NanoNEXT

Research Article

DOI: 10.54392/nnxt2542

Plasma-Assisted Synthesis and Engineering of Functional Nanomaterials: From Metal Nanoparticles to 2D Architectures

Ranjithkumar Rajamani [a, *], Chi Van Nguyen [b]

[a] Department of Biotechnology, Sri Ramakrishna College of Arts & Science, Nava India, Coimbatore-641006, India
[b] Faculty of Technology, Dong Nai Technology University, Dong Nai Province, Vietnam
* Corresponding author Email: biotechranjith@gmail.com
DOI: https://doi.org/10.54392/nnxt2542
Received: 19-07-2025; Revised: 23-11-2025; Accepted: 02-12-2025; Published: 11-12-2025

Abstract: Plasma-assisted synthesis methods offer a flexible, low-temperature and eco-friendly way to create nanomaterials with specific properties. This paper examines the basic interactions between plasma and materials that enable the creation and functionalization of advanced materials. We categorize plasma sources into four main types: DC, RF, microwave and dielectric barrier discharge (DBD). We also compare high- and low-temperature systems, focusing on how they deliver energy and create reactive particles. The review highlights plasma-liquid interfaces where solvated electrons and radicals allow for single-step, surfactant-free synthesis of metal nanoparticles. The paper explains how plasma induces etching, doping and defect formation in various materials such as catalysts, metal-organic frameworks (MOFs), quantum dots and 2D materials like graphene, hexagonal boron nitride (h-BN) and diamond. Plasma processes provide accurate control over nanoparticle dispersal, activating catalytic sites, generating quantum emitters and altering 2D heterostructures. However, challenges remain in scaling up these processes with controlling plasma in real time and maintaining the stability of treated surfaces. Finally, we discuss future prospects including integrating AI into plasma systems, greener starting materials and employing in-situ diagnostics. These advancements position plasma processing as a vital technology for developing scalable, programmable and multifunctional nanomanufacturing platforms.

Keywords: Plasma Processing, 2D, Nanoparticles, Metal Organic Frameworks (MOFs)

1. Introduction

The field of nanomaterials has experienced breathtaking development over the past two decades, revolutionizing our understanding of materials science and opening up new fields for technological advancements. Ever since the groundbreaking discovery of graphene in 2004 [1] and more recently magic-angle graphene [2, 3], research on two-dimensional (2D) materials has accelerated exponentially. Concurrently, metal nanoparticles, quantum dots (QDs),and porous networks have taken on important positions in emerging technologies. These functional nanomaterials are revolutionizing various areas of technology with their superior physical, electronic, optical and mechanical properties. 2D materials' atomic thickness gives a record-setting specific surface area with colossal potential for catalysis, energy storage and sensing [4-8]. Electronic properties of 2D materials vary incredibly from their bulk counterparts and have unusual properties such as giant carrier mobility and quantum confinement effects,[9] holding unparalleled opportunities in electronics [10-12]. On a mechanical side, 2D transition metal sulfides possess better elasticity modulus and strength of high interest for flexible elastomers and electronics [13]. They are also capable of supporting optical transparency and special properties that enable innovation in optoelectronics.

2D materials have been projected as the front runners of the post-Moore era for future computing technologies and integrated circuits [14]. They have been demonstrated to possess excellent performance in digital circuits, analog circuits, sensors systems, artificial intelligence chips, heterogeneous integration, and quantum computing platforms. Quantum confinement effect offers a new paradigm for quantum information technology with promising functionalities in quantum computing, communication and sensing [15, 16]. The characteristics of 2D materials not only promote paradigm-shifting achievements in basic research but also open up new possibilities for valuable applications in the fields of electronics and optoelectronics. Likewise, metal nanoparticles, especially gold and silver nanoclusters, have unique

size effects, surface plasmon resonance phenomena, as well as enhanced biocompatibility, with good prospects for mass application in biomedicine, optoelectronic devices, and catalysis [17-20]. Their nanometer dimension not only offers greater specific surface area but also enables large-scale manipulation of optical and electrical characteristics. Luminescence, photovoltaic conversion, and energy storage performances are excellent in carbon, silicon, molybdenum disulfide, black phosphorus, and chalcogenide semiconductor quantum dots [21-23]. With adjustable emission wavelength, quantum yield, and good stability, these QDs enable new design paradigms for optoelectronic devices.

New porous materials including metal-organic frameworks (MOFs), with their well-ordered porous structure, adjustable pore size, and abundant functionalized sites, have distinct advantages in gas separation, catalysis, drug delivery, and energy storage [24, 25]. The materials not only enhance efficiency in material transfer but also provide precise design and functional control. Though they promise much, there remain many challenges to the application of these new materials. The scaling down of electronic devices to the nanometer level calls for the employment of state-of-the-art semiconductors beyond silicon [14, 26]. Though 2D materials provide with their enhanced electronic properties [1, 27-35], there remain challenges. For example, in situ growth of 2D material onto random substrates is needed since transfer processes inevitably introduce contamination or damage [36, 37]. Also, 2D materials are extremely environment-sensitive, and it can ruin their electrical and optical properties and impact the devices' stability over longer periods. There is an urgent need for in situ synthesis strategies with real-time direct control over number of layers and composition.

Besides, it remains challenging to modify the 2D material properties via external control. Traditional chemical functionalization is difficult to manage and non-spatially selective, yielding randomized and inhomogeneous products that are unfit for mass production [38, 39]. Analogous to traditional metal nanoparticle syntheses, multiple processes and extra reducing agents are needed. The majority of carbon QDs are synthesized in sealed reactors under high temperature (200-300°C), high pressure (≈6 MPa), and extended reaction time (6-10 hours), which lead to energy-intensive processes with tremendous environmental effects. Plasma technology has emerged as a promising solution to these problems. The effect of plasma on material science has been significant, as capabilities for surface modification, cleaning, activation, and micro-nano-processing have significantly improved material surface quality, bonding strength, corrosion resistance, and have demonstrated advantages in environmental protection and energy savings [35, 40]. This has significantly broadened the range of applications for materials while promoting new material development and traditional material upgrading.

The plasma state, formally proposed by Langmuir in 1928 as part of his work on gas discharge oscillations [41]. The fourth state of matter—not solid, liquid, and gas by physical properties and principles. Plasma is essentially made up of free electrons and electrically charged ions [42], reactive radicals, quanta of electromagnetic radiation, and high electric fields that give it characteristic optical and electrical properties. These features facilitate extensive material physical and chemical interactions, such as defect modulation [43], heteroatom doping, and surface deposition. The new silicon technology already has plasma science well established in it. High concentrations of the active groups and energetic particles in the plasma state allow for surface cleaning, etching, and in situ material synthesis and modification [44]. One can choose suitable plasma processes to obtain required outcomes based on particular requirements. For example, plasma-enhanced chemical vapor deposition (PECVD) can synthesize films of various materials with variable thickness on large surfaces. Plasma-assisted dry etching, coupled with lithographic processes, can offer precise patterns up to nanometer scales—vitally important for nanoscale manufacture.

Plasma is broadly categorized as high-temperature or low-temperature. If electron temperature is the same as ion temperature, then it is high-temperature (equilibrium) plasma; otherwise, it is low-temperature (non-equilibrium) plasma [45]. Astrophysics and nuclear physics fields are primarily occupied with high-temperature plasma research, while low-temperature plasma is of immense interest in material science and chemistry. System particles and free radicals in low-temperature plasma exist in highly activated states, so reactions impossible under normal circumstances can occur. A plasma electrochemical reaction system is formed when one or both of the solid electrodes in an electrochemical system are replaced by charged and reactive contents of discharged plasma (electrons, ions, and other reactive neutral atoms and groups) [46]. The system utilizes plasma charge, charge energy, and reactive contents

at the liquid-plasma interface to transfer plasma reactivity to precursors without the requirement for additional chemical reagents. This enables easy synthesis of gold, silver, gold-silver alloys, carbon QDs, and other nanoparticles [47, 48]. Further, the plasma discharge gas species (nitrogen, oxygen, argon, etc.), discharge form (direct current, alternating current, pulsed, etc.), and solution structure provide wide reaction parameters, and thus nanomaterial synthesis can be efficiently controlled from both solution and plasma sides.

In recent years, major attempts have been made to translate plasma technology to 2D materials and their electronics. Significant progress has been made in the synthesis of plasma-assisted chemical vapor deposition of 2D materials and their subsequent processing, that is, phase engineering and surface functionalization [49-51]. Plasma-based low-temperature synthesis of large-area 2D materials like MoS_2, hexagonal boron nitride (h-BN), and Janus materials like MoSSe is a reliable material preparation technique today. Besides, 2D material properties can also be modified by phase transition induced by plasma, doping, and other methods. Technological advancements continue to create new avenues to explore the potential of 2D materials and electronic applications [52, 53]. Despite such advancements, systematic collection of plasma generation methods and mechanisms of interaction with 2D materials remains absent. Understanding these principles is necessary since they control the outcome of plasma-related processes and provide guidelines for designing and controlling protocols. To apply plasma technology in 2D materials and electronics better, it is necessary to re-understand these fundamental principles.

This review paper introduces the fundamental principles of plasma, including generation mechanisms and interaction mechanisms with various substances. We present the recent research on plasma-assisted synthesis of 2D materials like graphene, transition metal dichalcogenides (TMDCs), h-BN, and 2D Janus materials and its relevance to large-scale fabrication. We also take into account the potential implications of plasma treatment of 2D material modification and utilization in electronic devices, including plasma oxidation treatment of high-κ dielectric films, plasma doping, phase transition, and other methods for controlling and optimizing electronic properties. Finally, we summarize and offer future developments and benefits of application, opening broad prospects for future applications in applications ranging from electronics to energy storage, sensing, and quantum technologies.

2. Plasma Technologies: Mechanisms and Classifications

2.1. Concept of Plasma

Materials are composed of atoms and molecules microscopically. As the temperature rises, thermal motion of atoms and molecules overcomes intermolecular or interatomic forces and materials transform from solid to liquid to gas form. As the temperature rises further for a gas, electrons gain sufficient kinetic energy to be detached from atoms and form discharge. This emitted gas, since it is plasma, typically consists of electrons, charged ions, and uncharged atoms. Compared to conventional states of matter (gas, liquid, and solid), plasma is very dissimilar in terms of composition and properties [54]. Plasma can be thought of as a charged fluid that also responds to electromagnetic fields. Different types of plasma can be grouped on the basis of the place where they occur, the thermodynamic equilibrium phase, and the ionization degree. Natural plasma [55, 56], such as solar corona and lightning, exists naturally in the environment. Artificial plasma, however, is generated by introducing outside energy—electric fields, magnetic fields, radiation, or heat—to induce gas discharge. Artificial plasma is applied more practically since its properties can be precisely controlled based on the conditions of generation.

If categorized by thermodynamic state of equilibrium, plasma exists in three principal types: high-temperature plasma, hot plasma, and low-temperature plasma. In hot plasma, electrons, ions, and neutral atoms have the same temperatures (kinetic energies) and form thermodynamic equilibrium. Hot plasma doesn't have overall thermodynamic equilibrium but does have partial or local thermodynamic equilibrium with particle temperatures between 3×10^3 and 3×10^4 K. Arc discharge plasma in air is a type of hot plasma. Electron temperatures in low-temperature plasma are 10^3 to 10^4 K and ion and gas temperatures are 300 to 1000 K [57, 58]. The thermal non-equilibrium in this state is maintained by the incessant particle collisions that transfer kinetic energy. Low-pressure radio frequency discharge plasma and microwave discharge plasma are the examples of low-temperature plasma.

