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Tunable synthesis and in situ growth of silicon-carbon mesostructures using impermeable plasma

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In recent years, plasma-assisted synthesis has been extensively used in large scale production of functional nano- and micro-scale materials for numerous applications in optoelectronics, photonics, plasmonics, magnetism and drug delivery, however systematic formation of these minuscule structures has remained a challenge. Here we demonstrate a new method to closely manipulate mesostructures in terms of size, composition and morphology by controlling permeability at the boundaries of an impermeable plasma surrounded by a blanket of neutrals. In situ and rapid growth of thin films in the core region due to ion screening is among other benefits of our method. Similarly we can take advantage of exceptional properties of plasma to control the morphology of the as deposited nanostructures. Probing the plasma at boundaries by means of observing the nanostructures, further provides interesting insights into the behaviour of gas-insulated plasmas with possible implications on efficacy of viscous heating and non-magnetic confinement.

Thermal plasma because of its broad range of enthalpy is an ideal medium for readily tuning the total energy of a system of reactants¹. Of particular interest in this scenario is the nature of interactions between plasma and neutrals with regard to its potential applications in synthesis of new materials. In a quasi-steady plasma, these interactions can be subdivided into diffusion of fast neutrals and slow neutrals at the boundaries². If the plasma has a sufficiently high ion density, the slow neutrals which have a relatively lower temperature are readily stopped at the interface between the hot plasma and the cold gas blanket whereas the fast neutrals, due to their higher energies, can somewhat penetrate into the plasma before getting ionized and absorbed³. It is apparent that the temperature and therefore enthalpy of such a gas blanket system gradually increases towards the hotter core region of the plasma where the initial discharge channel under the source is located. At a hypothetical point where the temperature of neutrals gets comparable to that of the core owing to successive ion-neutral collisions, enthalpy reaches a critical value beyond which ionization has a noticeable effect on the plasma equilibrium. The resulting partially ionized boundary layer then effectively separates the plasma from the influx of impinging neutrals by balancing the pressure gradient⁴.

Within this boundary layer, there are at least two distinct regimes⁵ each with its own set of properties which can potentially affect the process of synthesis: 1) The outer *boundary region* where only the slow components perturb the steady state and 2) The inner *ionization region* where the fast neutrals are present. The former has a more turbulent nature and lower temperature due to the presence of neutrals while the latter because of the flow of transverse electric currents is essentially diamagnetic⁶ and therefore establishes a strong screening effect which minimizes ion loss. This special type of plasma is referred to as impermeable plasma suggesting that incorporation of both ions and neutrals at the boundaries can be closely controlled to give rise to a myriad of structures with customized properties. In this study we report a new method for systematic synthesis of virtually any mesostructure by utilizing these exceptional properties of impermeable plasma at high pressure differences of the order of 7500 Torr. Extremely rapid (typically a few seconds) growth of nanostructured thin films in a controlled manner is also demonstrated which can be attributed to the earlier introduced ion screening effect as well as the dissimilar potentials of non-identical ions⁷.

Introduction of silicon and carbon impurities to help with passively characterizing thermal plasma all the way down to nanoscale is another attractive capability of this approach which cannot be attained using the common intrusive probing techniques.

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Results

Impermeable plasma just like any other source of heat can be used to synthesize a variety of materials, but in order to demonstrate the versatility of this process, one must carefully choose the reactants to have distinct and stable products at different enthalpy levels. For this study we discuss the high temperature reaction of carbon and silicon given the countless energy-dependent structures it can create⁸. Furthermore the ability of carbon in forming a cascade of nanostructures due to the high flexibility of sp^n hybridization for $1 \leq n \leq 3$ (Ref. 9) is likely to prove advantageous in observing the effects of ion screening and element separation on the mechanism of growth. In other words we take advantage of a variety of nucleation growth pathways to synthesize distinct nanostructures which closely correlate with characteristics of plasma considering the temperature density during nucleation and growth are quite different for every structure.

