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Review

A review of cold plasma for catalyst synthesis and modification

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Abstract: Cold plasma has been extensively studied and developed in the field of energy storage and conversion, with a focus on its ability to assist in catalyst synthesis, surface modification, the introduction of heteroatoms, the generation of defects and vacancies, the improvement of catalyst dispersion, and the reduction of particle size. In contrast to conventional calcination and chemical methods, the energy from cold plasma can be transferred directly to the catalyst and carrier during the treatment process, which can improve the interaction between the loaded catalyst and carrier by changing the internal structure and surface morphology of the catalyst. Therefore, these properties make cold plasma quite green, safe, and efficient for catalyst synthesis and modification. In this paper, the characteristics and applications of various cold plasma technologies, as well as the synergistic treatment of cold plasma technology with thermodynamic principles on catalysts, are analyzed. Based on current research progress, this paper provides a summary and outlook on the synthesis and modification of catalysts using cold plasma.

Keywords: cold plasma; catalysts synthesis; surface modification; plasma dispersion

1. Introduction

Today, plasma technology has become the cornerstone of modern technology. It is a new catalyst preparation method to enhance surface defects and functional groups for surface treatment of special objects (**Figure 1**) and is widely used in fields such as medical and microelectronic industries [1]. Plasma consists of particles and ion groups. In a plasma, gas is ionized, which means that some or all of the atoms lose or gain electrons. These charged particles, including ions and free electrons, coexist in the plasma and interact via electromagnetic forces. These charged particles give plasma unique properties, such as electrical conductivity, response to electric and magnetic fields, and the ability to produce light. Plasma is found in a variety of natural phenomena, such as lightning, stars, and many man-made devices, such as fluorescent lamps and plasma televisions, and it includes neutral molecules and atoms, as well as excited molecules, clusters of atoms, and partially charged ions. All neutral particles have the same total number of positive and negative charges, and so they are electrically neutral at a macroscopic scale. The main modes of plasma production are air ionization and gas discharge [2]. All neutral particles possess the same total number of positive and negative charges, rendering the particles electrically neutral. The main methods for plasma generation are air ionization and gas discharge. Depending on the excitation sources, ionization can be classified as photoionization, radiation ionization and high temperature ionization. When a gas is subjected to an excitation source, if the energy contained in the source exceeds the first ionization energy of the gas molecule, electrons located in the outermost layer will gain enough energy to

overcome nuclear attraction and become ionized. This process gradually produces free radical substances, such as molecules and atoms in the ground or excited state, which eventually form a plasma. Gas discharge involves the insertion of two electrodes with a significant voltage difference into a gas flow, resulting in the formation of plasma [3].

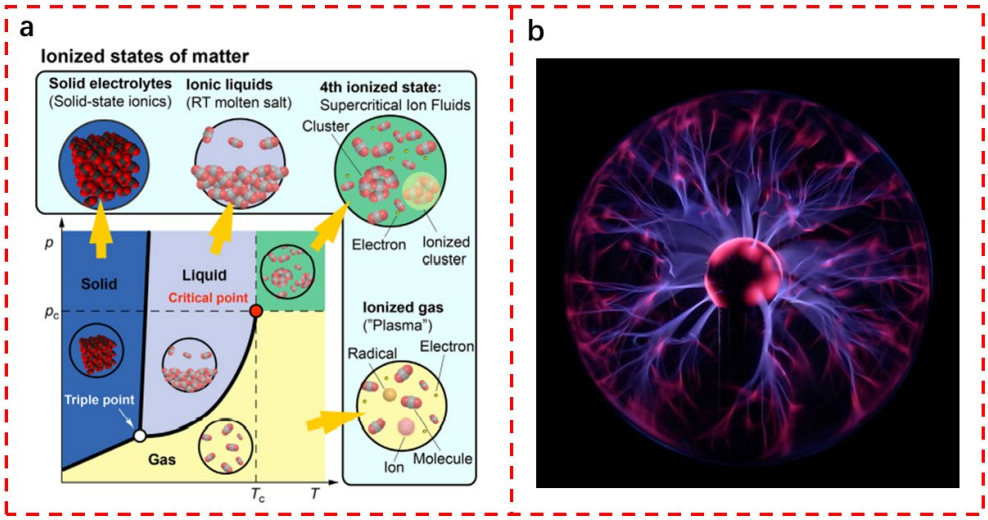

Figure 1. (a) Diagram of state of matter and **(b)** one type of plasma [1].

Plasma catalysis, a developing area in plasma processing, integrates expertise from various disciplines, such as physical chemistry, materials science, nanotechnology, plasma physics, plasma chemistry, and catalysis. Its primary objective is to enhance catalytic reactions through the incorporation of plasma into the reaction cycles. Given that catalysts predominantly consist of nano-structured materials, the interactions between specific plasmas and nanostructures can potentially yield synergistic effects. Nevertheless, current understanding of the underlying processes governing catalytic reactions has been limited thus far.

Based on the categorization of thermodynamic equilibrium, plasma can be classified into three types: fully thermodynamic equilibrium plasma, partially localized thermodynamic equilibrium plasma, and non-thermodynamic equilibrium plasma. In terms of the temperature range within a system, plasma can be further divided into high-temperature plasma and low-temperature plasma. High-temperature plasmas, such as those found in solar and other stellar environments, as well as fusion plasmas, are examples of thermal equilibrium plasmas. And the characteristic of high-temperature plasma is that its electron temperature is equal to the particle temperature, both of which are extremely high ($T_e = T_i$ = 106–108 K), and the plasma density is also very large. The plasma density is significantly high in various regions, such as the Earth's ionosphere, where the electron number density (n_e) reaches 105 cm^{-3} and the gas number density (n_g) reaches 1014 cm^{-3}. Generating high-temperature plasmas in a laboratory setting is generally challenging due to the requirement of large-scale devices, such as tokamaks. Low-temperature plasma is a form of non-thermal equilibrium plasma. It encompasses a broad research scope and finds extensive applications, and it is commonly generated through gas discharge in laboratory settings for ease of acquisition and maintenance. Low-temperature plasma can be

classified into two types: hot plasma and cold plasma. The formation of thermal plasma typically occurs through a dense gas (either atmospheric or high pressure) arc discharge within a system characterized by high and nearly equal electron excitation temperature and particle temperature ($T_e \approx T_i$), referred to as a near-equilibrium plasma or local thermal equilibrium plasma. Under specific conditions, an atmospheric pressure gas discharge can generate arc-discharge thermal plasma. Although cold plasma has a high electron temperature (1–10 eV, 1 eV = 11600 K), the temperature of the gas is similar to that of the surrounding room.

Moreover, based on the classification of the discharge process, plasma can be split into plasma-enhanced chemical vapor deposition (PECVD), dielectric barrier discharge (DBD), glow discharge (GD), atmospheric-pressure plasma jet (APPJ), corona discharge (CD), radio frequency discharge, and solution plasma processing (SPP) [4]. Relevant opportunities have been demonstrated by cold plasma in the fields of nano-material decomposition, catalyst reduction and regeneration, catalyst surface modification, environmental pollution control, and medicine [5]. Cold plasma technology is a key driver of the nanotechnology revolution due to its ability to induce unique physical and chemical reactions. Catalytic materials prepared using plasma systems exhibit numerous advantages, including rapid preparation time, low energy consumption, high specific surface area, excellent dispersion, abundant lattice defects, a single active component, and remarkable stability. Consequently, these prepared catalytic materials have demonstrated promising results and wide-ranging application prospects.

