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Plasma-nano-interface in perspective: from plasma-for-nano to nano-plasmas

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Abstract

This article introduces an updated focus of plasma nanoscience after a dozen years of successful international research efforts. The concept of plasma-nano-interface involves two fundamental options: plasmas in contact with nanoscale features and plasmas which have nanoscale dimensions on their own. Non-equilibrium and transient features pertinent to the both cases are discussed in view of the recent progress in the field. Plasma-like phenomena in nanometer-sized materials, the third dimension of plasma nanoscience, also benefit from the insights based on fundamentals of plasma physics. Opportunities for future science discoveries, cross-disciplinary collaborations and translational research and development are highlighted.

Keywords: plasma, nanoscience, nanoscale synthesis, plasma-specific effects

(Some figures may appear in colour only in the online journal)

Plasma nanoscience and three cornerstones. Plasma nanoscience [1] is broadly defined as a research field focusing on scientific research and practical applications arising from the consideration of the following three fundamental questions (figure 1):

- *Plasma-for-nano:* How to use plasma-specific effects arising upon contact of low-temperature plasmas with solid objects of nanoscale dimensions to create or modify nanoscale matter, virtually at will?
- *Nano-plasmas:* Is it possible to reduce the plasma size to the nanoscales, similar to other (solid, liquid, and gas) states of matter and utilize the arising exotic physical effects such as ultra-high-energy densities and extreme radiation?
- *Nano-plasma-effects:* How plasma-like collective excitations determine physical and chemical properties of nanoscale structures and how to utilize these properties in practical applications?

Localization. These questions are centered around plasmas, the fourth and most extreme state of matter on one hand, and nanoscale localization of energy and matter on the other. The energy and matter are carried by the elementary bits such as electrons, ions, photons, neutral and ionized atomic, molecular, and radical species as well as quasi-particles such as photons, phonons, holes, excitons and more complex formations such as bi-excitons, tri-excitons, quantum droplets, and some others. Localization within microscopic, and nanometer scales in particular, introduces several unique, often exotic conditions that do not persist in mesocopic and macroscopic environments [3, 4].

In other words, plasma nanoscience deals with interactions of the above bits of energy and matter that take place within very small spaces or over very small surfaces where at least one characteristic dimension belongs to the nanometer range (typically under 100 s of nm). Importantly, these interactions are either caused by the plasma-generated particles or exhibit plasma-like collective effects within the given spatial dimensions.

Space and time scales. Depending on the type and numbers of the particles involved, the temporal scales of the collective processes range from ultrashort, femtosecond ($\sim10^{-15}$ s) to days, years and even longer. For example, electron processes and the associated energy transfer typically take place over the scales shorter than picoseconds
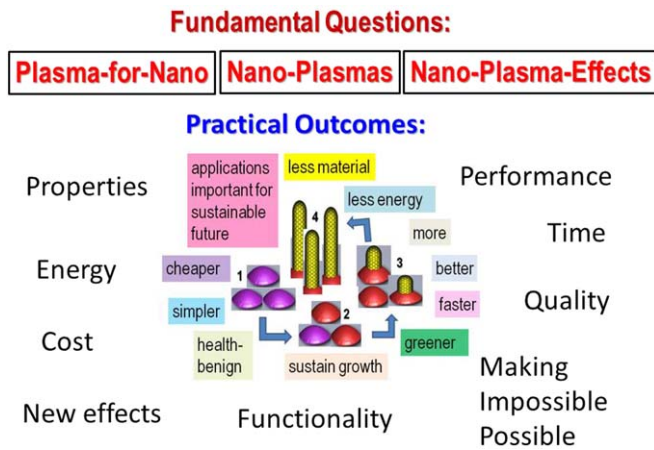
Figure 1. Fundamental questions, practical outcomes and specific objectives of relevance to plasma nanoscience research. Reproduced from [2]. Copyright © 2013, IEEE.
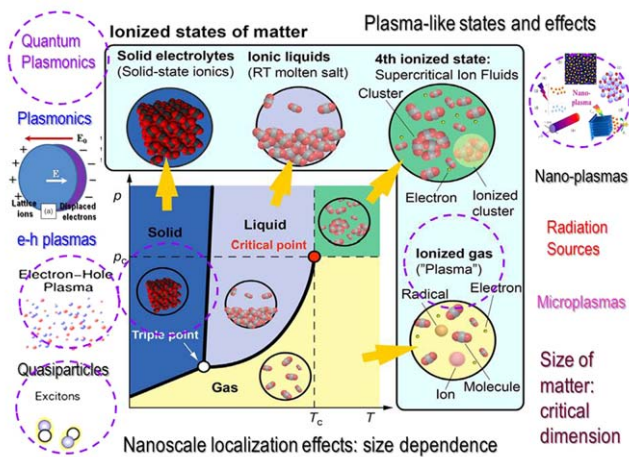