What differentiates impermeable plasma synthesis (IPS) from more conventional approaches is the unique property of its boundary layers which grants us the ability to closely tune the process. In order to control the size of the structures for example, we can simply disturb the growth process by regulating the population of the

impinging neutrals which on account of their lower temperature perturb the otherwise homogeneous hot plasma.

Theoretically the penetration length for fast neutrals exceeds that of slow neutrals by orders of magnitude given their higher energy level and the larger cross section for ion-neutral collisions compared to electron-neutral collisions (See Appendix A in supplementary information). However in laboratory experiments, this ratio conversely translates into a wider boundary region (see Fig. S1 in Appendix A for a qualitative diagram) as a result of the non-ideal compensation for ion outflux via diffusion. A more practical approach to modifying the extent of each regime therefore would be to monitor the permeability of plasma through different density balance conditions. Assuming an approximate isolation due to ion screening, in any practical case, changing the pressure of the blanket (influx) and the gas used to generate the column of plasma (outflux) can collectively influence permeability via critical density of ions and neutrals at the interface (See Appendix A in supplementary information)⁶. Consequently, higher permeability of the outermost layers leads to emergence of SiC nanocrystals in the vicinity of the blanket while those regions closer to the ionization region remain in a state of quasi-equilibrium to foster defect free microstructures (Fig 1a and 1.b.).