This review provides an overview of the advancements made in various fields utilizing different applications of plasma, as well as the different applications of plasma technology in catalyst synthesis and modification (**Figure 2**). The advantages and shortcomings of different classification studies are also analyzed, and the review looks for improvement methods for meeting these challenges. Low-temperature plasma irradiation of materials can yield various effects, including organic material breakdown for object cleaning and disinfection, increased wettability to facilitate even adhesion of ink and coating, and surface activation for enhanced adhesive strength. These properties make low-temperature plasmas valuable in the manufacturing of semiconductors and other industrial equipment. Furthermore, plasma technology offers chemical-free surface cleaning and disinfection that is safe for use across a wider range of fields, such as food processing and medical device production. The objective of gas processing is to either transform the composition of the gas or gas mixture into a different combination, such as in the case of CH_4 dry reforming, or facilitate the development of specific materials or structures from precursor gas molecules. An example would be utilizing plasma-enhanced catalytic growth to produce carbon nanotubes (CNTs). This field primarily involves employing cold plasma alongside heterogeneous catalysis (**Figure 3(a)**). Finally, the feasibility direction of realizing synchronous loading of gas-phase dispersed catalysts by plasma-spraying modification matching technology is prospected [6].

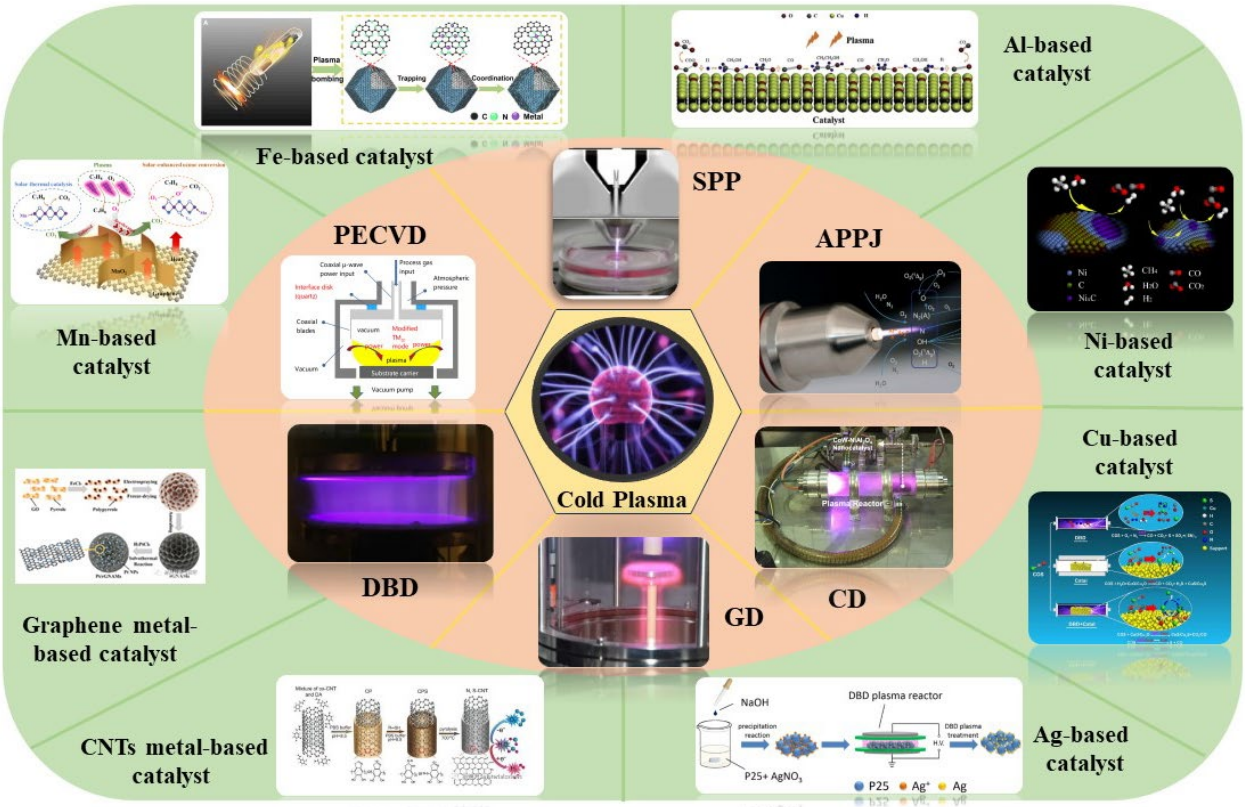

Figure 2. Images of various plasma types and catalyst treatments.

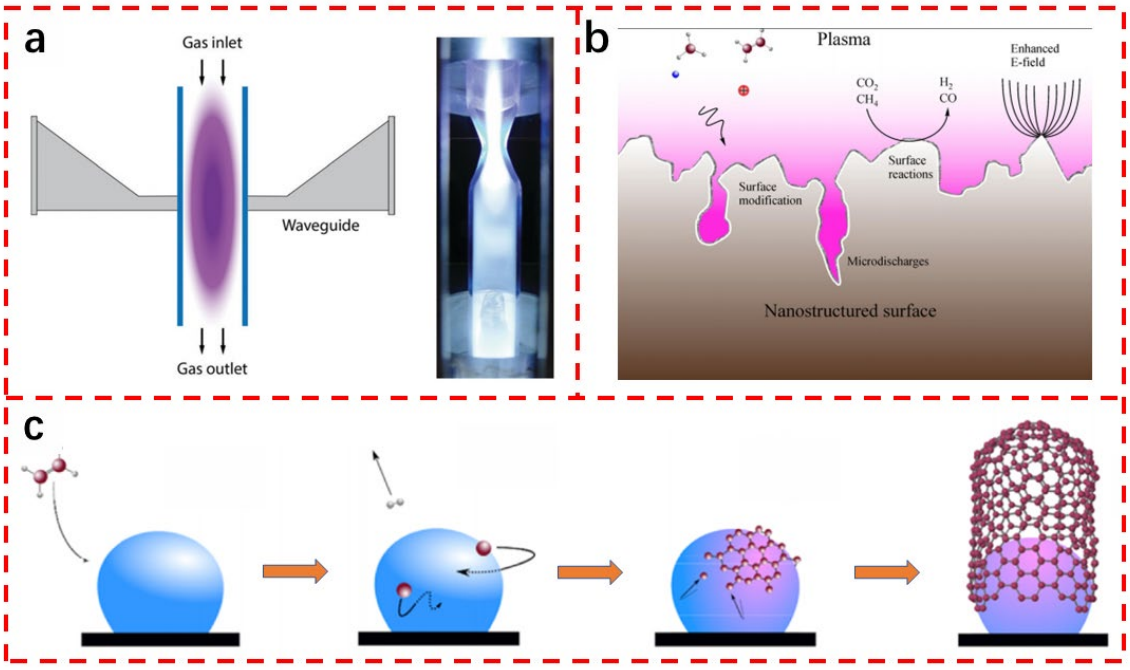

Figure 3. (a) Illustration and depiction of microwave discharge. **(b)** Diagram illustrating area of interaction between gas and catalyst that is pertinent to plasma-assisted catalytic conversion. **(c)** Adsorption of gas-phase hydrocarbon species on nano-catalyst particle application of VLS model in carbon nanotube (CNT) synthesis [6–8].

2. Plasma types and applications in catalyst synthesis

Cold temperature plasma [7] has shown unique effects in the synthesis of electrochemical catalysts and plasma surface spraying modification (**Figure 3(b)**). The method of treating catalysts by using a significant quantity of substances with high energy levels and free electrons or ion groups contained in it to replace traditional calcination has great advantages of increasing the surface functional groups and oxygen defects on the surface of catalysts, improving the internal grain structure, and enhancing the interaction between carrier materials and negative carrier catalysts. The catalytic effect is significantly increased compared with that in the thermal calcination of catalyst precursors (**Figure 3(c)**); in addition, the chemical stability and activation performance of catalysts prepared by the plasma method are greatly improved [8].