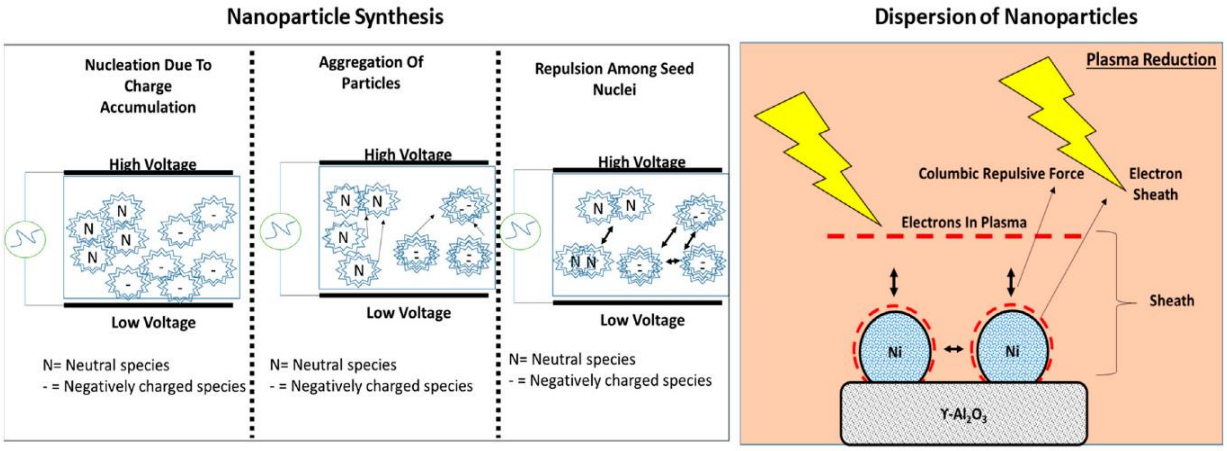

Figure 1. Mechanism of nanoparticles forging from medium and the dispersion of nanoparticles [59]

The applications of this type include material modification, waste treatment, sterilization, film growth, nanopowder preparation, plasma displays, and biotechnology.

The degree of ionization (α) is an important plasma characteristic parameter describing property. Its value describes the ratio of electron density (ne) to the sum of electron and neutral particle amount (ng) in the plasma. According to α, plasma is completely ionized (α = 1), partially ionized ($0.01 < \alpha < 1$), or weakly ionized ($10^{-6} < \alpha < 0.01$). For low-pressure plasma, typical ionization values range from 10^{-6} to 10^{-3}. In the case of charged particles externally controlled, such as in the case of electron cyclotron resonance plasma, ionization values as high as 0.01 or higher are realized. Charged particle density (n) is yet another highly significant plasma parameter. For $n > 10^{15}$-10^{18} cm^{-3}, the plasma is dense or high-pressure, and energy transfer includes significant roles by particle collisions. For $n < 10^{12}$-10^{14} cm^{-3}, particle collisions are negligible, and the plasma is dilute or low-pressure.

Observations from Figure 1 indicate that the presence of nanoparticles from a substrate/solution is charging process-dependent. The formation of nanoparticles starts with the nucleation/seeding process, then aggregation of the nanoparticles to form crystallites, and followed by sustained growth. Seeds or nuclei are developed by the accumulation of charges, either singly negative or neutral. The nucleation-formed particles are initially small and all singly charged negatively. Particles grow through the action of neutral nuclei particles and clusters. The process continues until the particles become larger than the parent. All particles are singly charged negatively now, and agglomeration is interrupted. Negative charge sheath is created around particles, and particles possess one or two elementary charges per nanometer of particle radius. Columbic repulsion comes into play for nanoparticle uniform dispersion. It can be that under the influence of a plasma catalyst, particles and/or crystallites act as an electron sink. The plasma treatment leads to the creation of a space-charge sheath on the catalytic surface and charges the material surface with a negative charge. Hence, there exists a repulsive Coulombic force between both these particles carrying an identical negative charge; this leads to the separation of one particle of the catalyst from another and in turn leads to enhanced dispersion and a decreased particle size.

2.2. Plasma Sources

As discussed earlier, gas and ion temperatures of low-temperature plasma are typically in the range of 300 to 1000 K, which needs additional external energy to ionize at these low temperatures. Low-temperature plasma generation techniques are classified into three categories: 1) Gas discharge plasma, e.g., DC glow discharge, high-frequency discharge, DC arc discharge, and corona discharge; 2) Thermal ionization plasma, e.g., high-temperature combustion and explosions; and 3) Radiation ionization plasma, e.g., X-rays, ultraviolet radiation, and other electromagnetic radiation. The most widely used method of generating low-temperature plasma involves electric fields in accelerating discharge processes.

The phenomenon can be classified into two modes: non-self-sustained discharge and self-sustained discharge. Non-self-sustained discharge maintains the discharge through combined action of external ionization factors and electric fields. Self-sustained discharge refers to processes maintained by only external electric fields. The most common method of producing low-temperature plasma is to utilize electric

fields to break down neutral gases. Currently, DC discharge, RF discharge, dielectric barrier discharge, microwave discharge, and corona discharge are the significant methods to generate low-temperature plasma, which are explained in the following sections.

2.2.1. DC Discharge

When DC voltage is applied between two parallel plate electrodes with working gas in between, electrons formed due to spontaneous ionization of gas molecules gain kinetic energy and collide with neighboring gas molecules. Inelastic collision results in energy exchange to enhance ionization. At the same time, positively charged ions and electrons move in the opposite direction, causing ion bombardment on the cathode that generates secondary electrons. Secondary electrons again collide with the neutral particles and generate more electrons and ions. When electrons and ions move in plasma, they also recombine into neutral particles. The rate of generation and recombination become equal when the process of discharge is self-sustaining. At this stage, the gas becomes conductive and gives off light—glow discharge. The process is advantageous in terms of energy efficiency being high, electron energy and density high, and it being the most stable type of discharge [60, 61].

Glow discharge has widespread applications in light devices. Neon lighting employs the phenomenon of luminescence, while helium-neon lasers employ distinct laser generation properties in the positive column region of glow discharge. Certain other applications include non-pulsed DC glow discharge plasma for the treatment of organic dyes, sterilization, and the growth of highly oriented BCN nanotube materials. Recent advances in DC plasma technology have enabled having control over plasma parameters with precision, and this has introduced new applications in nanomaterial synthesis and modification [62].

2.2.2. RF Discharge

With AC voltage supplied between parallel plate electrodes, an electric field oscillates periodically. When voltage supplied in each half-period is greater than the breakdown voltage of the working gas, an AC glow discharge occurs. Interestingly, as the electric field reverses direction, electrons and charged particles are forced to oscillate between electrodes and become trapped, leading to far more collisions. Therefore, resistivity of the gas between electrodes decreases, fostering the discharge process. Unlike DC discharge, radio frequency (RF) discharge has several advantages [63].

Secondly, RF discharge does not have conducting electrodes, and thus non-metallic materials can be employed as electrodes in RF plasma systems. RF power and plasma exchange through displacement current rather than real current, eliminating electrode-plasma contact and impurity contamination. The absence of electrode-plasma interaction improves reliability, reproducibility, and plasma lifetime. Secondly, inner as well as outer electrodes can support RF discharge plasma, but only inner electrodes can support DC discharge plasma. Moreover, RF discharge plasma possesses higher ionization efficiency and can be supported at comparatively low pressure. Therefore, RF discharge plasma is employed more universally in day-to-day uses [54]. Three principal methods deliver high-frequency power to plasma in general. Inductive coupling provides high-frequency power by means of induced high-frequency current dissipation due to Ohm's law through current flow generated by a high-frequency transformer. Capacitive coupling provides electron clusters with high-frequency power through high-frequency electric fields that are subsequently transported to plasma. Quasi-optical or microwave coupling is the third method. The interaction strength of radio frequency fields with plasma depends on three parameters: oscillation frequency, electron plasma frequency, and collision frequency. These are accountable for plasma conductivity, energy conversion frequency, skin depth, and other phenomena [64].

2.2.3. Dielectric Barrier Discharge

Dielectric barrier discharge (DBD) is a novel atmospheric pressure plasma discharge technique developed in recent decades. In contrast to RF discharge, insulating material covers at least one electrode in DBD systems, restricting current flow between electrodes. To initiate discharge, alternating current should be supplied on both electrodes since direct current cannot pass [65, 66]. At the same time, electric field intensity should be high enough to provide working gas breakdown to avoid arc development and gas heating. The charges built up in the dielectric barrier under external electric fields suppress new streamer formation, which allows discharge to spread homogeneously between electrodes and improves plasma stability. DBD can generate plasma at atmospheric pressure with working gas heating typically limited to several tens of Kelvins. All these

advantages make DBD widely applicable in various applications, including material property adjustment and contaminant treatment. Since the nineteenth century, plasma DBD has been shown to have the capacity to decompose various gaseous compounds, including NH_3, H_2S, and CO_2 [67]. Other applications include the production of semiconductors, sterilization processes, treatment of polymer surfaces, CO_2 lasers of high power used in welding and cutting metals, anti-pollution systems, and plasma display devices. DBD plasma finds its application in aerodynamic flow control and related processes. The relatively low temperature of DBD plasma makes it a viable method to form atmospheric pressure plasma. The recent enhancement in DBD technology has enabled plasma parameters at atmospheric pressure to be controlled with accuracy, opening the door for nanomaterial synthesis and surface treatment processes that were previously required to run in vacuum [68].

2.2.4. Microwave Discharge

Microwave plasma production is akin to RF plasma, utilizing 2.45 GHz frequency microwave sources for discharge. When magnetic fields govern electron movement, microwave electric field frequency and electron Larmor movement frequency resonate, which results in improved efficiency of energy transfer from microwaves to electrons. Gas molecules are ionized by microwave radiation, creating plasma made up of electrons and ions [54, 69]. Plasma mobility and stability are guaranteed by stable microwave energy. Compared to radiofrequency plasma, microwave electron cyclotron resonance creates denser plasma. High uniformity, high energy density, and the lack of inner electrodes are just a few advantages of microwave discharge plasma. Because of these characteristics, it can be used in a variety of chemical analysis and material fabrication applications [70]. Its applications are found in a number of industries, including material processing for thin-film deposition, etching and surface treatment; energy technology for fuel cells and plasma power production; and semiconductor chip manufacture for cleaning and surface activation [71]. The ability of controlled delivery of energy and absence of electrodes make microwave discharge most useful in sensitive material processing. Advances made in microwave plasma technology recently have enabled improved plasma parameter control and enhanced functionality for nanomaterial synthesis, particularly for carbon-based nanomaterials and 2D structures [72].

2.2.5. Corona Discharge

Corona discharge is a sustaining discharge phenomenon under non-uniform electric fields, with low energy density, low current density, and simple production [73]. It is free ion migration in air brought about by impressed electric fields, and the voltage and field strength increases proportionally speed up the ion motion. This motion creates electric current between electrodes. Low current is caused by low free ion concentration in the first instance in air. When they reach specific threshold voltages, ions near discharge electrodes gain increased energy and velocity. Positive and negative ions are formed through decomposition by collision with neutral atmospheric atoms. The associated reaction provides increased ion flow between electrodes, which strongly boosts electrode current (corona current). A light blue corona surrounds the discharge electrode—the corona—naming it the corona electrode. For example, gas molecules around metal tips discharge electrons under intense electric fields, which are common corona discharge reactions. Corona discharge plasma is particularly favorable for use in applications requiring low electron energy and density, such as medical diagnostics, plasma cleaning, and electroplating [74]. Soft plasma generated from corona discharge is beneficial for treating delicate materials and ultra-precision manufacturing. Recent advancements in corona discharge technology have created new fields of applications in surface treatment and functionalization of nanomaterials, particularly of polymer and carbon nanomaterials.

2.3. Classification of Plasmas by Temperature

Plasma systems are generally divided into two main types based on thermal equilibrium: thermal (or high-temperature) plasmas and non-thermal (or low-temperature) plasmas. Table 1 compares of Thermal and Non-Thermal Plasmas for Material Processing.The key difference lies in how energy is distributed between electrons and heavier species like ions and neutral atoms. Thermal plasmas, also known as equilibrium plasmas, maintain a uniform temperature across all components, including electrons, ions, and neutrals ($T_e \approx T_i \approx T_n$). These plasmas form under high energy conditions, usually at atmospheric or higher pressures, where the gas temperature often exceeds 10,000 K [57]. Arc discharges and inductively coupled plasmas are typical examples. Because of their extremely high temperatures, thermal plasmas are mainly used in processes like metal refining, waste

destruction, and high-temperature synthesis of materials such as diamond films and refractory ceramics [75].

Non-thermal plasmas, or cold plasmas, show a sharp difference in temperature between electrons and the heavier particles. Electron temperatures range from 1 to 10 eV (about 10,000 to 100,000 K), while ions and neutrals remain near room temperature (300–1000 K). These plasmas usually form at low or atmospheric pressures through methods like dielectric barrier discharge (DBD), radio frequency (RF) discharge, glow discharge, or microwave excitation. The high-energy electrons in such plasmas initiate various chemical and physical reactions—such as ionization, excitation, and dissociation—without significantly heating the gas. This property makes cold plasmas highly suitable for processing delicate surfaces and temperature-sensitive materials [76].

