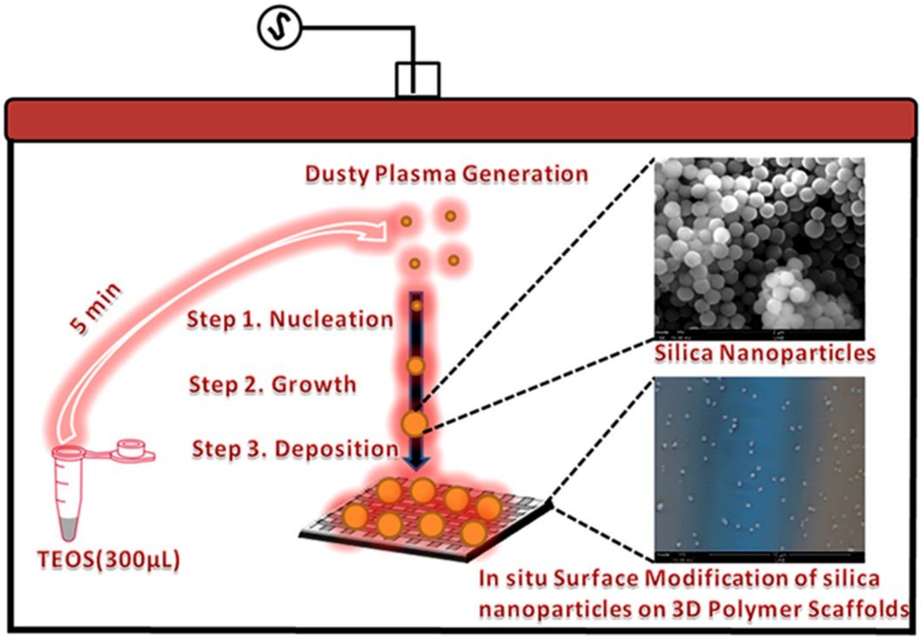

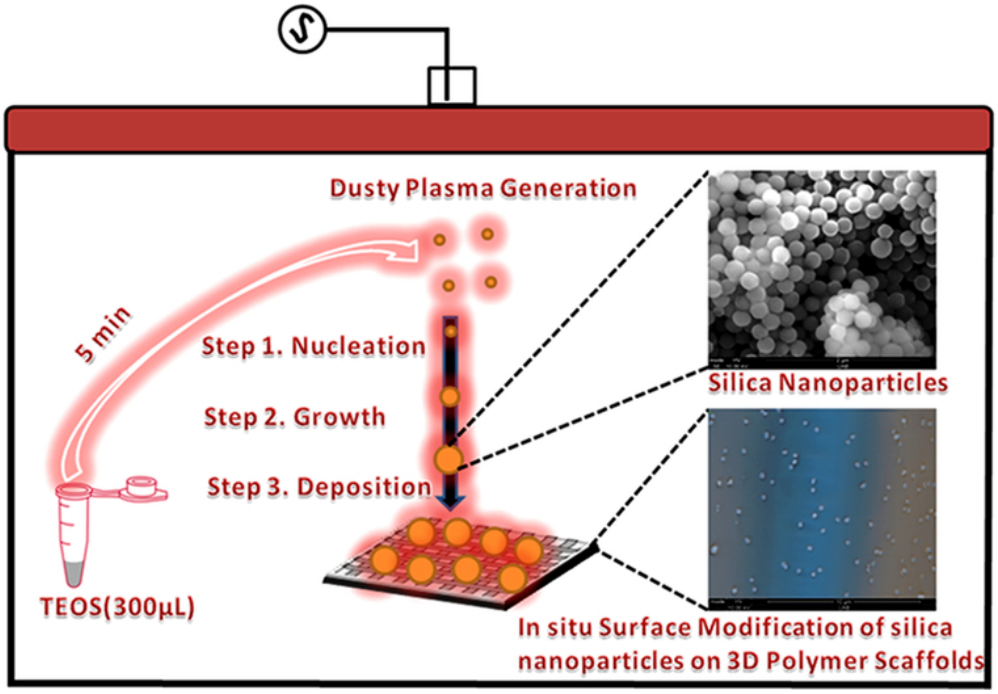

Non-thermal dusty plasma assisted in situ synthesis of silica nanoparticles and its application in modifying the surface properties of 3D printed polymer scaffolds

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