There are numerous physical methods for inducing gas ionization and generating plasma, including gas discharge (electric field effect), radiation (including X-rays, ultraviolet rays, and laser radiation), thermal ionization (high-temperature effect), and shock waves. Among these methods, gas discharge is the most commonly employed technique for inducing gas ionization. Clearly, based on the various types of excitations mentioned above, the methods can be categorized as follows: gas discharge plasma, radiation plasma (including laser plasma), thermal ionization plasma, and shock wave plasma.

The main characteristics of low-temperature plasma for applications lie in its higher temperature and energy density compared with conventional physical and chemical alternatives. The plasma has the capability to generate active ingredients that can initiate physical changes and chemical reactions that are either impossible or challenging to achieve through conventional chemical reactions. Reactive components encompass a range of entities, including UV and visible photons, electrons, ions, free radicals, etc. Additionally, there are highly reactive neutral components, such as reactive atoms (O, F, etc.) and excited atomic states. Furthermore, fragments of reactive molecules, such as monomers, also contribute to this category.

The low-temperature plasma discharge generates particles with distinctive chemical properties, which is a notable characteristic extensively utilized for the surface modification of materials. One of the advantages of plasma technology applications in comparison with conventional processes is that the inherent properties of the matrix remain unchanged, with modifications only occurring on the surface within a range of several to dozens of nanometers, such as in semiconductor nanoetching. Also, the entire dry treatment method (dry method), which does not involve the use of solvents or water, results in minimal pollution, thereby enabling energy conservation and cost reduction. Furthermore, the action duration is brief, the reaction rate is elevated, the processing scope is extensive, and there is a significant enhancement in product quality. The process is characterized by simplicity, ease of operation, controllable production, and consistent product quality. The process belongs to the health category, posing no harm to the operator's physical well-being. Due to these advantages, low-temperature plasma technology is widely utilized in various industrial sectors and has become increasingly significant, particularly in the field of material surface treatment, which plays a pivotal role in energy, matter and materials, environment, biochemistry, and other industries.

2.1. Plasma-enhanced chemical vapor deposition (PECVD)

PECVD has the benefits of rapidity, greenness, high efficiency, and good stability in the preparation of thin-film substances and finds extensive application in CNT surface modification, manufacture of solar cells, preparation of graphene materials, development and application of anti-corrosion and impact-resistant materials, micro-electromechanical engineering, and many other fields in system construction. The main principle of PECVD is to bombard the target precursor with a high-frequency pulse current with the aim to generate a large number of plasma nanoparticles to be deposited on the surface of the carrier after continuous convergence and finally form a compact nano-grain structure film. Different nano-particle films can be deposited by changing different precursors.

2.1.1. Synthesis of metal-based catalyst

The application of PECVD in the synthesis of various metal catalysts has incomparable advantages over traditional calcination and chemical methods. PECVD can be used at a low deposition temperature for good consistency and a high deposition rate, and the temperature range is from room temperature to 350 ℃. By operating at a low temperature and changing the plasma parameters, excellent control of material characteristics can be achieved.

Kato and Hatakeyama [9] developed a method for growing graphene on SiO_2 substrates without the need for transfer. This was achieved through rapid-heating plasma chemical vapor deposition (RH-PCVD). By employing this technique, it was possible to selectively grow high-quality monolayer graphene sheets with a hexagonal structure between the Ni films and SiO_2 substrates. Extensive research has demonstrated that the success of this unique approach relies on factors such as using a Ni layer with a relatively small thickness, implementing a rapid temperature increase, and utilizing plasma chemical vapor deposition (CVD). Piferi and Riccardi [10] carried out a study on the reduction of volatile organic compounds (VOCs) through the utilization of a plasma system that relied on a dielectric barrier discharge (DBD) occurring at the surface. On the other hand, the synthesis of bilayer graphene was achieved by Kato et al. [11] through a 30s application of hydrogen plasma on copper foils for treatment purposes at the temperature of 850 ℃, combined with the application of the joule-heating technique on the foils by excluding the utilization of methane, a gas containing carbon. This approach aimed to minimize the formation of nuclei density of graphene. The utilization of plasma resulted in the generation of active carbon atoms on the copper-based surface, facilitating the rapid and discriminatory establishment of AB-stacked bilayer graphene. Purushothaman and Jeganathan [12] conducted a study on the production of quasi-aligned GaN nanowires (NWs) on a Si (III) substrate using Ni as a catalyst through chemical vapor deposition. It was anticipated that during the growth process, nitrogen radicals would migrate onto the surface of the catalytic droplet and incorporate into the growing lattice via the solid-liquid interface. This occurred due to the limited solubility of N in Ni, preventing any alloying between nitrogen and nickel. Schmidt et al. [13] demonstrated that the utilization of non-thermal plasma (NTP) at ambient temperature and atmospheric pressure in air, combined with activated carbon filters, presented a superior approach

for eliminating VOCs from gas streams when compared with employing each individual technique separately.

Tang and Hong [14] employed a plasma-assisted chemical vapor deposition reactor with an Au catalyst to synthesize InGaN nanowires (NWs) on Si (100) substrates at a temperature of 700 °C. By increasing the indium vapor's pressure during the growth process to 53 MPa, InGaN nanowires underwent a transformation into less-curved NWs with a wide range of diameters ranging from 20 to 90 nm. Analysis using transmission electron microscopy revealed that the growth orientation shifted from being predominantly along for reduced vapor pressure of indium growths to primarily during the growth of indium when there was an increase in vapor pressure. Harling et al. [15] employed a packed-bed plasma reactor operating at atmospheric pressure and non-thermal conditions to investigate the impact of temperature on the plasma-catalytic process. Sarker et al. [16] conducted a study on the impact of phosphorus P-doping and the incorporation of multi-walled carbon nanotubes into a TiO_2 matrix, which was utilized for producing thin films of the photocatalyst. Plasma catalysis exhibited superior efficacy in benzene and toluene degradation compared with traditional thermal catalysis and plasma treatment alone. Irrespective of system temperature and reactor configuration, toluene demonstrated significantly higher efficiency in its destruction as compared with benzene. Based on the aforementioned study, Rao et al. [17] introduced a simple and highly effective plasma etching technique for the first time to produce diverse single-metal and dual-metal single-atom catalysts (SACs). The Cu-SAC/NC prepared in this manner exhibited exceptional performance in terms of oxygen reduction reaction (ORR) activity and long-lasting stability when tested under alkaline conditions (**Figure 4(a)**). The process of generating hydrogen through the technique of water electrolysis was described by Soares et al. [18], wherein photocatalyst activation occurred through catalytic reactions under the influence of UVA/vis light.

Moreover, Rao et al. [19] proposed a practical method for accessing the synthesis of SACs on a large scale. This approach involved exciting and stripping metal salts, resulting in the generation of mobile single-metal atoms through a treatment known as "plasma bombing" (**Figure 4(b)**). At the same time, they were simultaneously confined and secured by the faulty and nitrogen-rich locations of the supports. Additionally, the synthesis method employed was highly versatile and can be expanded to produce different types of SACs. To demonstrate this, exceptional ORR capabilities were exhibited by the SAC-Fe/NC sample. More importantly, in the construction of a zinc-air battery, battery performance was found to be outstanding when Cu-SAC/NC was utilized as the catalyst for the air cathode. In addition, the stability of Cu-po-N_3 sites with pyrrole-type tri-coordination was found to be significant according to density functional theory calculations. Also, the theoretical overpotential for this catalyst's main active center was determined to be merely 0.21 V, indicating the technique's high performance. Sitab et al. [20] employed the residual materials from chrome-tanned leather production as a source for obtaining collagen hydrolysate, which was then utilized in the creation of an electrospun nanofibrous membrane using polyvinyl alcohol, aiming at the removal of cationic dye from wastewater. Yao et al. [21] utilized conductive carbon materials to enhance the

conductivity of titanium dioxide and improve the sodium storage performance of TiO_2. This was achieved by introducing nitrogen atoms and oxygen defects on the surface through fluidized-bed-assisted plasma-enhanced chemical vapor deposition (FB-PECVD) (**Figure 4(c,d)**). Ho et al. [22] used plasma coating technology to study the preparation of CNTs/ZnO composites by directly coating ZnO nanoparticles on CNTs and used PECVD to make tapered graphite sheets (GSs) on ZnO coated with Ni particles. After a series of experiments, it was proved that the prepared hybrid ZnO/GSs possessed excellent field emission performance.