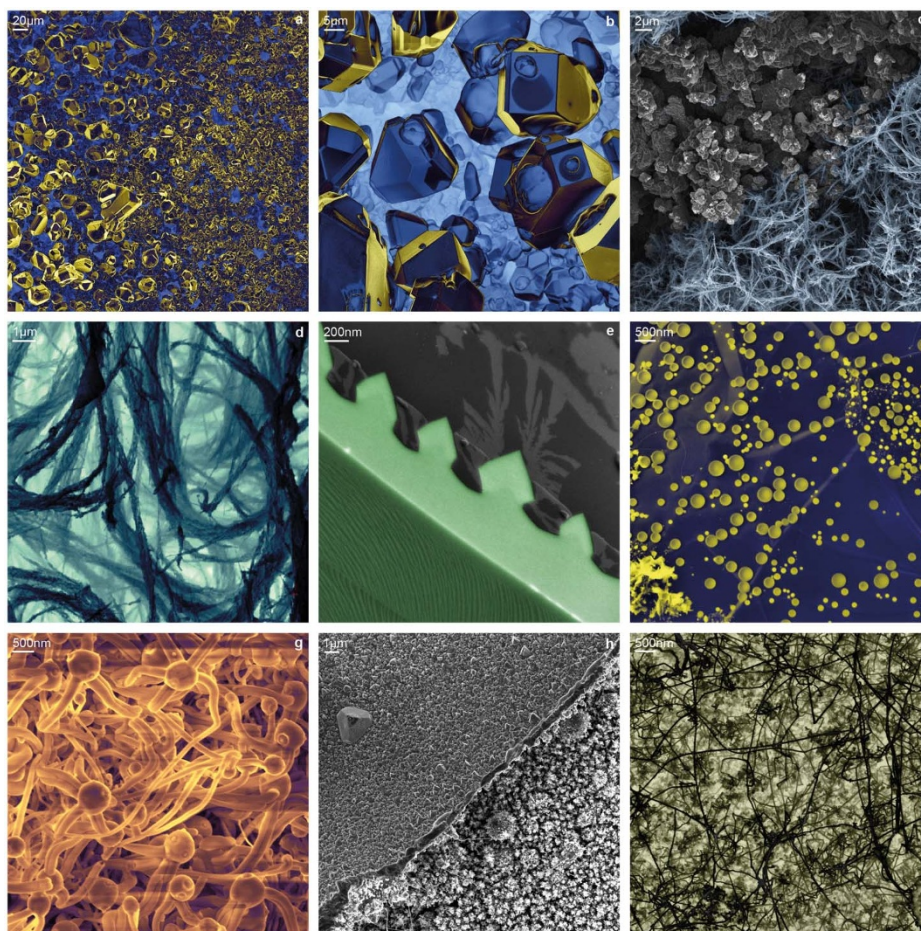


Figure 1 | A few of many meso and nanostructures synthesized using IPS. a) Sharp transition from microcrystals to nanocrystals at the boundary layers is clearly seen. b) A magnified view of microcrystals showing their perfectly faceted structure. c) Spatially well-defined growth of nanodendrites in the vicinity of ionization region is due to the presence of fast neutrals and diamagnetic properties of this layer. d) A magnified view of the nanodendrites with a depth of several microns. e) Uniform growth of graphitic carbon on an as-synthesized SiC crystal in the core region. Exfoliation and the consequent multi layer graphene are visible. f) Spherical quantum dots synthesized by adding carbon dioxide to the argon atmosphere. Large size of some of the dots (~ 200 nm) is associated with subtle concentration of impurities (see Fig. 2.a). g) The exotic nano-octopus structures synthesized under oxygen atmosphere show strong charging effects because of their large oxide content. Intricacy of this particular morphology makes it a good radiation absorbent. h) Pyramidal quantum dots synthesized by cyclic exposure of SiC microcrystals to boundary plasma. Size tuning of these structures should be possible by controlling the permeability during the second exposure. Note the well-defined interface and the unreacted region to the right. i) Nanowires formed through treatment of nanocrystals with boundary plasma have a uniform diameter of ~ 10 nm.



Beyond this outer boundary layer the temperature drop is steep preventing the occurrence of highly endothermic reactions, although nanoparticles may still be obtained (see Appendix B). The sudden decrease in temperature has origin in diamagnetic characteristic of the ionization region which effectively confines the ions. Ion screening, along with element separation, further gives rise to yet another interesting aspect of impermeable plasma; the extremely rapid in situ growth of nanostructured thin films of carbon on as-synthesized silicon carbide crystals.

It is evident from Fig. 1.c and 1.d that the morphology of the thin films is also a function of plasma permeability. Data from energy dispersive spectroscopy (EDS) confirm this idea by indicating that the nanodendrites grown in the close vicinity of the ionization region are largely carbon-based (up to 96%) and therefore the screening of carbon ions was effective. The exotic morphology of these nanodendrites can be attributed to perturbation of the quasi-steady plasma by the impinging fast neutrals. This is in agreement with previous observations that dendritic forms obey diffusion limited aggregation¹⁰ a process in which diffusion in a non-steady state is the primary means of transport in the system.

In the core region on the other hand, due to relative stability of the plasma, the process of growth takes a different turn producing pyrolytic carbon nanotubes¹¹ (refer to Appendix C) in short exposures (~10 seconds) and graphene (Fig 1.e) for longer exposures (~90 seconds). HRTEM image of carbon deposition on SiC

crystals can be found in Appendix D. The carbon nanodendrites, pyrolytic or otherwise, are in particular promising materials as electrodes in OLEDs¹² as well as batteries¹³ and for reinforcement of composites¹⁴. Graphene also has extraordinary potentials for high speed electronics¹⁵.

Morphological features in some cases are largely affected by composition. Quantum dots shown in Fig. 1.f for example were only obtained once the synthesis was performed under Ar+CO₂ (1:1 volumetric ratio) atmosphere. Due to considerable oxygen contents (16%), we believe that thermal decomposition of CO₂ had an essential role in disturbing the growth and emergence of these structures. Moreover the size of nanoparticles was observed to have direct correspondence to concentration of a number of impurities as suggested by EDS data presented in Fig 2.

In general, gases that are reactive at room temperature should likewise give more flexibility to IPS. To test this hypothesis, we used Ar+O₂ atmosphere to grow the exotic nano-octopuses of Fig 1.g. These structures owing to high oxygen content (37%) are not only good dielectrics but also because of their intricate morphology effectively absorb radiation. Micrographs of samples exposed to different doses of X-Ray can be found in Appendix E. The relative strength of only a few micron film of these structures in dissipating radiation into heat and their potential ability to spontaneously grow back make for attractive candidates for durable radiation shielding of spacecrafts¹⁶.