Low-temperature plasmas are widely used in nanomaterial synthesis and surface modification because they can carry out chemical reactions near room temperature. They enable controlled production of reactive species like radicals, ions, and ultraviolet photons, promote surface-level changes and defect creation without harming the bulk material, and support eco-friendly, one-step fabrication methods that do not rely on harmful chemicals. Recent advances have explored how non-equilibrium plasmas interact with liquids, especially in solution-plasma systems. Here, active species like electrons and radicals generated in the gas phase penetrate the liquid phase, allowing for the synthesis of nanomaterials such as metal nanoparticles (Au, Ag, Pt), carbon quantum dots, and metal-organic frameworks (MOFs) under gentle conditions [77].

At the gas-liquid interface, plasma triggers electrochemical reactions that produce reactive species like hydrated electrons, hydroxyl radicals (•OH), and hydrogen peroxide (H_2O_2). These species can drive reduction, nucleation, or surface functionalization, eliminating the need for chemical reducing agents [78]. Therefore, the classification of plasmas based on temperature strongly affects their chemical behavior, energy transfer patterns, and compatibility with different materials. High-temperature plasmas are vital for large-scale processing of heat-resistant materials, while low-temperature plasmas play a crucial role in modern nanotechnology due to their flexibility, scalability, and controllable chemistry [79].

Table 1. Comparison of Thermal and Non-Thermal Plasmas for Material Processing

Parameter	**Thermal Plasma (Equilibrium)**	**Non-Thermal Plasma (Non-Equilibrium / Cold Plasma)**
Electron Temperature (T_e)	≈ T_i ≈ T_n (10,000–30,000 K)	High (1–10 eV ≈ 10,000–100,000 K)
Ion / Gas Temperature (T_i, T_n)	High (same as electrons)	Low (~300–1000 K)
Energy Distribution	All species in thermal equilibrium	Strongly non-equilibrium; electrons >> ions/neutrals
Pressure Range	Atmospheric or high pressure	Low to atmospheric pressure
Typical Discharge Sources	Arc discharge, Inductive thermal plasma, Plasma torches	RF, DBD, corona, glow discharge, microwave
Material Interaction Mode	Melting, vaporization, thermal decomposition	Surface activation, etching, doping, functionalization
Common Applications	Metallurgy, thermal spraying, high-temp coating, diamond growth	Thin film deposition, nanomaterial synthesis, biomedical sterilization
Synthesis Suitability	High-temp bulk synthesis	Low-temp synthesis of nanostructures, surface engineering
Examples in Literature	Microwave plasma CVD for diamond	DBD synthesis of QDs, MOFs, graphene doping

2.4. Plasma–Liquid Interfaces and Their Role in Nanoparticle Synthesis

Plasma–liquid systems provide a soft and mutable medium for nanomaterial synthesis. For plasma-in-liquid and plasma-over-liquid configurations, plasma is located within the liquid or above it, respectively. The system has the ability to create a multiphase reaction zone wherein both physical and chemical processes exist. These interactions allow for localized energy transfer and generate reactive species for assisting formation, growth, and nanoparticle modification under gentle conditions [80]. It is at the heart of plasma–liquid systems that several mechanisms collaborate to drive nanoparticle growth. One such fundamental process is electron transfer. High-energy plasma electrons penetrate the liquid surface and reduce metal ions like Au^{3+}, Ag^{+}, or Pt^{4+} to elemental nanoparticles. This eliminates the need for external reducing agents, making the process cleaner and more sustainable [81].

Another key feature is the generation of reactive oxygen and nitrogen species (RONS). These include hydroxyl radicals (•OH), hydrogen peroxide (H_2O_2), superoxide anions (O_2^-), singlet oxygen ($^1O_2$), and solvated electrons (e^-_{aq}). Generated by plasma reactions in the gas phase and through interactions of UV photons, these species transfer to the liquid phase and participate in oxidation as well as reduction reactions to facilitate nanoparticle formation [82]. Plasma also assists in metal precursor activation. UV light and ionizing particle energy decrease the dissociation activation energy, allowing for nucleation to occur at a more rapid and homogeneous rate. DBD plasma, for instance, quickly disintegrates salts like $HAuCl_4$ into gold nanoparticles without triggering agglomeration and sedimentation [83]. Exposure to plasma also modifies local redox and pH conditions at the interface. These changes decide the size, form, and oxidation state of final particles, and it is possible to adapt synthesis conditions for different materials [84]. Additionally, strong electric fields at the interface can affect ion movement, double-layer formation, and stabilization of particles in solution [85].

These systems offer several advantages for nanoparticle synthesis. They allow direct formation of stable, surfactant-free colloidal nanoparticles, such as Au, Ag, Pt, Cu, and Pd. Particle size can be controlled by adjusting plasma power, exposure time, and gas environment. Since these processes can run at atmospheric pressure, they are easy to scale and repeat. Importantly, they also align with green chemistry by avoiding harmful chemicals. For example, Velusamy et al. produced copper oxide nanoparticles using a microplasma setup in an ethanol-based solution, achieving quick and uniform formation [86]. Similarly, Khatoon et al. used helium microplasma and a chlorinated carbonic acid precursor to synthesize gold nanoparticles. Their study showed that nanoparticle size can be controlled by varying plasma power, OH radical density, and precursor concentration [87].

Plasma–liquid systems are now widely used to synthesize metallic nanoparticles for catalysts, optical devices, and sensors; semiconductor quantum dots for imaging and electronics; and bimetallic or hybrid nanostructures for advanced applications. Their compatibility with different solvents and precursors makes them ideal for producing nanomaterials in a scalable and eco-friendly manner, especially for biomedical, environmental, and electronic uses [88]. Recent progress in this field has enabled precise control over the shape and composition of nanoparticles. This has opened new directions in designing materials with specific functions. The integration of in situ monitoring tools has also improved understanding of the formation process, making it possible to design complex nanostructures such as hierarchical assemblies and nanocomposites with greater accuracy [89].

3. Plasma–Material Interaction Mechanisms

Plasma–material interaction mechanisms play a significant role in the development of nanomaterials with accurate control over their surface structure, composition, and overall properties. The processes take place under a characteristic non-equilibrium condition, where ions, electrons, radicals, and photons interact with material surfaces by various mechanisms [90]. A correct understanding of the mechanisms proves helpful in the design of nanomaterials for electronic devices, catalytic reactions, energy devices, and biomedical devices.

3.1 Ion Bombardment and Sputtering

Ion bombardment is a very commonly used technique in plasma-based processes. Here, positively charged ions, driven by the electric field present in the plasma sheath, strike the material surface with regulated energy [91]. During impact, they transfer momentum to surface atoms. This can result in atom ejection (sputtering) or atomic structural

rearrangement. This method can be useful in etching, patterning of surfaces, thinning of layered structures, cleaning, and defect generation. The outcome depends on a combination of variables: ion energy (10–500 eV in RF equipment), type of ion (heavier ions like Ar^+ or Kr^+ impart more momentum), and angle of impact. For 2D materials such as graphene and TMDs, ion bombarding can be used to etch specific layers without shattering the underlying structure. This is achievable using low-energy plasmas or remote plasma setups that prevent excessive energy transfer [90, 92].

3.2 Surface Modification and Radical-Induced Reactions

Plasma also produces reactive neutral radicals that aid chemical processing of the surface [93]. These radicals are created when gas molecules are disintegrated by high-energy electrons. Hydrogen gas produces H radicals, oxygen produces OH and O radicals, and fluorinated gases like CF_4 produce F radicals. These radicals have three significant roles. First, they aid doping of materials with foreign atoms. For example, nitrogen doping of graphene or CNTs improves their electronics, but boron or sulfur doping can change catalytic properties [94]. Plasma methods allow such doping at lower temperatures than the traditional thermal process. Second, radicals graft functional groups onto surfaces, improving their compatibility with other materials. Fluorine or oxygen groups change electronic properties and surface wetting, while amine groups increase biological molecule compatibility. Thirdly, certain radicals have the capacity to selectively remove certain sections of a material. Fluorine, for example, attacks silicon to form volatile SiF_4 [95], whereas oxygen breaks down polymers into water and carbon oxides. The type of the radical and surface structure determines where and how the modifications occur. N_2 plasma would add nitrogen at the edge sites in graphene, for instance, while NH_3 plasma would favor nitrogen addition at the basal plane [96].

3.3 Role of UV and VUV Radiation

Plasma emits a wide range of electromagnetic radiation, including ultraviolet (UV) and vacuum ultraviolet (VUV) light. Such photons, especially in the 10–380 nm range, have enough energy to break chemical bonds, excite electrons, and cause some surface reactions. UV light finds application in breaking weak bonds, creating electron-hole pairs, desorbing surface contaminants, and triggering new chemical reactions. These effects are useful in uses like PECVD, where UV radiation improves film growth as well as quality. In materials like ZnO and TiO_2, UV light helps to trigger their surfaces for photocatalysis. UV exposure is also useful in generating defects in wide-bandgap materials and helps in local heating without elevating the temperature of the entire sample. In atomic layer deposition (ALD), UV photons enhance surface reactivity and allow for more efficient film formation at lower temperatures [97].

3.4 Defect Formation and Vacancy Control

Introducing defects in a controlled way is a highly effective method for adjusting the properties of nanomaterials without changing their overall structure [98]. Plasma can create a variety of defects, such as vacancies, dislocations, grain boundaries, or even voids. These defects affect electronic, optical, catalytic, and mechanical properties. For example, oxygen vacancies in TiO_2 or ZnO enhance gas sensing or catalytic activity [99]. Nitrogen vacancies in h-BN allow single-photon emitters to be formed, which are essential for quantum devices [100]. Similarly, defects in the edges of 2D materials can serve as nucleation sites for the immobilization of molecules or metal nanoparticles [98]. Through the modulation of plasma power, gas species, and exposure time, the number of defects that can be generated can be regulated. Plasma is kept comparatively cold in temperature, thereby preventing extraneous changes such as healing of defects that may take place in thermally activated processes [101].

3.5 Surface Energy and Wettability

Plasma can also be used to change the surface energy of the materials, and this determines how they will react in proximity to water, solvents, or other surfaces [102]. It is done by introduction of new chemical groups, removal of surface dirt, generation of nanoscale roughness, or adsorptive molecular bonding at the surface. The result depends on variables like the gas utilized (oxygen, nitrogen, fluorine), treatment duration, and power level. These changes enable enhanced blending of polymers or solvents with nanomaterials, composite bonding improvement, and enhanced performance in biomedical applications. For example, superhydrophilic or superhydrophobic coatings can be achieved through plasma treatment, which can be utilized for uses like anti-fog coating or self-cleaning coatings [103]. In a different study, fluorine plasma-treated boron nitride nanosheets

showed enhanced dispersion in solvent and enhanced bonding in composites because of new dipoles formed on their surface [104].

3.6 Depth Control and Spatial Precision

Another benefit of plasma-based methods is that they can alter only the surface of the materials and not the internal structure. This proves useful in the instance of delicate nanomaterials [105]. The level of alteration is ion energy, radical diffusion, and photon absorption dependent. Substrate biasing, remote plasma, or pulsed plasma are some methods that aid in controlling such effects. Plasma-liquid interfaces, however, allow for the injection of reactive species onto nanomaterials immersed in liquids, which is relevant to colloidal synthesis [106]. Such manipulation of space allows for tuning of surface properties, coating surface layers only, or treating localized zones like edges. New technologies such as microplasma jets or plasma printing now enable patterning in the micro- and nanoregimes to facilitate device development opportunities [107].

3.7 Plasma Heating Effects

Although plasma is a cold process, it has the ability to generate local heating. It is because of ions striking the surface, energy-releasing chemical reactions, electron collisions, and radiation emitted from the plasma [108, 109]. Such heating induces reaction, facilitates crystallization of materials, and removes defects. It also, in certain cases, triggers phase transformation in the material [110]. The degree of heating depends on plasma operation. In, for instance, the synthesis of nanoparticles, both plasma heating and gas cooling are used to control the size and morphology of resulting particles [111].