Figure 2. Various ionized states of matter, plasma-like states and nanoscale localization effects. Reproduced from [6]. © IOP Publishing Ltd.

($\sim 10^{-12}$ s); energy exchange interactions between electrons and ions/neutrals require $\sim 10^{-12}$–10^{-8} s; whereas atomic, radical, molecular etc processes on the surface and in the bulk usually last above 10^{-8} s [5]. The actual times are very sensitive to the environmental conditions that include the type of ionized state of matter, plasma-like excitations summarized in figure 2 as well as background particles and radiation. Interaction with the background is a determining factor on the specific types and rates of the multitude of collective interactions within the localized microscopic and nanoscale systems. If within a given volume, the density of particles is too low, they may not interact, for instance through collisions. Conversely, if the density is too high, the interaction may not only be strongly collisional, but may also lead to a certain degree of strongly coupled, potentially correlated interactions.

Plasma-nano-interface. These general features are common for the three key fundamental questions above and can be combined into a single concept of *plasma-nano-interface*. This concept reflects the confinement of the interactions rather than merely the nanometer scale atomic layer

on solid surfaces that directly face the plasma generated particles and are thus most affected by the plasma exposure. This concept may more broadly be understood as the interface between plasma science and nanoscience.

Such interfacing should be done with caution, because in most gas discharges, plasmas only exist beyond a few Debye lengths, which determine the spatial scales of charge separation, while plasmas are required to remain overall charge neutral. Hence, in nanoscale synthesis and processing plasmas extend over a very large number of nanostructures, even though the specific points of impact of plasma generated species onto the solid surface may be determined with nanometer, and even higher precision. These interactions and the effects they cause determine the nature of diverse physical effects that take place on plasma exposed solid surfaces during nanostructure formation or nanoscale surface modification, or in other words, the *plasma-for-nano* aspect (see figure 1 for relevant practical outcomes and their key criteria).

Plasma production: challenges. On the other hand, reducing plasmas into microscopic [7] and then nanometer [8] domain is extremely challenging because of the need to satisfy the Debye criterion for a reasonably large number of particles that are all confined within the domains with at least one dimension in the nanometer range. In other words, the electron Debye length should ideally be in the low nanometer range while the size of the overall charge neutral plasma cluster should still be in the sub-100 nm range to satisfy the broad definition of the nanometer domain. Production of such nano-plasmas and study of the associated extreme (e.g., XUV, x-ray etc) radiation and ultra-high-energy-density (UHED) effects form the second, *nano-plasmas* aspect of plasma nanoscience highlighted in top right corner of figure 2.