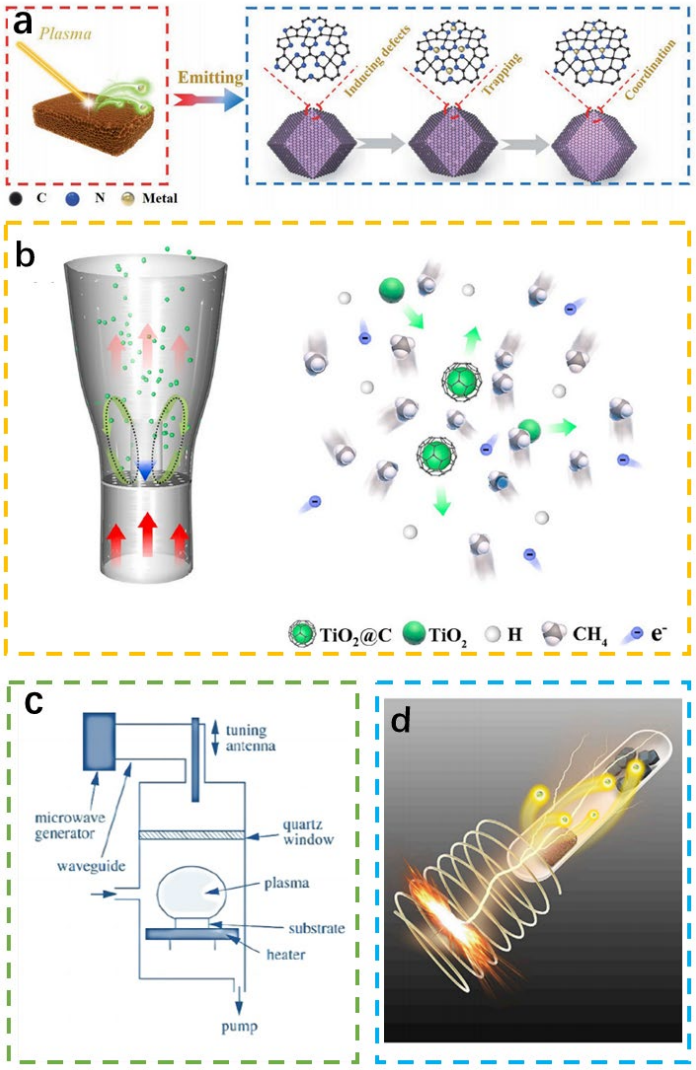

Figure 4. (a) Schematic illustrating process for synthesizing catalysts consisting of individual atoms. **(b)** Synthesis of TiO_2-C nanoparticles, **(c)** Device diagram of low-pressure microwave plasma CVD reactor. **(d)** Plasma bombing for creating SACs [17,19,21].

Based on such principles, various research organizations have carried out more in-depth explorations. In their study, Demidyuk and Whitehead [23] investigated how toluene decomposed when exposed to different types of alumina-based catalysts (Ag_2O-alumina, γ-alumina, and MnO_2-alumina) within a plasma-catalytic reactor. The researchers compared various systems including catalytic reactions alone, post-plasma

treatment with the catalyst present, and direct exposure of the catalyst to plasma at temperatures ranging from 150 ℃ to 400 ℃. Interestingly, they observed that both the catalytic reaction and post-plasma treatment systems exhibited similar activation energies. However, when the catalysts were placed inside the discharge area of a plasma reactor, it was discovered that plasma had an activating effect on certain alumina-based catalysts, such as silver-alumina, by reducing their activation energy requirements. Rao et al. [24] utilized a highly efficient "plasma-bombing" technique to create a single-atom catalyst composed of isolated Co atoms anchored on nitrogen-doped carbon (Co-SAC/NC). By achieving a high loading capacity of up to 2.5 wt%, the well-dispersed single Co atoms within the Co-SAC/NC structure exhibited robust performance in facilitating oxygen reduction reactions under alkaline conditions. Furthermore, when employed as the air-cathode catalyst in a zinc-air battery (ZAB), the catalyst demonstrated exceptional battery performance. Liang et al. [25] conducted a study on the breakdown of methylbenzene in a gas using non-thermal plasma with a ferroelectric catalyst under normal temperature and atmospheric pressure conditions. The plasma system was enhanced by incorporating materials with unplanned polarization ($BaTiO_3$) and photoactive catalyst properties (TiO_2). The research focused on investigating the efficiency of toluene degradation and particular energy density during the process of patient discharge. Additionally, an examination was carried out to understand the byproducts generated and the degradation mechanisms involved in the process. It was observed that merging non-thermal plasma technology with the catalyst resulted in an increased efficiency of toluene degradation.

Different from before, more research organizations added more detailed research on different kinds of catalysts. Luo et al. [26] successfully achieved the synthesis of vertically aligned single-walled carbon nanotubes (VA-SWCNTs) through plasma-enhanced chemical vapor deposition at temperatures ranging from 500 ℃ to 600 ℃. Ethylene was utilized as the carbon source, while a 1 nm Fe film served as the catalyst. To ensure the growth of high-quality VA-SWNTs within a plasma sheath, it was crucial to optimize both the input power and gas pressure in order to minimize undesirable ion bombardment etching effects. The resistance of the synthesized VA-SWNTs against such etching was found to be closely correlated with the growth temperature. Yamazaki et al. [27] utilized pulse-excited remote plasma chemical vapor deposition to grow CNTs at temperatures lower than 400 ℃. They also incorporated a biased plate-type screening electrode to eliminate charged particles, ions, and electrons. The study successfully achieved the growth of high-quality CNTs at a rate of 98 nm/min at 400 ℃. These findings suggest that the removal of charged particles and regulation of radical quantities are crucial for optimal CNT growth below 400 ℃. The synthesis of aligned gallium nitride (GaN) nanowires was carried out by Wang et al. [28] using a plasma-enhanced thermionic emission source chemical vapor deposition system. And in this process, GaN powder and nitrogen were utilized as the sources for gallium and nitrogen, respectively. By combining the growth mechanism of vapor-liquid-solid with the effects related to plasma, the fabricated GaN nanowires exhibited n-type characteristics with varying diameters.

2.1.2. Synthesis of carbon-based catalyst materials

Carbon materials, for example, CNTs, carbon black, and graphene, have the benefits of a substantial surface area and remarkable electrical and thermal conductivity, as well as resistance to corrosion, which is why they are often used as carriers of different types of catalysts (**Figure 5(a–f)**). Besides that, it is confirmed that the surface treatment of carbon-based carriers by plasma, such as plasma surface modification or chemical functional group modification, provides anchor points for nano-catalyst particles to deposit on, improves the interaction between the carrier and supported catalyst particles, and enhances both electrocatalytic efficiency and the long-term stability of the catalyst.