3.8 Computational Modeling of Plasma Effects

In order to develop a deeper understanding of plasma–material interactions, researchers nowadays employ advanced computer simulations across the broad range of time and space scales [112]. There are a number of approaches for a number of applications. Particle-in-cell with Monte Carlo collision (PIC-MCC) simulations simulate ions in the plasma sheath [113]. Molecular dynamics (MD) will be used to examine changes at the atomic level, and density functional theory (DFT) will compute chemical reactions and electronic behavior [114,115]. Computational fluid dynamics (CFD) will inform us how gases and particles will flow through the reactor [116].

These packages allow prediction of what the plasma will do to a material, so experiments can be improved. With the help of machine learning, it is now feasible to find correlations between plasma parameters and material outcomes at a faster rate, with reduced repetition of testing [117].

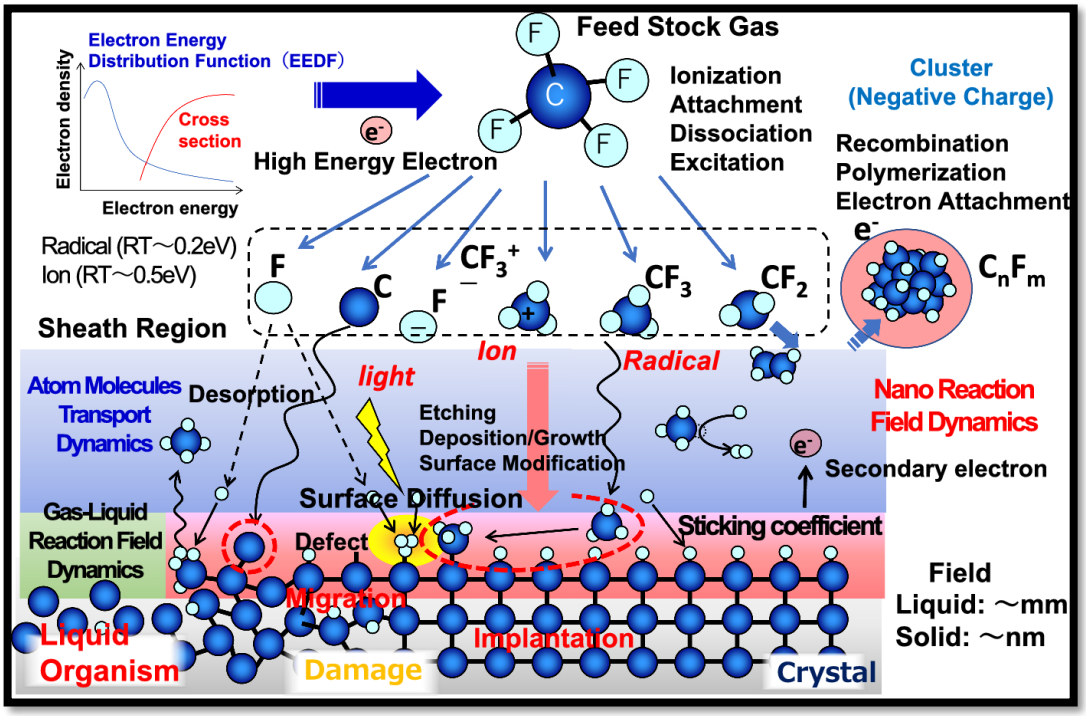

Figure 2. Schematic illustration of plasma-material interaction mechanisms [93].

Figure 2 provides an overview of a plasma-based process. In these systems, active components like ions, radicals, and photons are created through the ionization, attachment, dissociation, and excitation of gas molecules due to collisions with electrons. Reactive plasmas generate non-equilibrium physico-chemical reaction fields because they involve chemically active species, differentiating them from the physical fields linked to noble gas plasmas.

It is crucial to understand that the formation of radicals in plasma operates quite differently from the way molecules dissociate through thermal excitation or other means. When a molecule dissociates due to heat, its position and momentum change, causing the distance between nuclei along the dissociation potential curve to fluctuate. This raises the system's potential energy above the bond dissociation energy, leading to dissociation. On the other hand, in a plasma, collisions with electrons excite the molecules without altering their position or momentum, resulting in ionization and/or dissociation as described by the Frank–Condon principle. Therefore, when electrons with energies in the range of several electron volts collide with gas-phase molecules, they generate high-energy active species like ions, radicals, and photons. Unlike thermal methods that require temperatures of several thousand degrees, plasmas can achieve these results at relatively lower temperatures. The key plasma-material interaction mechanisms outlined in this chapter form the basis for the advanced strategies in nanomaterial synthesis and modification that we will explore in the following sections. By selectively utilizing these mechanisms through careful control of plasma parameters, researchers can effectively tailor the properties of nanomaterials for specific applications.

4 Plasma-Enabled Synthesis of Functional Materials

4.1 Metal Nanoparticles

Plasma-based techniques have become a promising method for synthesizing metal nanoparticles (MNPs), offering a cleaner and more efficient alternative to traditional chemical methods. These approaches can produce uniform, stable, and surfactant-free nanoparticles with controlled size and shape [118–120]. Unlike conventional routes that often depend on strong reducing agents, stabilizers, and high-temperature conditions—leading to impurities and requiring extra purification—plasma methods enable a simpler, single-step synthesis. The process takes place at ambient or near-room temperatures and combines reduction, nucleation, and surface modification in one setup [121]. In plasma–liquid or plasma–gas–liquid systems, nanoparticle formation follows several interconnected steps. First, the plasma generates reducing species like hydrated electrons (e_aq^-), hydrogen atoms (•H), and hydrogen peroxide (H_2O_2). These species quickly reduce metal ions such as Au^{3+}, Ag^+, Pt^{4+}, and Cu^{2+} to their metallic form [122]. The reduced atoms nucleate either in the solution or at the interface, and the nanoparticles grow as more atoms diffuse toward these sites. At the same time, functional groups formed by plasma—like hydroxyl (–OH) and carboxyl (–COOH)—along with surface charges, help to keep the particles dispersed and prevent aggregation, eliminating the need for surfactants [123]. Additionally, UV radiation and localized heating at the interface support precursor breakdown and speed up diffusion, making the synthesis quicker without affecting the bulk solution temperature [124].

Figure 3 shows the UV-Vis absorption spectra of Au, Pt, and Pd colloids produced using a surface dielectric barrier discharge (DBD) plasma at atmospheric pressure. The data include spectra after treatment and after 30 days, demonstrating the stability of the colloids [122].

A comparison (Table 2) between plasma-assisted and conventional synthesis methods highlights several advantages. Plasma processes rely on in situ reducing agents like electrons and radicals, whereas chemical methods usually need external agents such as sodium borohydride or citrate. Plasma eliminates the need for surfactants, works at lower temperatures, and generally takes less time. It also avoids toxic waste and results in purer nanoparticles. Plasma techniques offer better control over size and distribution and help to prevent clustering. Crystalline forms can develop during the process itself, and catalyst surfaces can be tailored more easily. Moreover, the process is flexible and can be paused or adjusted mid-way—unlike traditional setups, which are often continuous and harder to control.

Gold nanoparticles, due to their distinct optical and catalytic features, have been widely explored. A plasma jet applied over an aqueous solution of $HAuCl_4$ produced nearly 10 nm-sized Au nanoparticles in under 5 minutes, without any stabilizers. The size was easily adjustable by changing plasma power and exposure time [125]. Similarly, silver nanoparticles synthesized in $AgNO_3$ solution using DBD plasma had narrow size distributions (5–15 nm) and exhibited strong antimicrobial properties.

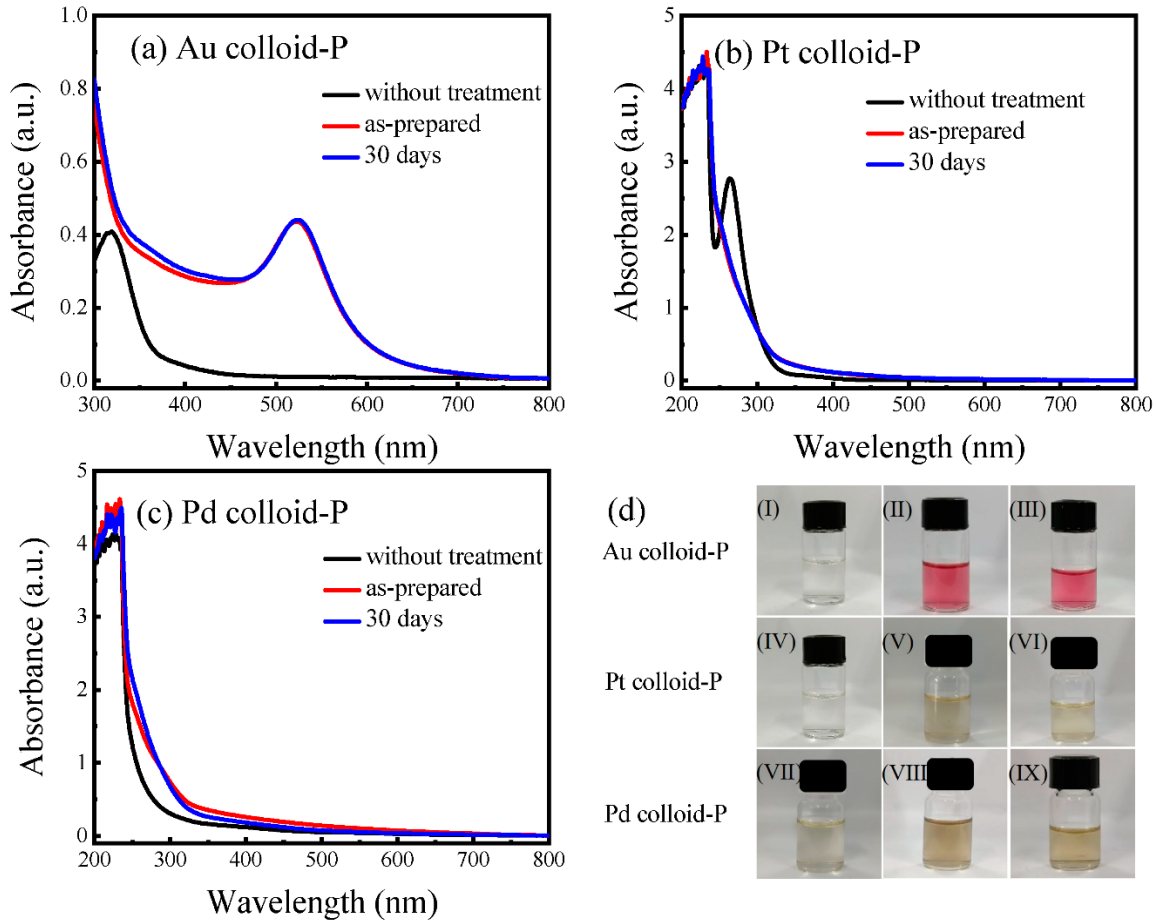

Figure 3. UV-Vis absorption spectra of **(a)** Au colloid-P, **(b)** Pt colloid-P, and **(c)** Pd colloid-P (using H_2PdCl_4 as Pd precursor) prepared by surface DBD cold plasma at atmospheric pressure and after 30 days of storage, and **(d)** corresponding photos before and after treatment and after 30 days of storage (gold colloids: (I)–(III); platinum colloids: (IV)–(VI); palladium colloids: (VII)–(IX)). [122]

Table 2. Comparison of Plasma-Assisted and Conventional Methods for Nanoparticle and Catalyst Synthesis

Feature / Parameter	Plasma-Assisted Method	Conventional Chemical/Physical Method
Reducing Agent	In situ (e_aq^-, H_2, •H) from plasma	External (e.g., $NaBH_4$, citrate)
Surfactant / Stabilizer	Not required	Often required to prevent aggregation
Energy Input	Localized, low-temperature	Bulk heating required
Operating Temperature	Low	High
Treatment Duration	Short (minutes)	Long (hours)
Synthesis Environment	Solvent- and ligand-free	Aqueous or organic solvents with additives
Environmental Impact	Green, minimal byproducts	Often generates toxic waste
Nanoparticle Purity	High (no purification needed)	Often low (requires post-treatment)
Nanoparticle Size	Easily controllable (2–10 nm)	<10 nm is difficult to achieve
Agglomeration Control	High (plasma prevents clustering)	Poor (requires stabilizers)
Size Distribution	Narrow and tunable	Broad, less controllable
Nanoparticle Growth	Irreversible, stable	Reversible, prone to reshaping
Crystalline Form Synthesis	Possible directly during process	Often requires post-annealing
Catalyst Surface Tuning	Enabled by plasma-specific activation	Limited or not possible
Process Interruptibility	Can be paused or modulated mid-process	Typically continuous, difficult to halt

Plasma-induced hydroxylation further enhanced their colloidal stability [126]. Platinum nanoparticles have also been prepared through microplasma reduction of H_2PtCl_6 in water. These sub-5 nm particles showed high catalytic performance in oxygen reduction reactions, important for fuel cells. Particle size and crystal structure varied with gas type and exposure time [127]. Copper nanoparticles, which tend to oxidize easily, were synthesized successfully by reducing Cu^{2+} in an ethanol–water mixture. The plasma process formed a thin carbon layer from solvent breakdown, protecting the Cu surface from oxidation [128].