Plasma-like excitations also appear in solid and liquid media under various types and levels of external excitations. For example, plasmonic excitations are the results of collective oscillations of de-localized (e.g., free) electrons in metals or semiconductors around the ions firmly fixed in crystalline lattice serving as a charge compensating background [9]. These plasmonic oscillations are described by the same collective electron oscillation formalism and resonant plasma frequency $\omega_p = (4\pi e^2 n_e/m_e)^{1/2}$ (where e, n_e, and m_e are the electron charge, concentration, and mass, respectively) as the classical plasma oscillations in gas discharge plasmas (e.g., various eigenmodes in discharge plasmas [10]). Moreover, across-bandgap photonic excitations in semiconductors lead to the creation ('ionization') of two types of space-separated charge carriers, namely electrons and holes. The holes represent positively charged quasiparticles that act like ions in gaseous plasmas in terms of charge compensation and shielding of negatively charged electrons. The electron-hole oscillations are the examples of possible plasma-like collective effects in solid-state plasmas with two types of photo-excited charge carriers. Depending on the density and energies of the electrons and holes, more complex coupled states such as excitons and bi-excitons may exist. Importantly, the level of localization of the plasma-like excitations as well as coupling and correlations between the charged and neutral species involved strongly depends on the scale of localization

determined by the size of nanoparticles or quantum well at the interface between the solid materials. When such scales are reduced to the low-nm domain, quantum non-locality and spatial correlation effects come into play and enrich the diversity of the physical effects even further. The study of these interesting, and in many cases size-dependent effects forms the third, *nano-plasma-effects* aspect of plasma nanoscience. The various possibilities that arise at different levels of particle and energy coupling in the localized nanoscale systems are summarized on the right hand size in figure 2.

In this *Perspective article*, we highlight some of the key achievements in the field in these three aspects mostly over the last dozen years and map some of the most promising areas for the future scientific research and technological development.

Plasma-for-nano. This area is the most traditional for the plasma nanoscience research. Starting from earlier works on plasma-assisted synthesis of mostly carbon- and silicon based nanostructures in 1990s to early 2000s [11–23], research expanded into a large variety of materials systems, including organic and inorganic materials; materials made of the same atoms (e.g., pure metals) as well as binary, ternary, quarternary and even more complex compounds; single-phase and composite nanomaterials; materials with diverse surface features and several others [24–43]. Exposure of these materials to plasmas of various types has produced a large variety of nanoscale structures and features, which are either grown by addition (e.g., deposition) of materials onto the substrate (which is termed bottom-up nanoscale synthesis in nanoscience) or formed by removing material from the material (e.g., by reactive chemical etching using ion beams or chemically reactive plasmas). Importantly, the interactions between the plasma-generated species (e.g., ions, radicals) and these nanostructures or nano-features are localized within nanometer scales and proceed in many cases very differently compared to the processes on solid surfaces exposed to neutral gases (e.g., in thermal chemical vapor deposition). Significant research efforts have been devoted to better understand the many unique and interesting physical and chemical effects that could be generated through such nanoscale localizations of multi-phase interactions at plasma-solid interfaces under non-equilibrium conditions.

Series of experimental and theoretical research efforts on nucleation and growth of various nanoparticles in the plasma bulk as well as nanostructure and nano-feature formation on plasma exposed surfaces revealed that plasma-specific effects manifest themselves over several spatial scales representing different levels of organization of the system [44]. For example, in the growth of vertically oriented carbon nanotubes (both single- and multi-walled), six levels of interfacing plasma and solid could be identified: (1) plasma-whole substrate in the reactor (e.g., tens of cm across); (2) plasma sheath between the solid surface and plasma bulk (e.g., tens of micrometers to millimeters); (3) dimensions of nanostructure patterns on the surface (e.g., sizes of growth domains produced by patterning); (4) length and thickness of individual nanotubes in the patterns/arrays; (5) sizes of catalyst particles
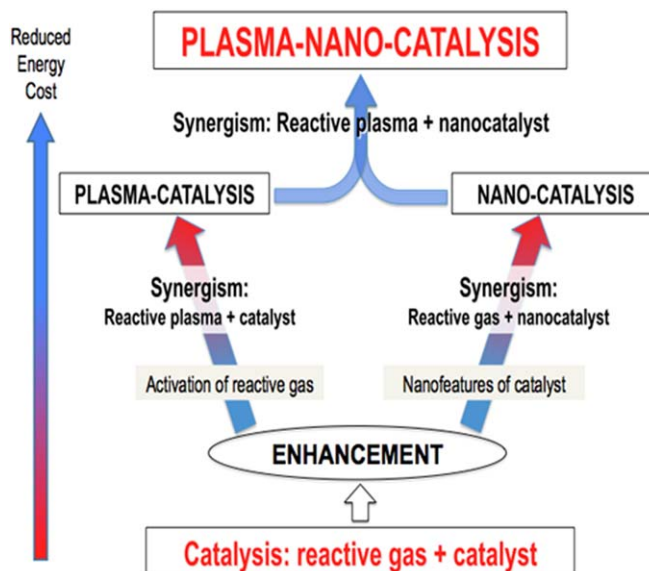