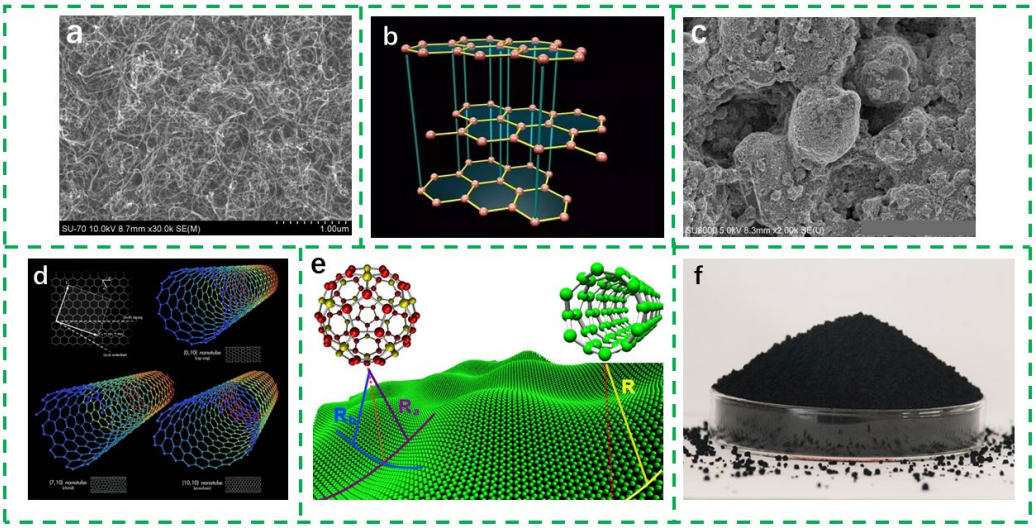

Figure 5. (a) SEM image of carbon nanotube. **(b)** Diagram of graphite lamellar structure. **(c)** SEM image of carbon black. **(d)** Micro-morphology of CNTs. **(e)** Surface micrograph of graphene. **(f)** Carbon black powder.

Through long-term research and using the accumulation of the carbon element, Sahoo et al. [29] successfully converted the naturally hydrophobic vertical graphene nanoplates (VGNs) into nanoplates with super-hydrophilic properties through the application of oxygen plasma deposition. Remarkably, they were able to maintain the distinctive 3D interconnected porous network structure. After the plasma treatment of the exposed VGN structure, the oxygen content on the surface increased, the surface of the VGNs changed from the hydrophobic state to the super-hydrophilic state, and the surface area infiltrated by the electrolyte was enhanced. From oxygen plasma spraying, the area capacitance of the super hydrophilic VGN electrode increased by 10 times compared with that of the inherent hydrophobic electrode. Hussain et al. [30] took advantage of PECVD and assisted chemical vapor deposition (CVD) to grow CNTs, where CNTs with bamboo-like and multi-walled structures were grown on different types of substrates (silicon wafer, copper, MEAs, carbon paper, and graphite).

The modification of CNTs by plasma treatment and MnO_2 electrodeposition is used to optimize the characteristics of carbon nanotubes in terms of their physical and chemical attributes. Plasma treatment has been found to enhance the capacitance and

surface area of CNTs, making them more appropriate for electrochemical, biological, and environmental uses when compared with untreated CNTs.

Because of their special tubular hollow structure, ample surface area with significant dimensions, remarkable heat transfer capability, conductivity of electricity, mechanical strength comparable to that of metal materials, and excellent thermochemical stability, CNTs are provided with special catalytic properties due to their spatial stereoselectivity and strong interaction between metal catalysts and carriers. Combining CNTs with a nano-metal catalyst by plasma chemical vapor deposition is able to improve the catalytic activity, stereoselectivity, and chemical stability of the catalyst, and the introduction of plasma technology solves the problems of easy agglomeration among single CNTs and low catalyst loading and makes CNTs a more excellent catalyst carrier.

2.2. Dielectric barrier discharge (DBD)

Atmospheric-pressure DBD is a discharge phenomenon in non-equilibrium gas, which is capable of being produced at standard atmospheric pressure. The insulator initiates discharge to prevent the generation of high-frequency and high-voltage current at atmospheric pressure. DBD plasma is able to generate excitation discharge with a simple device and higher power density (**Figure 6(a,b)**), and it can be discharged under different gas phase conditions and sometimes applied in a liquid-phase environment [31,32]. Due to the presence of a dielectric barrier in the discharge space, current growth is restricted, thereby preventing the formation of sparks or arcs. Dielectric barrier discharge can generally be categorized into filament discharge, uniform discharge, and spot discharge, with the specific manifestation depending on factors such as the type of the discharge gas, properties of the medium, voltage value of the input electric field, and frequency of the high-voltage power supply. There are multiple variations of DBD electrode structures. DBD involves the presence of a specific working gas between two discharge electrodes, with one or both electrodes being coated with an insulating material, or alternatively, the medium can be directly suspended within the discharge space or filled with a granular substance. Upon the application of a sufficiently high AC voltage across the electrodes, the breakdown of the gas occurs, which leads to the generation of a dielectric barrier discharge. In practical applications, tubular electrode structures find extensive uses in various chemical reactors, while plate electrode structures are widely employed for industrial purposes, such as polymer and metal film/plate modification, grafting processes, surface tension enhancement, cleaning operations, and hydrophilic transformation.

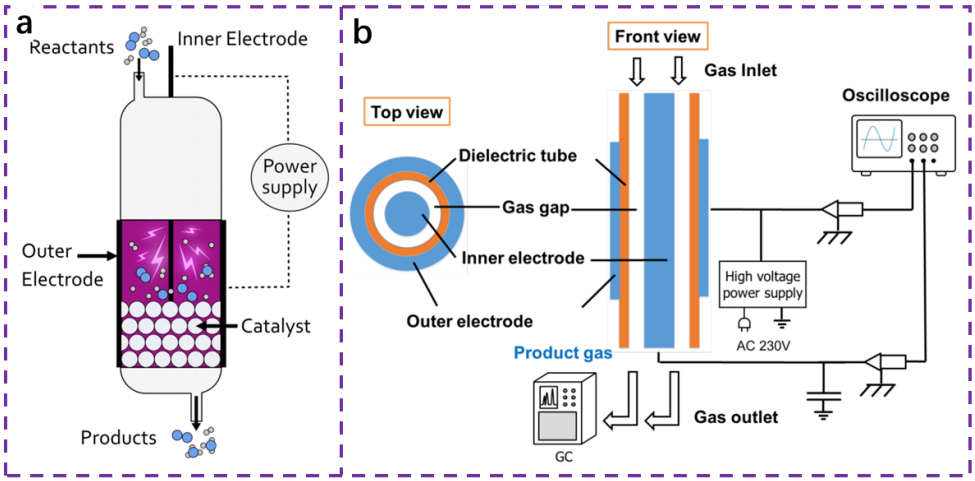

Figure 6. Schematic diagram of dielectric barrier discharge (DBD) [31,32].