Several parameters influence the outcome of plasma-based nanoparticle synthesis. Plasma power determines the amount of electrons and radicals available, affecting how quickly particles form. The type of gas used, such as hydrogen or argon, supports the stabilization of metal atoms in their reduced state. Precursor concentration impacts the density of nucleation sites, while longer exposure times allow more particle growth, often leading to larger sizes. These plasma-made nanoparticles serve a wide range of applications. In catalysis, their clean and active surfaces boost reaction rates. Their size and shape can be adjusted for use in plasmonic devices, where precise control of localized surface plasmon resonance (LSPR) is important. Silver and copper particles provide effective antibacterial coatings. Their electrical conductivity and stability make them ideal for electrochemical sensors and biosensors [129]. Overall, plasma-assisted synthesis presents a fast, clean, and tunable method for making high-quality metal nanoparticles. It works well in both water and organic solvents, suits large-scale production, and integrates smoothly with continuous-flow systems, making it a practical choice for future nanoparticle manufacturing.

4.2 Catalysts

Catalyst performance depends heavily on surface structure, particle dispersion, defect concentration, and the oxidation states of active components. Plasma-assisted methods have emerged as powerful tools in catalyst development, particularly for synthesis, surface activation, and fine-tuning of properties. These methods make use of high-energy species generated during plasma discharge, which help in surface cleaning, creation of oxygen vacancies, and uniform dispersion of particles. Importantly, all this is achieved without high-temperature calcination or the use of harmful solvents [14]. In plasma catalysis, non-thermal plasma (NTP) plays a key role in promoting chemical reactions and modifying catalyst surfaces. It can create new active sites by inducing defects or doping elements, and it produces reactive species such as atomic oxygen, hydrogen radicals, hydroxyl radicals, and electrons. These species reduce the energy needed for reactions to proceed. Plasma also improves the way molecules stick to and leave from catalyst surfaces. Additionally, ultraviolet radiation and energetic ions from the plasma can break chemical bonds and rearrange molecular structures. This combined effect during catalyst preparation leads to improved dispersion, altered morphology, and increased catalytic efficiency and stability [130].

One of the major improvements brought by plasma is better dispersion of catalytic particles. Plasma treatment breaks up clusters of metal precursors and helps spread nanoparticles evenly across supports like alumina (Al_2O_3), ceria (CeO_2), or carbon nanotubes (CNTs). The reactive species in plasma prevent particles from sticking together and increase the number of exposed active sites, which enhances performance [131]. Plasma can also engineer defects, especially oxygen vacancies, on catalyst surfaces. Treatments using gases like hydrogen or argon can pull out oxygen atoms from the lattice or replace them with other atoms, creating sites that make it easier for reactants such as CO_2 or CH_4 to bind. These vacancies also help in transferring charges and support the formation of electron-rich centers, especially on materials like ceria, which are known for their redox properties [132]. For example, exposing MnO_x catalysts to argon plasma increased surface defects and improved their activity in low-temperature CO oxidation. Another advantage of plasma treatment is its ability to reduce metal oxides or convert amorphous materials into crystalline phases without heat. This is useful when dealing with sensitive systems like metal-organic framework (MOF)-based catalysts. In one case, platinum particles supported on nitrogen-doped carbon were successfully reduced from H_2PtCl_6 using nitrogen plasma, without any chemical reducing agent, and showed excellent performance in oxygen reduction reactions (ORR) [123].

Table 3 summarizes several catalyst systems improved through plasma processing. For instance, dielectric barrier discharge (DBD) plasma helped in dispersing Ni on Al_2O_3, enhancing CO_2 methanation activity [133]. Nitrogen plasma reduced platinum precursors directly on carbon supports, boosting ORR activity in fuel cells [134].

Table 3. Catalyst systems improved through plasma processing

Catalyst System	Plasma Type	Effect	Application	Ref
Ni/Al_2O_3	DBD	Enhanced dispersion and surface reduction	CO_2 methanation	133
Pt/Carbon	RF plasma (N_2)	Direct reduction of Pt precursor, improved ORR activity	Fuel cells	134
MnO_x	Ar plasma	Defect engineering, oxygen vacancy enrichment	CO oxidation	135
$Co–CeO_2$	Air plasma	Improved redox cycling and lattice oxygen mobility	VOC degradation	132

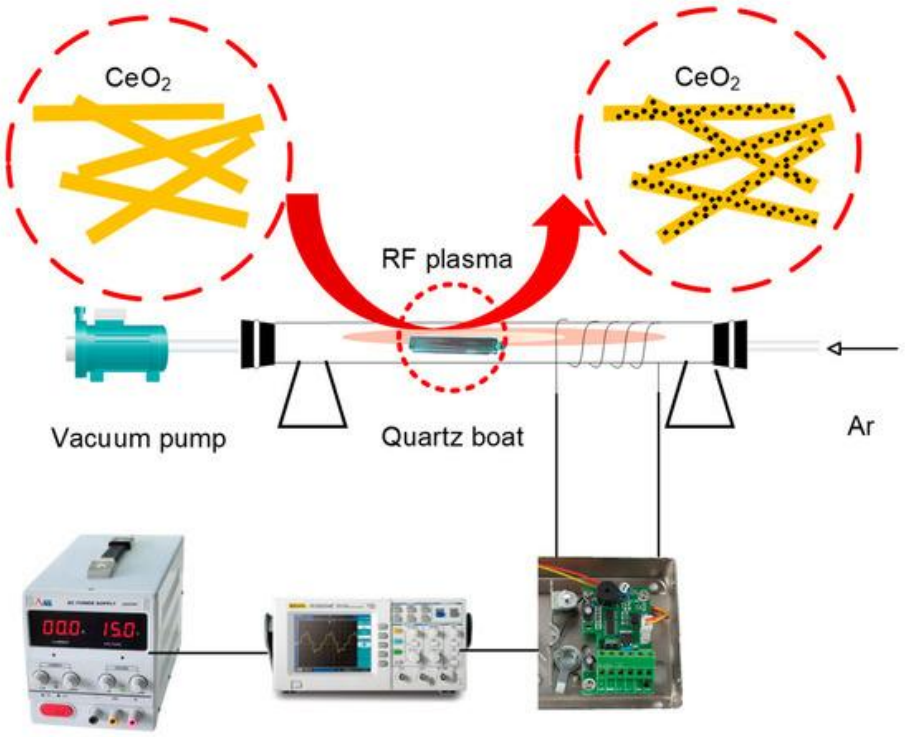

Figure 4. A scheme showing CeO_2 by RF plasma modification [132]

Argon plasma created defects in MnO_x, improving its function in CO oxidation [135]. Similarly, air plasma enhanced redox behavior in $Co–CeO_2$ systems, making them suitable for VOC degradation [132].

As illustrated in Figure 4, radio frequency (RF) plasma treatment of CeO_2 can significantly change its surface properties [132]. Plasma techniques provide several benefits in catalyst design. They eliminate the need for high-temperature processes, which helps retain nanoscale features. The process is environmentally friendly, as it avoids harmful chemicals and solvents. Plasma allows one-step functionalization and activation, saving time and simplifying the procedure. Also, changing the plasma gas or exposure time helps control surface properties with high precision. Plasma can also be combined with other synthesis methods like atomic layer deposition (ALD), sol-gel processing, or microwave techniques to develop advanced catalyst systems with better structural control.

Although these benefits occur, there are limitations. Plasma effects are generally primarily surface, generally on the order of a few nanometers, and possibly will not fully activate bulk catalysts. It is difficult to uniformly treat large amounts of powder, affecting scalability. Fine-tuning plasma parameters—power, pressure, and gas composition—may be difficult to control without introducing defects like over-reduction or particle growth due to sintering. Research is addressing these challenges. Technologies such as rotating DBD reactors, plasma microfluidic systems, and in-line diagnostics are opening doors towards controlled and scalable catalyst synthesis. Overall, plasma-assisted methods are revolutionizing catalyst development by offering clean, rapid, and tunable

solutions for particle dispersion enhancement, functional defect engineering, and surface chemistry modification. Such methods are especially beneficial in applications like low-temperature catalysis, energy, and environmental clean-up, where efficiency and surface activity are imperative.

4.3 Metal–Organic Frameworks (MOFs) and Quantum Dots (QDs)

4.3.1 Plasma Functionalization and Synthesis of MOFs

Metal-organic frameworks (MOFs) are porous crystalline materials. They form when metal ions connect to organic linkers. These materials have a high surface area and their structure can be tuned. Due to these properties, they find use in various fields, including gas storage, catalysis, sensors, and drug delivery. However, two main issues often limit their widespread application and scalability: their chemical stability and the complexity of their preparation methods. Plasma-based techniques are now being explored to modify MOFs after synthesis. These methods help add new surface groups, create defects, and tune chemical reactivity without damaging the crystal structure [123]. Dielectric barrier discharge (DBD) plasma is useful in introducing functional groups like hydroxyl, carboxyl, and amine on MOF surfaces. This improves interaction with water and ions, and also increases compatibility with other materials [136].

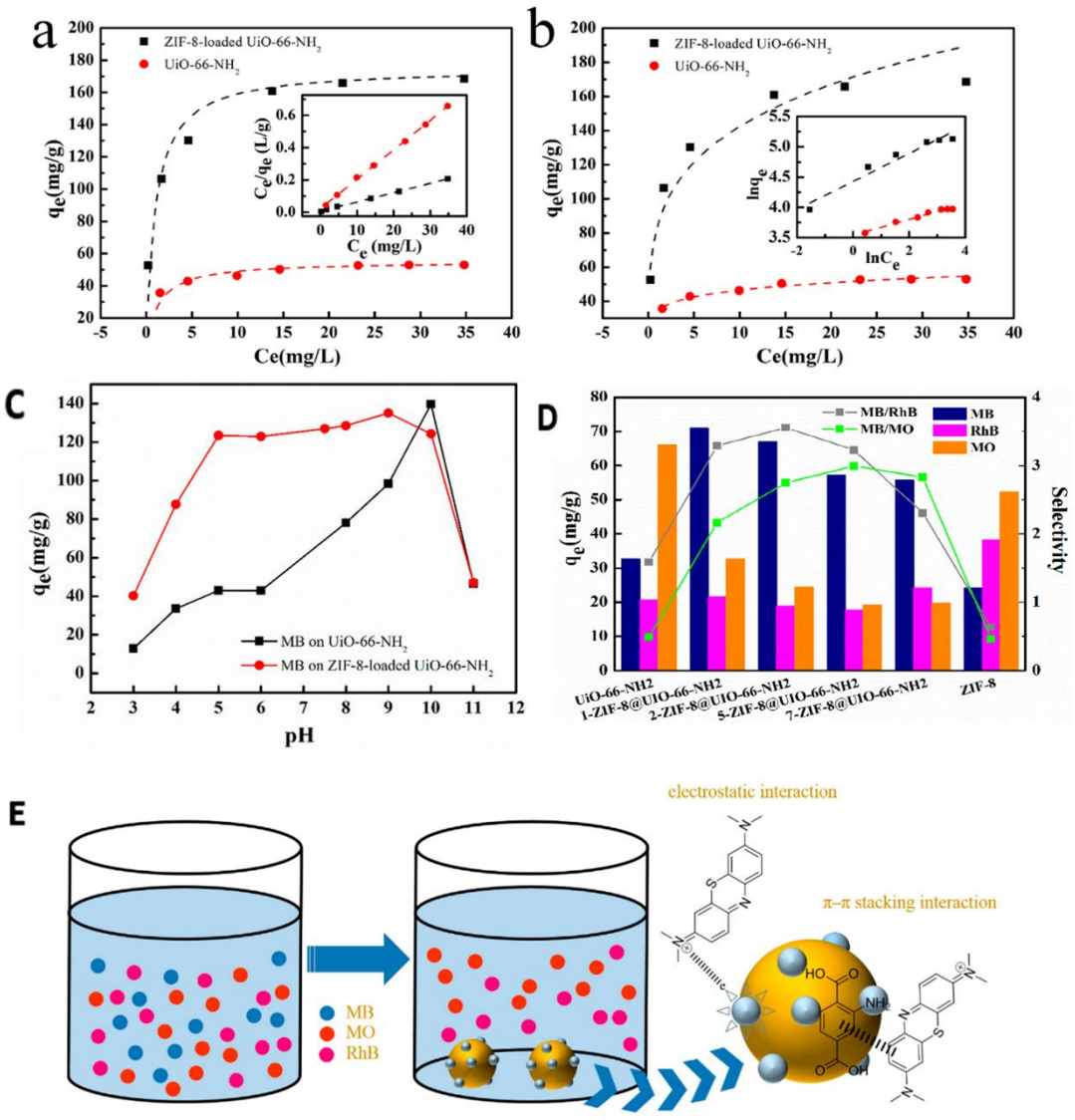

Figure 5. (A) Langmuir and (B) Freundlich isotherm models for the adsorption of methylene blue (MB) on UiO-66-NH2 and zeolitic imidazolate framework-8 (C) The effect of pH on methylene blue (MB) adsorption onto UiO-66-NH2 and zeolitic imidazolate (D) The selective adsorption of different adsorbents in mixed dyes (E)The possible adsorption mechanism of dyes adsorption on zeolitic imidazolate framework [139]