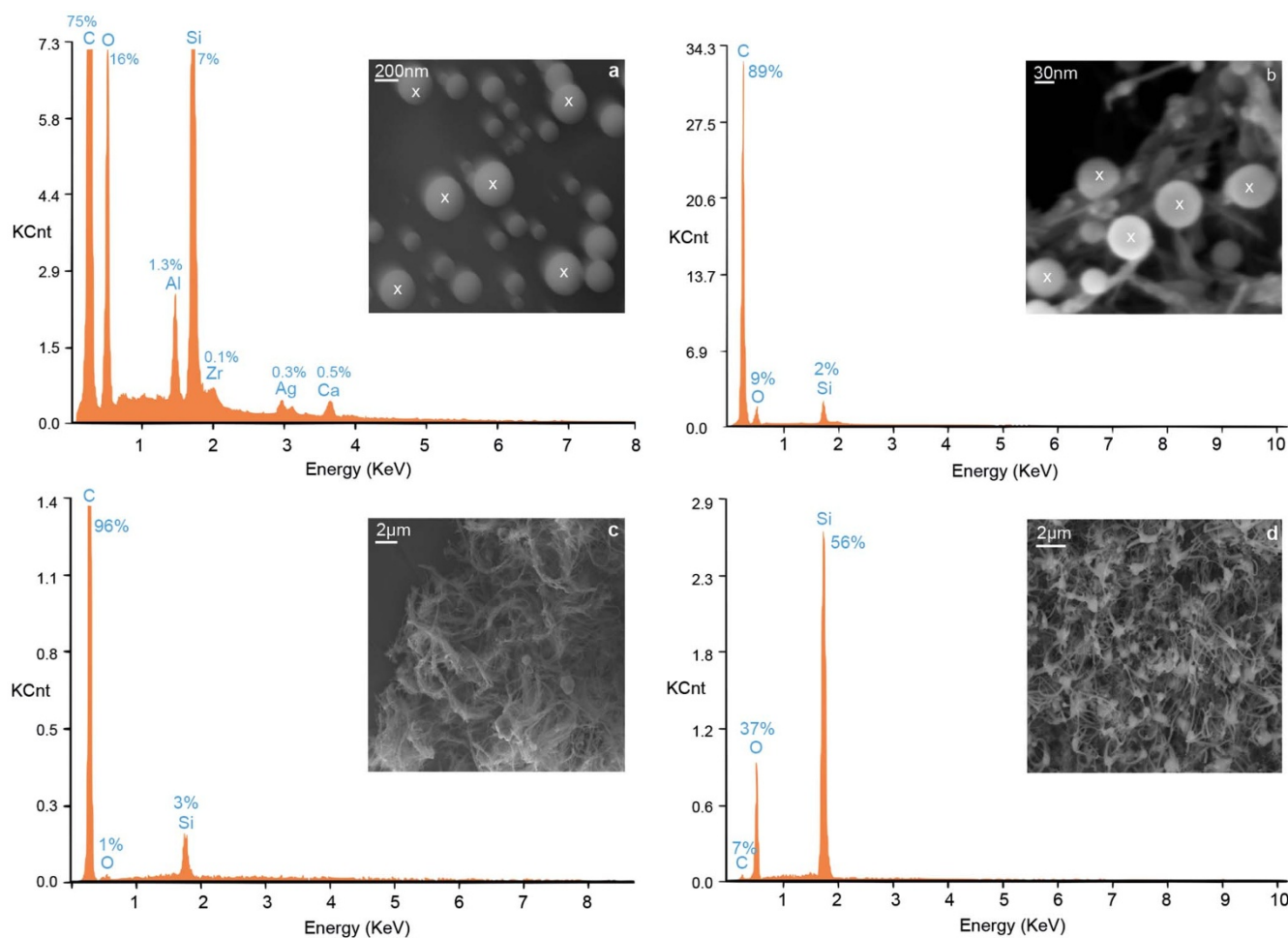


Figure 2 | Energy dispersive spectra of selected structures manifests morphology- and size-dependency on composition. The insets are secondary electron images of the corresponding structures. a, b) EDS for large (~200 nm) and small dots (~40 nm) are shown. Note the presence of impurities in large dots. c) Spatially well-defined growth of nanodendrites with large carbon contents indicates how the screening effect confined the carbon ions within the core. d) Significant oxygen content of nano-octopus structures is clearly detected. Lack of large concentration of carbon can be related to heavy oxidation.