2.2.1. Synthesis of metal catalyst by DBD plasma

The utilization of the plasma effect may lead to notable alterations in both the surface morphology and inner structure, as the catalyst's surface experiences substantial influxes of plasma matter. These include a significant quantity of high-energy ions, electrons, and radicals, which are likely to induce specific modifications in the oxidation state and stability of the surface faceting structure. The study conducted by Wang et al. [33] examined the combined impact of a catalyst and low-temperature plasma on the dry reforming of methane in a plasma fluidized bed using Ni/g-Al_2O_3 in the capacity of the catalyst. From temperatures ranging between 648–798 K, it was observed that the synergetic effect resulting from the interaction between the catalyst and plasma was evident. The evaluation of this synergetic effect, measured by comparing its conversion ratio to that achieved solely with plasma or only with catalyst, indicated the superior performance of the plasma fluidized bed over a certain temperature range when compared with that of a packed bed configuration utilizing only plasma. Wang et al. [34] examined various ways in which plasma interacted with a produced catalyst, focusing particularly on their combined effects. They investigated how a commercially available Ni/Al_2O_3 catalyst performed when exposed to cold plasma generated by a DBD system for methane dry reforming within a coaxial DBD reactor. Experimental results revealed that through assistance from in-situ plasma, it was possible for an unreduced catalyst present within an annular discharge gap to undergo reduction during reactions at approximately 673 K. Nevertheless, compared with using the produced catalyst, this approach exhibited lower synergistic effects and resulted in greater carbon deposition on the catalytic surface. Sentek et al. [35] investigated the performance of a hybrid plasma-catalytic system using different types of catalytic packing materials, including a carrier made of a ceramic material with alumina composition and two catalysts, which were Al_2O_3/Ag and Pd/Al_2O_3. The experimental setup involved converting a mixture of methane and CO_2 at 1.2 bar of pressure in a DBD reactor operating at a frequency range of 5.7–6 kHz. Notably, non-volatile byproducts, such as carbon deposits and macromolecular substances, were observed on both the quartz dielectric barrier and metal electrode surfaces. When the Pd/Al_2O_3 catalyst was employed, the overall conversion rate for methane was found

to be between 30%–50%, with the conversion of methane specifically into C_2-C_4 hydrocarbons reaching up to 22%. Rico et al. [36] conducted atmospheric-pressure dielectric barrier discharge (DBD) combined with a copper-manganese oxide catalyst to achieve the simultaneous direct decomposition and steam reforming of methanol for hydrogen production, as well as the selective oxidation of CO. And extensive experimental research conducted by Nozaki et al. [37] focused on the utilization of barrier discharges with a Ni/SiO_2 catalyst for the steam reforming of methane. The presence of barrier discharge at 400 ℃ clearly demonstrated the chemical activity of the nickel catalyst. Methane conversion significantly surpassed the equilibrium rate of conversion, while product selectivity tended to align with the equilibrium composition at a given temperature, resulting in an energy cost and efficiency achievement of 134 MJ/kg and 69%, respectively. Di et al. [38] prepared a Pt/TiO_2 mesoporous photocatalyst by an atmospheric-pressure DBD cold plasma device (**Figure 7(c)**). It was found that the plasma treatment of DBD reduced H_2PtCl_6 to metallic Pt nanoparticles, and the Pt particles were smaller after the application of plasma. The photocatalytic activity of the Pt/TiO_2 mesoporous catalyst for the photodegradation of methylene blue (MB) was twice as high as that of ordinary mesoporous TiO_2. Xu et al. [39] investigated the Pd/Al_2O_3 catalyst using a simple method of impregnation, with $Pd(NO_3)_2$ and $PdCl_2$ as precursors, by employing atmospheric-pressure DBD cold plasma. The catalytic oxidation activity of CO on Pd/Al_2O_3 samples prepared by cold plasma treatment using the same Pd precursor was found to be higher compared with those prepared through conventional thermal reduction. Furthermore, when utilizing $Pd(NO_3)_2$ as the precursor, smaller Pd nanoparticles were observed in the resulting Pd/Al_2O_3 catalyst, with a majority of these nanoparticles distributed on the surface of the Al_2O_3 support material. This phenomenon proved that the utilization of cold plasma demonstrated efficacy in the preparation of Pd/Al_2O_3 catalysts with superior performance. Li et al. [40] attracted a lot of attention that utilizing a novel technique involving plasma decomposition via dielectric barrier discharge (DBD) to synthesize a Ni/MgO catalyst. The application of the DBD plasma treatment significantly enhanced the interaction between Ni/MgO catalyst and metal support, leading to the formation of smaller Ni particles. The plasma-treated Ni/MgO catalyst exhibited a substantially improved performance in low-temperature activities and demonstrated exceptional stability in CO_2-assisted methane reforming. Gallon et al. [41] observed the conversion of NiO into metallic Ni and investigated the reduction process of a NiO catalyst by CH_4 in a coaxial double-DBD reactor at low temperatures. The experimental findings indicate that, at atmospheric pressure, the plasma catalytic reaction achieved a CH4 conversion rate of 37%, with an impressive selectivity of 99% towards H_2 and solid carbon. Tu et al. [42] introduced a functionalized Al_2O_3/NiO catalyst with plasma-assisted reduction into Ar/H_2 DBD at ambient pressure and reduced temperature (<300 ℃). The performance of the discharge power improved by increasing the generation of supplementary conductive metallic Ni within the discharge gap while undergoing the plasma-reduction procedure. And it was found that the original size of the Ni particles remained unchanged after the plasma therapy. In another study, Tu et al. [43] examined the impact of incorporating TiO_2 on the electrical and spectroscopic properties of N_2 DBD in a single-stage plasma catalysis

system. The inclusion of TiO_2 pellets within the discharge led to a significant enhancement in the vibrational temperature of N_2 within the DBD, indicating that there was a pronounced influence of the interaction between the plasma and catalyst on the electron energy distribution function within the discharge.

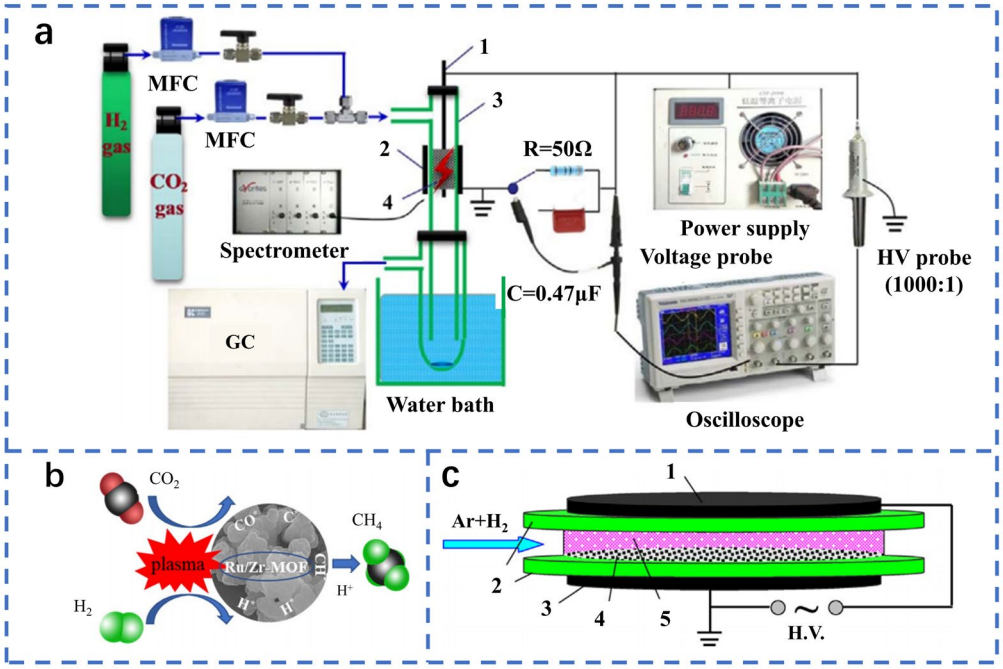

Figure 7. (a) Schematic illustration depicting plasma system utilizing DBD technology for CO_2 hydrogenation. (1: discharge electrode, 2: ground electrode, 3: DBD reactor, and 4: catalyst). **(b)** Proposed mechanism of hydrogenation of CO_2 to methane. **(c)** Schematic illustration depicting cold plasma device utilizing DBD at atmospheric pressure (1: electrode for discharging, 2: quartz material made of amorphous silica, 3: grounding rod, 4: exemplar, and 5: cold plasma) [38,44].