Figure 6 (a) The process involves washing the fish, removing the head, tail, fins, and then filleting. **(b)** Fish fillets undergo treatment with PC pigment in preparation for plasma treatment. [140]

Plasma can also help in partial replacement or addition of linkers, which gives dual functionality to MOFs without needing full reconstruction [137]. Modified MOFs also show improved stability, as plasma helps strengthen the bonding between metal centers and ligands. These changes happen at or near room temperature, avoiding damage to MOFs that are sensitive to heat.

In one study, Hou *et al.* [130] used DBD plasma to prepare europium-based MOFs (Eu–BTB). The process was fast, completed within 20 minutes at room temperature and normal pressure.

The resulting material emitted red light at 617 nm due to Eu^{3+} ions and showed good selectivity in detecting Fe^{3+} ions. Compared to traditional fluorescent materials, these MOFs were cheaper, easier to produce, and had better optical properties, making them suitable for sensing applications. Using DBD plasma, bimetallic metal-organic frameworks (MOFs) have been effectively produced. A novel iron-based bimetallic MOF was created by Jin *et al.* [136]. Comparing this material to its single-metal competitors, it showed better thermal stability. Jiang *et al.* [138] have prepared additional bimetallic MOFs, including $Tb_{1.7}Eu_{0.3}(BDC)_3(H_2O)_4$ and UiO-66(Zr/Ce), using the DBD plasma technique. Their method had a major advantage over conventional synthesis techniques in that it sped up the synthesis process and produced well-formed crystalline structures faster [47].

Another example is ZIF-8, a subclass of MOFs. When treated with air plasma, ZIF-8 showed improved ability to adsorb dyes and detect metal ions [139]. In one case, ZIF-8 was loaded on UiO-66-NH_2, increasing its capacity to adsorb methylene blue (MB) from 55 mg/g to 173 mg/g. This improvement was mainly due to enhanced electrostatic attraction after adding ZIF-8. The material worked best at pH 5, with performance remaining stable across a wide pH range. Even after four reuse cycles, the structure remained intact, making it suitable for water purification. Figure 5 illustrates isotherm models for the adsorption of methylene blue and proposed mechanism behind this dye adsorption on ZIF-8-loaded UiO-66-NH_2 [139].

Figure 6 shows a different application of DBD plasma, where fish fillets were treated to reduce microbial contamination [140]. During treatment, plasma produced reactive species such as ozone, hydroxyl radicals, and UV light, which damaged bacterial membranes and disrupted biofilms [141, 142]. These species also included hydrogen peroxide, which entered cells and caused oxidative damage [143]. Increasing the treatment time and voltage improved the penetration and effectiveness of these reactive species. Pigment compound (PC) was also used for its antibacterial and antioxidant properties. It entered cells more easily after DBD treatment and increased the antimicrobial effect. In experiments, raising the voltage from 70 to 80 kV and extending treatment time from 2 to 5 minutes led to better bacterial reduction. Combining DBD and PC gave better results than using either method alone [140].

4.3.2 Plasma-Assisted Synthesis and Doping of Quantum Dots

Quantum dots (QDs) are small semiconductor particles that show size-dependent optical and electronic behavior due to quantum confinement. Plasma-based methods offer a fast and eco-friendly way to produce QDs, especially carbon, graphene, and metal chalcogenide types. These methods allow precise control over size and emission, and also support doping to improve performance. Plasma can drive QD formation quickly, reducing synthesis time from hours to minutes. Factors like plasma power, gas type, and exposure time influence the size, structure, and optical properties of the QDs. Using gases such as nitrogen or argon during plasma treatment introduces elements like N or S into the QD matrix, enhancing emission and stability. Plasma also passivates surface defects, improving the quantum yield. Since strong acids or bases are not required, this method is safer and greener.

In one approach, N-doped carbon dots were prepared using microplasma at atmospheric pressure [144]. Nitrogen atoms entered the structure as N–H and pyrrolic groups. Optical emission spectroscopy was used to study the active species and mechanisms. The QDs showed excitation-dependent emission with a quantum yield up to 9.9%. Plasma duration and voltage influenced carbon content, nitrogen doping, and particle size. Electrode size had a small impact on QD yield, ranging from 0.31% to 0.42%. Another team, Mohammadzaheri *et al.* [145], used a cold atmospheric plasma jet to make N-doped carbon quantum dots. Their synthesis took 30 to 60 minutes. UV–Vis spectra confirmed the carbon structure and surface functional groups. FTIR results showed the presence of carbonyl and amide groups. The main control factors in plasma-QD synthesis are listed in Table 4.

Plasma-modified MOFs and QDs are now being used in various fields. In photocatalysis, they help break down dyes or produce hydrogen. In electrocatalysis, they support reactions like CO_2 reduction and water splitting. In biology, QDs are used for imaging due to their low toxicity and bright emission. Flexible electronics also use MOF–QD hybrids in sensors and devices. One example is a flexible blue-light photodetector made from plasma-treated carbon QDs, which showed better response and sensitivity [146]. In summary, plasma techniques offer controlled, low-temperature, and eco-friendly ways to develop advanced MOFs and QDs. By adjusting the plasma conditions, scientists can fine-tune chemical properties and surface features. This opens new opportunities for applications in energy, environment, health, and electronics.

5. Plasma Engineering of 2D Materials

5.1 Graphene

Graphene consists of a single layer of carbon atoms arranged in a hexagonal structure, bonded through sp^2 hybridization. It offers excellent electrical, thermal, and mechanical characteristics. However, its applications remain limited due to the absence of a bandgap, low chemical reactivity, and limited ability to form functional derivatives. Plasma techniques provide a controlled and eco-friendly approach to modify the surface, structure, and chemical properties of graphene, even at atomic scales, allowing low-temperature and scalable processes [147].

5.1.1 Plasma Etching and Layer Reduction

Through plasma etching, multilayer graphene can be thinned down to a single layer. Oxygen and hydrogen plasmas remove material by oxidation or hydrogenation. The etching rate depends on the presence of defects and edge exposure. Shen et al. used CF_4 plasma to reduce graphene thickness. The fluorine atoms formed bonds with the surface carbon atoms, leading to surface fluorination [148]. Shi et al. used hydrogen plasma to form different nanostructures on graphene, including superlattices, triangular islands, and ribbons as narrow as 10 nm [49]. To minimize ion-related damage during treatment, a remote plasma setup was proposed, where only neutral species like H, F, and O interact with the graphene surface [149]. Another method uses pulsed plasma, where the plasma source cycles between on and off states. During the on phase, radicals, ions, and electrons are generated. Once the plasma is off, these species decay through recombination processes, avoiding direct ion bombardment [150].

In Figure 7a, the sheet resistance increases with the D band intensity, particularly when I(D)/I(G) exceeds 1.0. When the graphene becomes highly disordered, the D band intensity plateaus. Figure 7b compares the density of states for pristine graphene, graphoxide, and graphane. Figure 7c shows the NH3 gas-sensing performances of pristine graphene, graphane, graphoxide, and Ar-treated graphene at 273 K. The sheet resistance increased proportionally with the NH3 gas pressure.

Table 4. Control Parameters and Optimization

Parameter	Effect on QDs
Plasma power	Controls nucleation rate and defect density
Gas type (e.g., N_2, Ar)	Influences doping species and surface chemistry
Precursor composition	Determines emission wavelength and optical gap
Exposure time	Affects QD size and surface functionalization

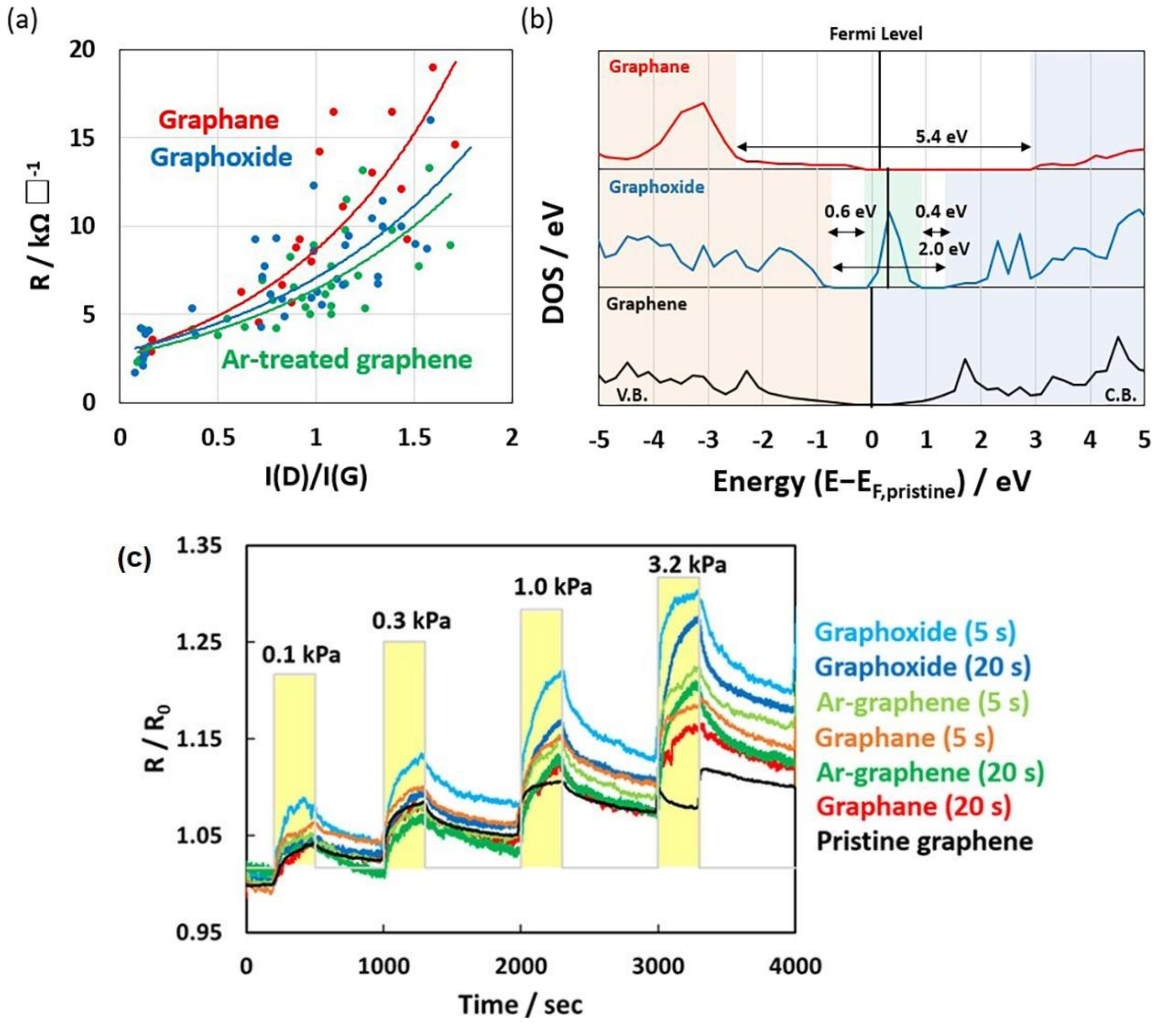

Figure 7. (a) Changes in sheet resistance with D/G intensity for different plasma treatments. **(b)** DOS of graphene, graphoxide, and graphane. Black bars represent the Fermi levels. **(c)** Responses of pristine graphene, graphoxide, graphane, and Ar-treated graphene to NH3 gas pressures of 0.1–3.2 kPa. [151]

Graphane shows higher sheet resistance than both graphoxide and argon-treated graphene, as hydrogen treatment leads to more sp^3 carbon. Though ideal graphene has no bandgap, real graphene has a small bandgap of around 0.01 eV, as seen in temperature-dependent sheet resistance measurements. Graphane and graphoxide have larger bandgaps—5.4 eV and 2.0 eV, respectively—due to hydrogenation and hydroxyl group insertion. In graphoxide, oxygen introduces a mid-gap band, effectively splitting the original 2.0 eV bandgap into smaller gaps of 0.6 and 0.4 eV. Electrons can move either directly across the gap or through this intermediate band, depending on their proximity to oxygen-functionalized carbon atoms. These changes in band structure are reflected in the sheet resistance values, showing semiconductor-like behavior for all three materials [151]. Controlled O_2 plasma treatment can also produce narrow graphene ribbons, useful for biosensing and nanofluidic devices [49, 148].