In IPS, further tuning of mesostructures is achieved by exposing the sample to plasma in a cyclic manner. Microscale crystals of Fig. 1.b, initially synthesized with 90 second exposure, were quenched to room temperature right after synthesis by purging the chamber with high pressure (15 bars) flow of argon and were subsequently treated again with plasma for 30 seconds to give SiC pyramidal quantum dots of Fig 1.h (see Appendix F for a closer look). Nanocrystals undergoing the same procedure transformed into SiC nanowires shown in figure 1.i. Large scale synthesis of pyramidal quantum dots due to their strained structure¹⁷ and nanowires for their superior properties especially ballistic conductance¹⁸ is attractive for optoelectronic applications.

Discussion

In principle there are countless structures that can be synthesized using IPS and we cannot possibly go through each of them here given that other than the prominent effect of permeability, smallest changes in exposure time alone can give rise to new morphologies. For instance for intermediate exposures (20 seconds) the twisted nanotubes of Appendix C unfold and at 30 seconds, by introducing carbon dioxide, large hollow onions start to grow at the end of the each tube (see Appendix G). These or other resulting structures may

have different properties and thus different applications, however all can be synthesized using the universal approach described here. The relative isolation and the quasi-steady state of impermeable plasma due to ion screening offer a significant level of control over the total energy level in the system and that is how altering any parameter even slightly leads to new products.

Achieving such a versatility using a typical thermal plasma is not feasible mainly because of substantial heat conduction via ion loss to the surrounding¹⁹ which can in turn alter the kinetics of reaction. Additionally an arc channel developed under the sole effect of Ohmic heating is limited in dimension to the size of the electrode²⁰ and is not homogenous owing to lower collision frequency in the absence of screening.

In impermeable plasma, on the contrary, the higher rate of ion-ion collisions in the core which is due to ion screening induces viscous heating²¹. For high pressure differences of the order of +7500 Torr (the plus sign indicates higher pressure of the influx), this effect were found to be the dominant source of enthalpy in which case heating is essentially due to dissipation of kinetic energy during Coulomb collisions. Even though this secondary heating mechanism is similar to neutral beam injection in principle²², through conservation of ions in the core, it is to a large extent self-sustaining. As represented in