Figure 3. Synergistic effects in plasma-nano-catalysis.

that support nanotube nucleation and growth; (6) interatomic spacings and precise positioning of heteroatoms over the surface or within the nanoscale catalyst particles (the latter is often referred to as coordinated atomic sites in catalysis science).

Owing to the interfacing levels of different complexity, plasmas, plasma generated charges, species, and electromagnetic fields interact with the solid surfaces and affect energy and matter organization at each of these levels. Under favorable (e.g., optimum) conditions, these interactions may lead to a number of fundamental synergies. The interactions appear synergistic when the outcome of the two interactive effects exceeds the combination of the outcomes of two separate processes under the same reaction conditions (1 + 1 > 2) [45]. Synergies arise at each of the six hierarchical levels mentioned above.

In terms of practical utility, it is instructive to examine the synergies arising in plasma catalysis when plasma species, electric fields, catalyst particles, precursor, intermediate, and product species interact within nanometer areas, wherein the localization is determined by, e.g., the catalyst nanoparticle size. The desired catalytic effects appear through localized nanoscale interactions at the plasma interface. These effects enable several advanced applications of low-temperature plasmas in micro- and nanofabrication, nanoscale materials synthesis and processing, industrial catalysis, new sustainable industrial processes based on green-chemistry approaches [46].

An example of synergies arising in plasma catalysis [45] that relies on nanometer-sized catalyst particles is presented in figure 3. Indeed, there are two common ways to enhance interactions of reactive gas and catalyst particles. First, is to activate the source gas, by using plasmas, while nanoscale features of the plasma-activated catalyst help ensure the key requirements of product selectivity [47, 48]. In this way, plasma enhances the activity while nanoparticles enhance the selectivity and under optimum conditions this interaction can

be synergistic as has very recently been demonstrated by several research groups [49, 50]. It is worth emphasizing that the entire series of processes involved in the catalytic conversion of abundant or waste gases into valuable products, e.g., conversion of natural gas CH_4+CO_2 into $CO+H_2$, is localized over nanoscale areas on the catalyst particles. Quite similar localized nanoscale plasma chemistry was shown to take place in plasma-assisted growth of carbon nanotubes and semiconducting (e.g., Si) nanowires, through nanoscale plasma-surface interactions [44, 51], which appear to be quite similar to interactions of plasmas with small solid dust particles [52].

A large and ever increasing number of publications suggest that many exotic effects appear when the size of the plasma-solid interface is reduced into nanometer domain. Apart from the challenging a decade ago but now common place plasma-nano catalysis [45], reforming of natural carbon-based resources into chemicals, fuels, and multipurpose functional materials (e.g., for catalysis, energy storage etc) may lead to green and sustainable nanotechnology [46].