5.1.2 Doping Through Plasma

Plasma enables the incorporation of other elements into graphene by turning feed gases into

reactive species, which then attach to the surface. For nitrogen doping, gases like N_2 and NH_3 generate species that form pyridinic, graphitic, or pyrrolic nitrogen sites. These sites increase surface activity, modify electrical behavior, and enhance catalytic performance [152]. A short exposure of about five minutes provides optimal doping for catalysis, especially in oxygen reduction reactions, by increasing the spin density around nearby carbon atoms [147]. Fluorination using CF_4 or SF_6 plasma introduces carbon–fluorine bonds, converting graphene into fluorographene, an insulating material with high chemical stability and a wide bandgap [154, 155]. Hydrogen plasma or mixtures of argon and hydrogen introduce C–H bonds, which open up a bandgap and improve compatibility with polymers [156]. Pulsed plasma systems, such as those using RF cycles or on/off biasing, offer better control of how deeply atoms penetrate and where they bind. This approach helps achieve uniform doping with less damage to the lattice [152, 157].

5.1.3 Managing Defects and Functional Groups

Plasma treatment naturally creates defects like vacancies and disordered edges, which are helpful for adding functional groups or catalytic sites. However, too many defects can weaken the structure and reduce electronic mobility [158]. Remote or pulsed plasma configurations help avoid over-etching, allowing graphene to retain high mobility, especially in devices like field-effect transistors [157].

5.1.4 Applications and Performance Benefits

Graphene modified with plasma techniques finds use across many fields because of its adjustable surface chemistry and strong bonding with other materials [159]. Table 5 lists the applications of Plasma-Functionalized Graphene Nanomaterials. Plasma can add different groups such as hydroxyls, carboxyls, amines, or heteroatoms, improving dispersion, interfacial bonding, and electrical performance. In structural composites, functionalized graphene improves strength and thermal performance, seen in materials like epoxy, PI, and HDPE. For lubricants, treatments using ionic liquids or urea improve water compatibility and wear resistance. In electronics, reversible chemistries introduced via plasma enable flexible and self-repairing circuits, with improved dielectric properties and mechanical recovery.

Table 5. Applications of Plasma-Functionalized Graphene Nanomaterials

Application Area	Plasma Functionalization Role	Performance Improvement	Reference
High Thermomechanical Materials	Improves dispersion and bonding in polymers	Up to 130% increase in strength; 200% better thermal conductivity	[160–163]
Packaging Materials	Enhances bonding through covalent and π–π interactions	Thermal conductivity increased 38 times; modulus increased by 1000%	[164–165]
Lubricants	Introduces hydrophilic surfaces using urea or ionic liquids	Wear rate reduced by 60%; improved anti-friction properties	[166–168]
Flexible Electronics	Adds reversible functional groups for self-healing	14x higher dielectric constant; 60% more elongation	[169–170]
Optical Limiting Devices	Deposits metal or oxide nanoparticles	Lower threshold (as low as 4 μJ); dual optical and antibacterial functions	[171–173]
Supercapacitors	Enhances surface area and wettability	81% capacitance retention; 37 Wh/kg energy density	[174–176]
Fuel Cells	Improves catalyst support and oxygen reduction	Lower catalyst use; better long-term activity	[177–179]
Solar Cells	Boosts dye loading and charge transfer	Up to 10% rise in efficiency; better device stability	[180–182]
Sensors (Electrochemical/Biosensors)	Enables bio-molecule or MIP attachment	Detects biomolecules at picomolar levels; higher selectivity	[183–186]

In optoelectronics, plasma-modified graphene enhances performance in optical limiters, solar cells, and sensors. It boosts sensitivity, optical response, and carrier mobility. Energy storage and conversion devices such as supercapacitors and fuel cells benefit from increased surface area, porosity, and better catalyst dispersion. Functionalization also supports clean processing by reducing the need for harmful chemicals. The diverse benefits of plasma treatment make graphene a strong candidate for various applications, ranging from materials engineering to energy and biosensing.

Plasma technology offers a clean and adjustable way to change graphene's properties. Methods such as remote plasma, pulsed discharge, and element-specific doping open up new possibilities for electronics, sensors, and energy devices. Future work may explore real-time diagnostics, atom-level simulation of defects, and integration with other 2D materials for multifunctional systems.

5.2 Hexagonal Boron Nitride (h-BN) and Boron Nitride Nanosheets (BNNS)

Hexagonal boron nitride, also called "white graphene," is a two-dimensional material made of alternating boron and nitrogen atoms arranged in a hexagonal pattern. It has a large bandgap of about 5.9 eV, excellent thermal conductivity, strong chemical stability, and high dielectric strength. These properties make h-BN important for applications such as gate dielectrics, deep-ultraviolet optoelectronics, and quantum photonics [187, 188]. However, the chemical inertness of h-BN restricts easy doping, defect creation, and solution processing. Plasma-based methods provide a low-temperature, environmentally friendly, and substrate-compatible way to overcome these limitations by enabling synthesis and functionalization [189].

5.2.1 Plasma-Enhanced Chemical Vapor Deposition (PECVD) of h-BN

PECVD has become a useful method for growing high-quality h-BN thin films on substrates like silicon, quartz, or copper. Using RF or microwave plasma, precursors such as diborane (B_2H_6) and ammonia (NH_3) break down into reactive species that assist film growth at relatively low temperatures between 400 and 800 °C [190, 191]. This process allows catalyst-free growth, with good control over the film's thickness and crystallinity. It also produces large-area films with uniform dielectric properties, making them suitable for electronic devices [192]. For example, Yamamoto and colleagues grew about 15 layers of h-BN on silicon and quartz substrates without any catalyst using inductively coupled PECVD at 400–500 °C. The films showed an optical bandgap near 5.8 eV, consistent with reported values. The Raman spectra revealed a full width at half maximum (FWHM) of 32–33 cm^{-1}, comparable to commercially produced multilayer h-BN on copper foils. These films also exhibited low leakage current, similar to mechanically exfoliated h-BN [190]. Plasma-assisted growth offers potential for low-temperature synthesis on more sensitive substrates and holds promise for industrial scale-up.

Merenkov et al. reported vertical growth of h-BN nanowalls with heights from 50 to 250 nm via plasma-assisted methods. They suggested that collisions between crystalline domains during growth led to vertical alignment of the h-BN structures relative to the substrate [193]. In general, growing 2D materials with uniform planar orientation reduces grain boundaries, lowers defects caused by grain edges, and decreases charge scattering. This improves carrier mobility and enhances device performance. Huang et al. achieved uniform h-BN crystal orientation by adjusting hydrogen and argon gas flow in inductively coupled PECVD. They found that hydrogen plasma at certain temperatures corroded the copper substrate slightly, causing wavy surface patterns which affected growth [194]. Using h-BN as an insulating layer opens opportunities to combine it with other 2D materials like graphene or transition metal dichalcogenides (TMDCs) to create novel heterostructures and devices [190].

5.2.2 Plasma-Assisted Defect Engineering and Doping

Plasma treatments using gases such as nitrogen (N_2), argon (Ar), hydrogen (H_2), or oxygen (O_2) can introduce vacancies, interstitial atoms, and substitutional dopants in h-BN. These defects and dopants change the optical and electrical properties of the material [195, 196]. Controlled plasma exposure can produce boron or nitrogen vacancies that serve as reactive or luminescent centers. Doping with foreign atoms like oxygen, carbon, or fluorine is possible through plasma with O_2, CH_4, or CF_4 gases, respectively. These dopants can adjust the bandgap or change surface properties such as hydrophobicity [197]. For instance, Liu et al. applied four different plasma atmospheres—N_2, O_2, H_2, and Ar—to perform

nitriding or denitrification, oxygen functionalization, reduction, and etching of boron nitride. Two kinds of nitrogen defects appeared during plasma treatment. Among these, a "TBC"-type defect formed by nitrogen plasma etching acts as an active site for catalyzing the oxidative dehydrogenation of propane to propylene [196]. Zhong et al. prepared fluorinated BN nanosheets (F-BNNS) through dielectric barrier discharge (DBD) plasma treatment using boron fluoride nitride. The fluorinated nanosheets showed improved dispersion and interfacial compatibility. Molecular dynamics simulations revealed that fluorination increased the bandgap and created deep trap levels at the interface. These traps prevent continuous charge injection and regulate carrier movement, improving the composite's insulating properties [197].

5.2.3 Quantum Emission via Plasma-Treated BN

Point defects created by plasma in h-BN can work as single-photon emitters (SPEs) at room temperature, emitting light between 550 and 800 nm. These color centers are important for quantum communication, sensing, and computing [198]. Plasma treatment using argon, hydrogen, or oxygen gases allows control over defect density without needing annealing steps. The plasma power and thickness of the h-BN flakes influence the number and quality of the emitters. For example, H_2 and Ar plasma treatments on exfoliated BN nanosheets produced dense, stable single-photon emitters with control over polarization and nanoscale localization [198].

5.2.4 Functional Surface Engineering of BNNS

Exfoliated BN nanosheets modified by plasma gain functional groups such as hydroxyl (-OH) and carboxyl (-COOH). These groups increase surface energy and chemical compatibility with polymers or nanofillers [197]. h-BN is emerging as a promising host for bright, stable, and tunable single-photon emitters with narrow linewidths at room temperature. These quantum emitters can form from defects created randomly during growth or exfoliation from bulk crystals. Zeng *et al.* produced high-density single-photon emitters in exfoliated h-BN flakes using H_2 and Ar plasma followed by air annealing. They found that plasma power and flake thickness were key factors in the efficiency of SPE production. Compared to Ar plasma, H plasma enhanced emitter creation more due to combined physical and chemical etching, requiring lower plasma power [199]. Plasma functionalization also helps anchor nanoparticles, bind quantum dots, and conjugate biomolecules. It improves dispersibility in polar solvents and strengthens mechanical interlocking in nanocomposites. Polymer composites with plasma-treated BN nanosheets show better interfacial adhesion and enhanced heat dissipation [197]. Table 6 lists the Applications Enabled by Plasma-Modified h-BN.

Plasma synthesis and modification of h-BN and BN nanosheets offer a controllable, scalable, and low-temperature way to tailor their structural, electronic, and optical properties. Combining plasma doping, surface chemistry adjustment, and defect activation has made plasma technology a vital tool for advanced uses—from quantum emitters to high-performance nanocomposites. Future work may focus on real-time plasma diagnostics, modeling of interfaces, and hybrid plasma–thermal methods to further develop boron nitride–based 2D materials.

5.3 Diamond

Diamond is a remarkable wide-bandgap material, with a bandgap around 5.5 eV. It offers excellent thermal conductivity of approximately 2000 $W \cdot m^{-1} \cdot K^{-1}$, strong chemical stability, and high carrier mobility.