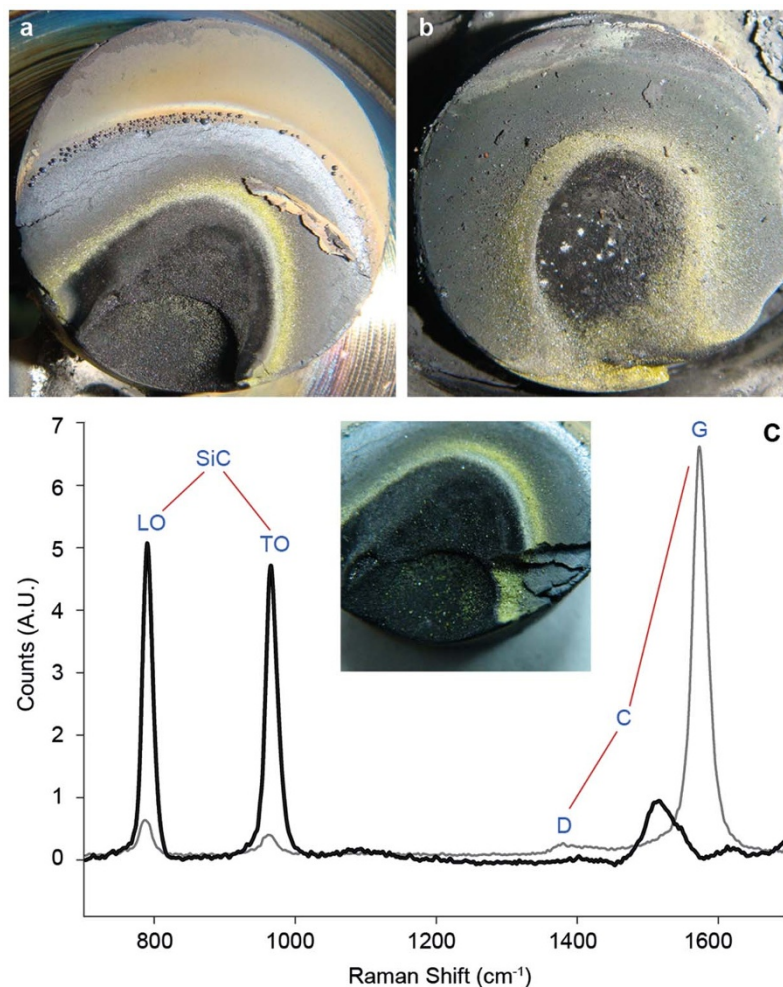


Figure 3 | Advantage of impermeable plasma over permeable plasma: All samples are 2 cm in diameter. a) IPS at 100A exhibits great yield despite of low current discharge. The secondary source of energy, viscous heating was dominant. The boundary acted as a physical barrier and the influx of cold gas pushed the plasma to the opposite side. See Appendix H for a schematic diagram. b) With a negative influx, the plasma is largely permeable and therefore no viscous heating takes place. Even though a larger discharge current of 300A was applied, the yield is minimal. Note the reaction zone is nearly centred and the thick boundary regions are not well-defined meaning that neutrals could readily penetrate deep into the core. c) Raman spectrum of SiC crystals (thicker line) in the boundary region versus that of carbon nanodendrites of the ionization region is given. In situ growth over as-synthesized crystal is evident. The inset depicts removal of carbon nanostructures to reveal the SiC crystals beneath.



Fig. 3.a, a sample synthesized at 100A for discharge current shows higher yield of synthesis using impermeable plasma (positive flux difference) whereas for the sample of Fig. 3.b even though the current was threefold (300A) the negative pressure difference (-7500 Torr) made the plasma largely permeable and thus the synthesis had a substantially lower yield. This can be attributed to the fact that in impermeable plasma the highly ionized column rapidly spreads from the initial channel ($1/8''$ in diameter) toward the boundaries generating a homogeneous medium with the same size as that of the torch (1 cm in diameter).

The observation that in our experiments viscous heating surpassed the common Ohmic heating hints at possible applications in nuclear fusion studies where currently the inefficiency of resistive heating at elevated temperatures due to high conductivity of plasma is a major barrier²³. A similar analogy applies to the case of electric propulsion systems where heat loss to the walls limits the efficiency of ion thrusters and the costly magnetic confinement is the only solution at the moment²⁴. For such applications, further work is required to determine the behaviour of gas-insulated plasma under case-specific conditions for which utilization of spatially resolved emission spectroscopy techniques is necessary considering the plasma core is surrounded by the blanket as well as several boundary layers. Current double-pulse techniques with their millimetre resolution²⁵ limit our ability in analyzing the boundary regimes which can sometimes be as small as 100 microns in width, but future progress is expected to improve our understanding of IPS, efficacy of viscous heating in thermonuclear reactors and non-magnetic confinement.

In regard to synthesis of mesostructures we demonstrated that composition, size and morphology can be effectively tuned by altering the permeability conditions, exposure time, reaction atmosphere and concentration of impurities. Element separation due to dissimilar ionization potentials in parallel with ion screening was also shown to cause in situ growth of nanostructured thin films over as-synthesized crystals. Contrary to other methods where a diverse collection of nanostructures are produced together needing an ex situ separation through chemical or physical treatments, in our method different regimes of an impermeable plasma are responsible for production of spatially homogeneous, yet versatile meso and nanostructures both in composition and size.