Distinctive features of more recent (last few years) state of-the-art in the field is convergence with advanced thermal [53], ionic [54] and other processes to control macroscopic properties of materials by precise manipulations of atomic bonds, atoms and defects at nanoscales. Precise defect engineering of nanoscale materials leading to advanced functionalities and enhanced performance has marked a notable paradigm shift in nanoscale synthesis and processing. In this regard, plasma ions hold enormous potential and are now increasingly regarded as a useful and effectively controlled tool that can be used for precise manipulation of matter at nanoscales, for example nanopore shrinking, localized phase transitions and atomic bond reconstruction upon exposure to energetic ions beams [54]. Another example demonstrates that gentle ion bombardment by low-energy ions with the energy in the specific range helps heal atomic defects in the single-atom-thin carbon sheet at the early stage of nucleation of single-walled carbon nanotubes [55]. Ion bombardment has largely been considered detrimental even a decade ago, and present-day advances in control capabilities is one of the key factors facilitating this paradigm shift, leading to the previously challenging precise treatment of delicate nanomaterials such as graphene and other two-dimensional materials [56–58].

Major advances have been seen in the applications of plasma-produced nanocrystals, nanostructures and nanomaterials in practical devices [59–61]. For example, silicon and other semiconducting nanocrystals synthesized in plasmas have been integrated into electronic and optoelectronic devices [31]. On the other hand, metal oxide nanowires, presently being produced at ever increasing scales (e.g., quantities per hour of reactor operation), are very promising for applications in industrial catalysis and energy storage devices and systems. Acting in synergy with advanced chemical engineering methods, significant opportunities for industrial applications and entrepreneurship arise, for example in the development of high-performance, durable membranes for water purification to address the escalating issue of scarce potable water supply [32].

Nano-plasmas. Generation of nano-plasmas under extremely non-equilibrium conditions, while being a dream of theoreticians for decades, has only recently become a well-established and reliable experimental reality [62, 63]. This advance is underpinned by the advents of extremely powerful and fast (e.g., femtosecond) radiation sources capable to generate extremely non-equilibrium matter featuring high-energy-density and UHED states on one hand, and ultrafast, time-resolved spectroscopy capable to image femtosecond and even shorter processes with unprecedented accuracy and reliability [64]. Importantly, nanoscale interfacing of solid targets and powerful excitation sources makes it possible to produce nano-plasmas, for example through fs laser induced explosion of atomic clusters or nanoparticles (typically under 100 nm in size). In this case, up to several tens of electrons can be extracted from inner atomic shells, thus producing atomic ionization numbers of the order of +50 and higher. Given that the electrons can be generated even with sub-relativistic energies, the extra-high values of energy-density, extending into UHED domain, may be generated for the development of next-generation extreme (THz to x-ray) radiation sources [65]. These and several other major advances in the area of nano-plasmas generated by intense radiation have recently been critically examined from the plasma nanoscience perspective [8].

The greatest challenge in this area is the very early stage of research which is still very far from practical applications. Even though extra-powerful nano-plasma bursts can presently be generated in a controlled and reproducible way, the time scales of existence of such nano-plasmas (e.g., from hundreds of fs to few ps) are very short which makes it very challenging to develop applications that specifically aim to capture the benefits of the nanometer stage of the nanoparticle/nanocluster explosion. Science-wise, even though nano-plasmas do satisfy the plasma criteria (and can be regarded as 'proper' plasmas) their status as nanoscale objects still remain elusive, mostly during the transitional stage preceding the nanoparticle explosion and during the early stages of the explosion. Moreover, size-dependent effects that are very clearly manifested for nanoscale solid, liquid, and gaseous states of matter still require significant attention for nano-plasmas. Very high costs and reliance on expensive radiation sources make experimentation in this area very challenging. However, microexplosions have recently been demonstrated using small scale table-top fs laser sources, which brings us a hope that by combining small nanostructures and such table-top sources one could produce and characterize nano-plasmas that might potentially be suitable for compact ultra-powerful radiation sources (e.g., 'pocket synchrotrons') [8].