Different from the above, some studies chose some precious metals to carry out similar experiments. Xu et al. [44] applied DBD to the CO_2 hydrogenation of Ru/Zr-MOF plasma (**Figure 7(a)**). The experimental findings revealed that the combined influence of plasma and Ru/Zr-MOF catalyst resulted in a remarkable increase in methane selectivity (94.6%) and yield (39.1%) during CO_2 hydrogenation. XRD and SEM analyses demonstrated that the fundamental crystal structure and morphology of Zr-MOF and Ru/Zr-MOF remained unaffected after exposure to DBD plasma, indicating their stability under plasma conditions (**Figure 7(b)**). The utilization of plasma-assisted Ru/Zr-MOF exhibited exceptional catalytic activity and durability for converting CO_2 into methane, which holds significant implications for employing plasma and MOF materials in CO_2 hydrogenation processes. And later, Di et al. [45] fabricated an Au catalyst supported by the commercial TiO_2 Degussa P25 (Au/P25-P) via the deposition-precipitation method using cold plasma generated by DBD under normal air pressure and investigated the effects of plasma reduction time and calcination on the performance of the Au/P25-P catalyst. Interestingly, transmission electron microscopy (TEM) results showed that the Au nanoparticles were small in size and high in distribution. DBD cold plasma accelerated the preparation of the

Au/P25-P catalyst, and the Au/P25-P revealed exceptional CO oxidation performance attributed to the full reduction of Au compounds and reduced utilization of oxygen vacancies.

2.2.2. Preparation of catalyst by gas-assisted plasma

Mizushima et al. [46] developed a novel catalyst for a plasma reactor using a membrane-like alumina tube. By subjecting the pure alumina membrane to nitrogen-hydrogen plasma, they observed an increase in ammonia production under various reaction conditions. Furthermore, when the catalyst was loaded with ruthenium, there was an additional enhancement in ammonia synthesis. These findings clearly demonstrate the combined effect of plasma and catalysis from both alumina and ruthenium on ammonia formation. Through a series of verification experiments, Mizushima et al. [47] conducted a study on the synthesis of ammonia at atmospheric pressure using a DBD plasma reactor that featured a metal-loaded membrane-like alumina tube as an electrode catalyst. The introduction of unadulterated aluminum oxide into N-H plasma led to an enhanced production of ammonia, which was further improved by incorporating Ru, Pt, Ni, and Fe onto the alumina surface. These findings clearly demonstrate the catalytic properties exhibited by both metals and alumina during the reaction involving plasma. Yu et al. [48] proposed to remove vehicle exhaust gas by a novel plasma-driven catalysis reactor with a special structure. The coaxial DBD reactor consisted of a trio of quartz tubes and a pair of copper electrodes. A nano-titanium dioxide film, prepared using radiofrequency magnetron sputtering, was applied onto the outer wall of the middle quartz tube to separate the catalyst from the high-voltage electrode. Continuous operational tests demonstrated that a stable performance with no deterioration in catalytic activity was sustained for over 25 h. It is interesting to note that after treatment, the concentration of HCs (hydrocarbons) in the vehicle exhaust gas treated by the PDC (plasma-driven catalysis) reactor reduced significantly compared with the result from the NTP (non-thermal plasma) treatment. Hou et al. [49] successfully cultivated superior-grade straight GaN nanowires through the reaction of Ga vapor with N_2 plasma in a horizontally positioned furnace equipped with DBD technology. The diameters of the GaN nanowires varied between 70–100 nm, depending on the size of Au catalyst particles, while the lengths extended to multiple microns. These findings highlight the effective utilization of DBD-type N_2 plasma in inducing superior growth conditions for single-crystalline GaN nanowires within the furnace.

However, the reduction in NO concentration was only minor. This observation suggests that the PDC reactor was more effective in reducing HC emissions compared with NO emissions in the specific context of vehicle exhaust gas treatment. The PDC reactor combined the use of plasma and catalysts to facilitate chemical reactions and convert pollutants into less harmful compounds. The precise mechanisms at play can vary depending on the specific design and operating conditions of the PDC reactor. Further investigations and optimization of the PDC reactor's operation parameters may help enhance the performance in reducing NO emissions as well, potentially leading to more balanced pollution control in vehicle exhaust gas treatment. Mei et al. [50] presented a cylindrical DBD reactor designed for the conversion of undiluted CO_2 into CO and O_2 at atmospheric pressure and low temperature. The effects of

incorporating $BaTiO_3$ and glass beads into the discharge gap were investigated, both in terms of their physical properties and chemical impact on reaction performance. Optimal results in terms of CO_2 conversion and energy efficiency were obtained when the discharge gap was fully packed with $BaTiO_3$ beads. It was observed that the addition of $BaTiO_3$ beads to the plasma system led to a twofold increase in the average electric field and mean electron energy within the CO_2 discharge, thereby significantly enhancing CO_2 conversion, CO yield, and the overall energy efficiency of the plasma process. Yu et al. [51] conducted a study on the breakdown of CO_2 in a plasma reactor filled with dielectric materials. The research revealed that the properties and structure of these dielectric pellets had significant implications for the reaction, as they impacted the distribution of electron energy within the plasma. Additionally, investigating the reverse reaction of CO_2 decomposition—namely, CO oxidation—provided further insights into understanding how the dielectric materials influenced plasma reactions. Using similar theoretical and strategic approaches, Scapinello et al. [52] explored the catalytic impact of electrode surfaces in a DBD process involving CO_2 and CH_4 at atmospheric pressure. The study revealed that copper and nickel electrodes led to increased production of carboxylic acids, particularly formic acid, indicating that the metal surface facilitated CO_2 hydrogenation reactions. Additionally, Krawczyk et al. [53] employed a plasma-catalytic system that combined both plasma and catalysts to facilitate the oxidative coupling of methane with CO_2. They investigated the impact of temperature (ranging from 130 ℃ to 340 ℃) and the gas flow rate on the conversion rates of methane and CO_2 using a DBD reactor operating at approximately 6 kHz of frequency. Hydrogen, carbon oxide, hydrocarbons, and alcohols were successfully produced by utilizing plasma and the Fe/Al_2O_3 catalyst system. The system without packing but with a carrier (Al_2O_3) demonstrated the highest yield of methanol and ethanol. Spencer and Gallimore [54] conducted an experimental investigation on the conversion of CO_2 into CO and O_2 using a microwave plasma/catalyst system operating at atmospheric pressure. Initially, the CO_2 gas was subjected to plasma treatment alone, followed by a combination of plasma treatment and utilization of a rhodium (Rh) catalyst material. The temperature measurements during plasma operation indicated that thermal equilibrium between the vibrational temperature and the rotational temperature occurred within the range of 6000–7000 K. Pietruszka and Heintze [55] conducted a study on the co-reforming of methane using oxygen and steam in non-thermal plasma or dielectric barrier discharge. The activation of plasma promoted the production of CO as the primary output, which subsequently underwent oxidation to form CO_2 when the catalyst became active at temperatures above 300 ℃. Introducing steam into the reactants led to increased generation of hydrogen under conditions where complete conversion of oxygen occurs.