We hope that this report serves as an introduction to infinite possibilities IPS can offer and encourage the scientific community to explore new aspects of this approach for synthesis of other mesostructures. Further work to improve precision and controllability of this method is in progress and more thorough analysis of the novel materials synthesized using this method will be published soon.

Methods

Sample preparation. 99.9% pure silicon and graphite powders (max particle size: 45 and 75 microns respectively) were dried overnight at 150°C . The dried powders were subsequently blended using a planetary ball mill with zirconia beads (1 cm in diameter) for 4 hours at 300 RPM after which the powders were mixed (1:1 molar concentration) using the same equipments for another 8 hours. The mixed powder were then compacted into tablets (2 cm in diameter) using a hydraulic press at 13 metric tons. Similar results in the case of using a silicon wafer along with a carbon-seeded thermal plasma is expected, however the morphologies might be affected by the substrate.

Experimental setup. A DC source (max output: 300 A) was used to create an arc discharge between a water-cooled cylindrical tungsten electrode $1/8''$ in diameter and a homemade steel chamber which was grounded. The sample was placed in the cavity of the chamber right under the electrode. The good conductivity of graphite helps with maintaining the arc. The sample and the electrode should initially be in contact until the arc is established after which the electrode should be lifted to a distance comparable to the diameter of the torch to avoid damaging the chamber.

The argon plasma was ejected from an alumina torch (1 cm in diameter) at the sample for different durations (10–120 seconds). Pressure of plasma outflow (from torch) and that of blanket (influx) as well as discharge current were set at different values to record their effect on plasma permeability and yield of synthesis. The cold gas was injected from an inlet (1 cm in diameter) on the side of the chamber and continuously exhausted from another hole (same diameter) on the opposite side. A schematic diagram of the setup is available in Appendix H.

Monitoring permeability. Upon sublimation of carbon, the blue colour plasma of argon becomes bright red. A simple method to monitor the permeability of plasma is to qualitatively measure the carbon contents in the exhaust through cooling. If the plasma is partially permeable the exhaust gas produces carbon flakes, whereas if the plasma is impermeable, no carbon should be observed in the tank considering the ions are effectively screened at the boundaries and cannot leave the plasma core in large numbers. Note that carbon gas has a temperature beyond 4000 K and therefore the transparent tank used for monitoring if made from plastic is easily damaged by the lava-like carbon flakes as they solidify. A quartz tank is therefore preferred.

Caution. If the cavity inside the chamber is too large, the cold gas may accumulate inside the chamber over long exposures. The entrapped gas upon receiving enough heat through interaction with the core may break the impermeability of plasma leading to uncontrolled release of heat and eventually violent explosions. When designing the chamber, the ratio between the chamber cavity and gas inlet/outlet is critical. A ratio of at least 4:1 (cavity diameter: inlet/outlet diameter) is recommended to allow for a constant flow of neutrals. In addition, the experimental setup has to remain stationary while in operation. A rotating plasma if not confined by external magnetic fields can give rise to uncontrolled instabilities mainly due to ion drift.

Characterization. Morphologies were analyzed using a Zeiss Auriga Field-Emission Scanning Electron Microscope (FESEM) at 5–10 kV. For colour-enhancement, exclusion and difference filters available in commercially available graphical software packages were applied. Chemical compositions were initially studied using Energy Dispersive Spectroscopy (EDS) on Zeiss Auriga. Raman spectra were obtained on a Renishaw inVia Micro-Raman equipped with an Olympus microscope. An excitation wavelength of 325 nm (UV) from a 20 mW HeCd laser at 50% power was used. Exposure time was 30 seconds.

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Author contributions

A.Y. designed and performed the experiments as well as the characteristics. Both authors interpreted the data and wrote the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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