Nano-plasma-effects. Nano-plasma effects have been actively studied in plasmonics field. These studies have been traditionally focused around either metal nanoparticles for localized surface plasmons [66] or thin metal slabs for surface plasmon polariton [67] excitations, although the range of viable (e.g., relatively low loss) plasmonic materials and metamaterials (e.g., graphenes, MaXenes, nitrides, 2D

materials, etc) has recently seen strong expansion. While traditional pure electronic plasmon excitations show nano-plasma-like behavior while excited and localized in nanoparticles, there is no consensus in multidisciplinary community whether these excitations can be considered as nano-plasmas, without deliberate ionization of matter as is commonly done in the *nano-plasma* case discussed above. Nevertheless, the plasmonic oscillations show a very clear size dependence. Moreover, when nanoparticle sizes shrink into the low nanometer range, the quantum effects of electron delocalization become not only non-negligible but even possibly dominant. This interesting phenomenon requires the development of quantum physics based theories that ulti-mately bring into consideration coupling of electrons and photons within localized nanometer spaces, thereby opening the now advanced field of quantum plasmonics [68–71].

Situations when both positive (holes) and negative (electrons) charge carriers are generated by intentional photo-excitation (see figure 2 on the left hand side) of semi-conductor heterostructures and quantum wells, clear overall charge neutral plasma-like states may exist and even possibly be localized within the small nanometer interfacial transition layer, although the latter aspect presently is not very clear. Under favorable conditions, exciton, bi-exciton and even more complex coupled, quasiparticle states may form, pos-sibly on the plasma background. As the quasiparticles con-sume electrons and holes, the density, and hence the frequencies of plasma eigenmode oscillations of these plas-mas become lower. Interestingly, the sizes of such quasi-particles determined by the extent of localization of electron wavefunctions in confined space, can be in the nanometer range as was recently demonstrated for the quantum droplet (dropleton) case [72]. However, given the ambiguity asso-ciated with defining the localization and confinement scales in quantum wells for various types of correlated collective coupled excitation (e.g., excitons, bi- and tri-excitons) makes it presently challenging to clearly define size-dependent effects associated with such undoubtedly very interesting nano-plasma effects. These and other important questions, especially related to practical applications of the intriguing quantum phenomena, still remain essentially open and present excellent opportunities for cross-disciplinary collaborations in the near future.

Generic opportunities. The opportunities for plasma nanoscience research in all areas are expected to be enhanced by more proactive engagement of cross-disciplinary platforms such as plasma-materials informatics. This can be done, e.g. in a way similar to the virtually non-existent a decade ago, presently rapidly emerging advanced functional materials discovery platforms based on big data science, new approa-ches for machine learning, and artificial intelligence [73]. These enabling technologies combine to drastically augment human intelligence capabilities in materials design, fabrica-tion, performance testing and process/product-specific applications. Relevant platforms are currently most advanced and widespread in health-related areas such as drug discovery using advanced big data-enabled genomics, proteomics, and epigenomics [74]. This obviously creates opportunities for

plasma researchers to actively engage with data science, artificial intelligence, robotics and intelligent industrial pro-cess engineering to contribute to the upcoming digital tech-nology driven industrial transformations supported by the global internet of things, Industrie 4.0/5.0 and other emerging platforms. One could expect many radical developments in these areas that are expected to significantly stimulate plasma science and applications in the coming years, to materialize the ultimate ambitious goals of plasma-enabled transforma-tive industrial technologies towards prosperous and sustain-able society.

Closing remarks. The three cornerstones of plasma nanoscience articulate the focus and scale of this undoubtedly very interesting, dynamic and promising multidisciplinary research field. The few arguments presented in this Perspec-tive article suggest that important fundamental and practical advances might be expected in the near future and therefore more attention of the plasma physics community to the arising collaborative opportunities might be desirable.

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