Table 6. Applications Enabled by Plasma-Modified h-BN

Application	Plasma Role	Enhancement Achieved
Gate dielectrics in FETs	PECVD growth of thin h-BN	High-uniformity, breakdown-resistant insulation [191]
Quantum photonics (SPEs)	Defect creation via N_2/Ar plasma	Room-temperature single-photon emission [198]
Thermal interface materials	Surface functionalization of BNNS	Better matrix adhesion and heat transfer [200]
Filtration membranes/coatings	plasma fluorination and etching	Improved chemical resistance and selectivity [197]

These properties make diamond well-suited for applications in high-power, high-frequency electronics and quantum technologies. Plasma techniques, particularly microwave plasma-enhanced chemical vapor deposition (MPCVD), provide precise and scalable methods to grow and modify diamond films. These methods serve as effective alternatives to traditional high-pressure high-temperature (HPHT) growth processes [201].

MPCVD remains the most common plasma-assisted technique to synthesize diamond films. In this method, a methane-hydrogen gas mixture is energized by 2.45 GHz microwave plasma, producing CH_3 radicals that serve as building blocks for sp^3 carbon, while hydrogen atoms remove unwanted sp^2 carbon phases [201]. Jia et al. demonstrated that hydrogen-methane plasmas support the formation of diamond nanoparticles in the gas phase. The plasma's non-equilibrium nature promotes the generation of reactive species such as H atoms, C_2, and CH_3 at moderate temperatures, which stabilizes these nanoparticles. Their study revealed that an increase in C_2 concentration correlates directly with diamond phase formation, emphasizing C_2's crucial role in nucleating diamond nanoparticles [202]. Growth typically proceeds at substrate temperatures between 700 and 1000 °C, methane content of 0.5–2%, and pressures from 20 to 200 Torr.

Studies on diamond growth on sapphire and MgO substrates coated with iridium (Ir) buffer layers have offered insight into growth mechanisms. Before deposition, the Ir buffer surface is atomically smooth, but bias-enhanced nucleation (BEN) introduces ridges where diamond islands begin to form. On Ir/sapphire, diamond islands shaped like quadrangular pyramids with {111} facets grow first, then sidewall facets change to {011}, leading to coalescence along the 〈010〉 direction. On Ir/MgO, similar pyramid islands grow, followed by columnar growth, but coalescence takes longer than on Ir/sapphire. Detection of Ir on the diamond island surfaces suggests a catalytic role for the buffer layer in early-stage growth. X-ray rocking curve and transmission electron microscopy confirm the diamond films exhibit low defect density dominated by edge-type dislocations [203]. High-quality single-crystal diamond films on Ir/MgO grown by MPCVD show excellent crystallinity and low leakage currents, making them suitable for high-voltage field-effect transistors [202].

Plasma also enables controlled doping of diamond films, which are normally insulating, to achieve functional electronic and quantum properties [204]. Boron doping is achieved by introducing B_2H_6 into CH_4/H_2 plasma, resulting in p-type conductivity. Such boron-doped diamond finds use in thermistors, temperature sensors, and even cryogenic superconductors [201].

Nitrogen and phosphorus doping, using N_2 and PH_3 plasmas respectively, aims for n-type conductivity, though incorporation remains challenging. Nitrogen doping creates nitrogen-vacancy (NV^-) centers, which serve as stable single-photon sources and quantum sensors operating at room temperature [205]. NV centers in diamond are promising for quantum sensing, but current devices fall short of theoretical sensitivity limits. Enhancing spin dephasing time, improving readout fidelity, and optimizing diamond host properties appear to be the best routes to improve performance. NV^- centers formed by nitrogen plasma treatment show long spin coherence and strong photostability, essential for quantum magnetometry and spintronics [206].

Surface modification through plasma etching and activation provides fine control over diamond morphology. This enables surface roughening to boost light extraction in photonic devices, tuning of wettability, and enhanced biocompatibility. Selective etching with O_2, Ar, or CF_4 plasmas allows precise micro- and nanoscale patterning [207-209]. For example, H_2 plasma etching of diamond surfaces exhibits orientation-dependent rates, with the {110} planes etching faster due to increased hydrogen reactivity [209]. Bias-assisted plasma etching further allows anisotropic patterning useful in MEMS/NEMS fabrication and helps remove amorphous carbon contaminants.

Table 7 summarizes key applications where plasma techniques enhance diamond properties. These include high-power electronics through MPCVD growth and boron doping, quantum devices by generating NV^- centers via nitrogen plasma, MEMS/NEMS systems using plasma etching for wear resistance and precise structuring, and biomedical surfaces functionalized to improve cell adhesion and protein binding [210].

Plasma-based processes especially microwave PECVD enable atomically controlled growth, doping, and surface modification of diamond for a wide range of emerging technologies. From spin qubit engineering to wear-resistant microelectronics, plasma offers unmatched versatility for diamond functionalization.

Table 7. Application Integration

Application Area	Plasma Role	Impact
High-power electronics	MPCVD growth + B doping	High breakdown voltage, p-type control [201]
Quantum devices	NV^- center formation via N_2 plasma	Single-photon emission at room temperature [205]
MEMS/NEMS systems	$CF_4/O_2/Ar$ plasma etching and roughening	Wear resistance, precise patterning [208]
Biomedical surfaces	Plasma functionalization (e.g., NH_2/OH groups)	Enhanced cell adhesion and protein immobilization [210]

Future research needs to target real-time diagnostics, plasma–substrate interface modeling, and multi-dopant co-integration to fully unlock diamond's potential in quantum, thermal, and optoelectronic applications.

6. Challenges and Prospects

Plasma-assisted synthesis of nanomaterials has also been one of the main facilitators of high-precision, low-temperature, and green manufacturing in a range of fields from catalysis and optoelectronics to quantum technologies. There remain, however, a number of outstanding scientific and engineering issues that continue to prevent reproducible performance as well as commercial scaling. Overcoming these will be to the fore of the evolution of plasma-based material platforms.

6.1 Contemporary Challenges

Plasma synthesis of nanomaterials is a new method of high promise for environmentally friendly, controlled, and low-temperature synthesis. It is applied in catalysis, optoelectronics, and quantum technology. However, there are still some engineering and scientific limitations that prevent homogeneous outcomes and manufacture on the industrial scale. Those have to be abolished for plasma-based material technologies' synthesis. One of the main constraints is uniformity maintenance and scaling up the process. Plasma-plasma interactions are highly reliant on local parameters such as electric fields, sheath properties, and reactor geometry. Scaling from small sources of plasma such as dielectric barrier discharge jets or microplasmas to big substrates involves inhomogeneous plasma density, energy flux, and species distribution in most situations [211]. These consist of making arraylike plasma and revolving substrates in a bid to facilitate greater uniformity over large sizes in wafer-scale or batch nanoparticle production.

Another issue is precise control of plasma parameters in real time. It is difficult to monitor and control large variables such as electron density, ion energy, gas temperature, and radical flux with consistent results. This brings in batch-to-batch variability and reduces reproducibility [212, 213]. Coupling optical emission spectroscopy, Langmuir probes, and mass spectrometry with machine learning-driven feedback control can help design adaptive and reproducible plasma processes. Defect control and doping at atomic precision remain a challenge, especially for two-dimensional materials like graphene and hexagonal boron nitride. Damage or loss of crystallinity occurs due to overexposure to plasma or uncontrolled energy [214, 215]. Using remote plasma sources, pulsed radio-frequency discharges, and bias-modulated plasma, better control over energy delivery is possible and the structural integrity of the material is preserved.

Plasma interactions with liquids are another aspect that needs to be understood. Some nanoparticle and quantum dot fabrication methods rely on plasma-liquid interfaces, yet boundary chemistry remains empirical. Solvated electrons, radicals, and charge transfer mechanisms require more research [47], [118]. Advanced tools such as time-resolved optical spectroscopy, advanced plasma–electrolyte modeling, and density functional theory simulations can add depth to such processes. Material stability after plasma treatment is another concern. Plasma-implanted dopants, vacancies, or surface groups can be degraded by exposure to air, water, or light and adversely affect device performance in the long term [216]. Protective techniques like atomic layer deposition coatings, in situ plasma annealing, and passivation layers are being developed to enhance longevity. In the future, combining plasma technology with artificial intelligence has great potential. AI systems could adjust plasma parameters dynamically in real-time based on real-time diagnostics, allowing processes to be more consistent and efficient. Machine learning techniques from spectroscopic information are able to predict optimal

process conditions and identify faults at an early point [212].

Green plasma processing is also emerging into the spotlight with new chemistries using ambient air, aqueous, or biomass-derivative precursors. These processes avoid toxic solvents and high heat and enable cleaner manufacturing goals [217]. Plasma-assisted 3D structuring through lithography, etching, and templating also has the potential to synthesize complex hierarchical architectures for photonics, memristive devices, and microfluidics. Plasma hybridization with additive manufacturing techniques would additionally enhance spatial control. Quantum devices and materials will benefit from the ability of plasma to create quantum defects with tunability, e.g., nitrogen-vacancy centers in diamond and single-photon emitters in h-BN. Superconducting and spintronic oxides surface engineering by means of plasma processing is also possible, enabling integrated quantum photonic circuits [205]. In biomedical uses, atmospheric non-thermal plasma is promising for drug delivery, sterilization, and tissue scaffolds with good chemical selectivity and high biocompatibility [54], [208].

6.3 Future Research Directions

Multiscale plasma–material interface modeling, modular adaptive control plasma reactors with AI integration, and lifecycle studies of plasma-functionalized materials must be the research direction in the future. During treatment and growth, in situ diagnostic tools will enable process optimization and monitoring. Materials with multiple uses and controllable characteristics can be made possible through hybrid processing that combines thermal, chemical, and plasma techniques. For green nanomanufacturing, plasma-assisted synthesis is evolving from a specialized laboratory approach to a common platform. The main drivers of broader industrial use will be scalability, accuracy and dependability, particularly through AI-orchestrated management and thorough interface knowledge. With the great potential of quantum, green, and biomedical technologies, plasma engineering will transform the functional material frontiers of the future.

7. Conclusion

Plasma-based synthesis and engineering are now a versatile and effective method for creating functional nanomaterials. This approach helps overcome several long-standing challenges in nanotechnology, materials science and device fabrication. This review has explored how various plasma techniques such as dielectric barrier discharge, radio-frequency plasma, plasma–liquid interactions and plasma-enhanced chemical vapor deposition offer precise control over nanomaterial composition, structure, surface chemistry and properties. Plasma processing allows for one-step surfactant-free synthesis of highly pure metal nanoparticles with enhanced dispersion and catalytic activity. Plasma processes facilitate low-temperature activation and functionalization of metal–organic framework and quantum dots, which are important for sensoric and optoelectronic applications. Atomic doping and etching of the graphene and hexagonal boron nitride two-dimensional materials are facilitated by plasma techniques, thus allowing their introduction into electronics, photonics, and quantum devices. Furthermore, plasma can enable room temperature-controlled growth and doping of diamond films for high-performance electronics and quantum technologies. Localized energy input, tunable reactive species, and friendly compatibility with sustainable chemistry are the most important strengths of plasma techniques. All these factors give a clear advantage over traditional chemical or heat-based methods. Several challenges remain including achieving large-area uniformity, enhancing real-time diagnostics, identifying plasma–liquid interfaces and ensuring the long-term stability of treated materials.

In the coming years, the interplay among machine learning, real-time monitoring of processes, and sophisticated modelling will likely revolutionize plasma processing through better control and reproducibility. New technologies like quantum materials, neuromorphic devices, biomedical surfaces and sustainable nonmanufacturing will benefit heavily from further plasma innovation. Briefly, plasma-assisted nanomaterial engineering is evolving beyond exploratory research and becoming a cornerstone of scalable, programmable, and sustainable nanofabrication. The progress will rely on the integration of close interaction among plasma physicists, materials scientists, and device engineers to utilize plasma technology maximally for sculpting future functional materials and next-generation devices.

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Author Contribution Statement

Both the authors equally contributed to this work.

Declaration of generative AI and AI-assisted technologies in the writing process

The manuscript's language was refined using ChatGPT 5.1 to improve clarity and grammar. No AI system was involved in generating content, conducting analyses or interpreting results. The author(s) reviewed all suggestions and accept full responsibility for the final text.

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The Authors declares that there is no conflict of interest anywhere.

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