2.2.3. Surface treatment of catalyst by DBD plasma

Compared with conventional thermal or chemical techniques, the utilization of DBD plasma for catalyst surface treatment enhances the dispersion of surface particles. Additionally, it maintains the original crystal structure of the catalyst, while reducing particle size due to its milder reaction conditions and heightened reactivity. DBD plasma treatment technology is different than traditional physical and chemical treatment methods, as it can not only simplify the operation process of the traditional

catalyst preparation and shorten the preparation time but also shows the advantages of a high degree of plasma ionization and decomposition without a pollution source. And its safety factor is high, which shows a unique aspect that is not possessed by chemical and thermodynamic methods. When high-speed electrons collide with gas molecules and atoms in the surrounding environment, a significant number of excited state particles or ions are generated through ionization. These active species possess exceptional physical and chemical properties, as they can transfer energy to third parties through contact collisions. Surface modification occurs when interacting with material surfaces. Cold plasma is commonly employed for surface treatment and catalyst modification purposes. The objectives of surface treatment primarily encompass defect construction, surface doping, fabrication of active sites, and modification of surface functional groups on catalysts.

Before all others, Tu et al. [56] designed a coaxial double DBD reactor to explore the plasma-catalytic conversion of CH_4 and CO_2 into valuable products, such as syngas. The impact of incorporating Ni/Al_2O_3 catalyst pellets into the gas gap on the discharge's electrical characteristics was examined. The presence of these catalyst pellets resulted in a shift in the discharge behavior from a typical filamentary micro-discharge to a combination of spatially limited micro-discharges, with a predominant surface discharge occurring on the catalyst surface. Additionally, it was observed that fully packing the reduced catalyst within the discharge area led to a significant decrease in the breakdown voltage for the CH_4/CO_2 discharge.

Chen et al. [57] used DBD plasma to synthesize CH_3OH from CH_4 directly at normal temperature and pressure. The methane conversion rate and methanol yield can be changed by changing the discharge frequency of plasma, the power supply of the equipment, and gas circulation time and composition. The influence of inert gas doping in the plasma discharge system on the results was studied. The experimental results showed that the plasma discharge intensity and efficiency obviously improved by adding inert gas, and the methane conversion rate and methanol yield were higher. Li [58] first studied the decomposition of CO_2 into CO on CeO_2 doped with Mo in oxygen-free plasma, and the test results showed that the conversion rate of CO_2 doped with CeO_2 was about 20 times higher. Plasma increased oxygen vacancies (VO) on the catalyst surface and formed Ce^{3+}-VO-Mo nodes, which made VO sites show great catalytic stability. Adding N_2 and Ar improved the conversion rate of CO_2 in the plasma process and N_2 was used as the scavenger of oxygen to promote chemical balance and inhibit the reverse reaction of CO_2 generation. Dong et al. [59] deposited silver nanoparticles (Ag-NPs) on powder P25 by DBD cold plasma treatment at atmospheric pressure without using any reducing agent harmful to the environment and biology, and then completely reduced to metal state by DBD cold plasma treatment at atmospheric pressure (**Figure 8(a,b)**). The obtained product showed high dispersibility, improvement in photocatalytic degradation of methylene blue (MB), and an antibacterial effect on *Escherichia coli* and *Staphylococcus aureus*.

Tu and Whitehead [60] reported a coaxial DBD reactor under different catalysts of $Ni/\gamma\text{-}Al_2O_3$. Compared with the fully filled reactor, the discharge volume of the DBD reactor was significantly reduced and the discharge mode was changed. The catalyst partially filled with $Ni/\gamma\text{-}Al_2O_3$ clearly showed strong filiform discharge in

both radial and axial directions, which significantly enhanced the physical and chemical interaction between the plasma and the catalyst. The experimental results showed that the methane conversion rate and hydrogen production almost doubled and the synergistic effect of plasma catalysis was helpful to significantly improve the energy efficiency of greenhouse gas conversion. Chen et al. [61] drew support from DBD in conjunction with Cu/γ-Al_2O_3 catalytic technology to degrade carbonyl sulfide (**Figure 8(c)**). It was found that the best effect was achieved by using the 5wt% Cu/γ-Al_2O_3 catalyst in conjunction with DBD, where the removal efficiency reached 98.9% at 16 kV and the gas product was without H_2S and SO_2 (**Figure 8(d)**). Adding DBD plasma to the catalyst also reduced energy consumption.

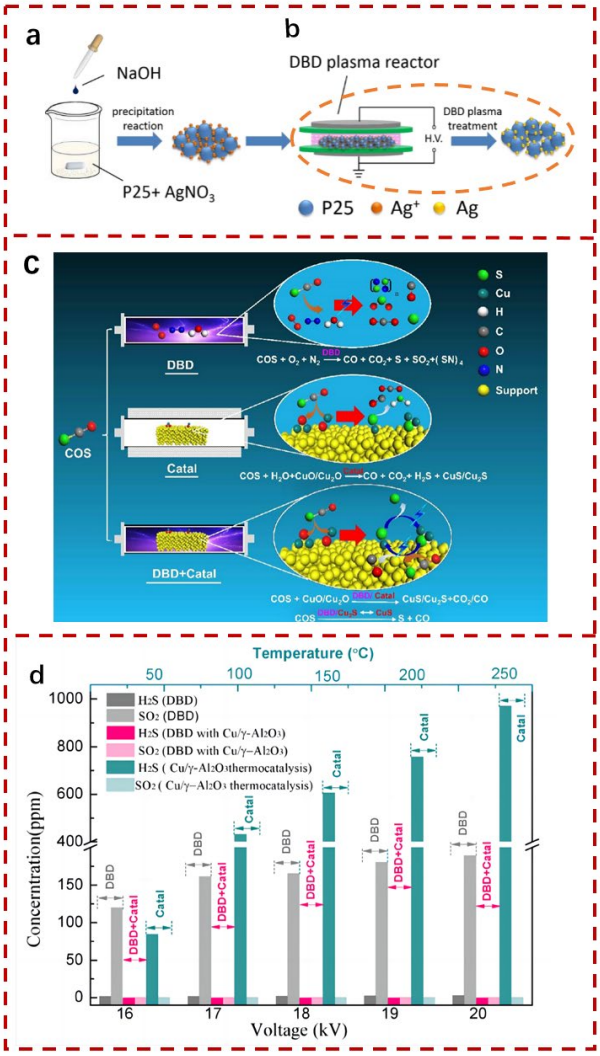

Figure 8. (a) Schematic of two-stage synthesis of Ag-TiO_2 nanocomposites, showing precipitation reaction and **(b)** followed by DBD plasma reduction. **(c)** Reaction mechanism diagram of three systems. **(d)** Generation of H_2S and SO_2 in the reaction [59,61].

DBD plasma has gained extensive utilization in catalyst preparation, surface alteration, and surface hydrophilicity modification, which improves the efficiency of material preparation, reduces the complicated treatment process, reduces the

granularity of catalyst materials, and improves the stability and working efficiency of catalysts. However, there are still some processes to be improved and studied, such as the selection of the optimal concentration of the carrier, the preservation of the integrity of the catalyst during preparation and treatment, the controllability of the shape and size of the catalyst particles, and the high dispersion of the surface of the catalyst carrier, which need to be further explored.

2.3. Glow discharge (GD)

GD is formed when a high-voltage DC power supply is connected between two plates and the gas in the interval is highly ionized to produce plasma. After crossing the corona discharge area, if the external circuit resistance is reduced or the whole circuit voltage is increased, the discharge current will continue to rise. Light gradually expands to the entire discharge space between the two electrodes and becomes brighter. According to its voltammetry characteristics, glow discharge can be divided into three different stages, namely, pre-glow, normal glow, and abnormal glow. The transition region between the corona discharge and normal glow is called preglow. The volt-ampere characteristic corresponds to the normal glow discharge, which is characterized by the discharge current increasing with the increase of the input power of the electric field, but the electrode voltage remains almost unchanged and is significantly lower than the breakdown voltage, showing the self-sustaining property of the discharge. After the normal glow, the voltage value of the volt-ampere characteristic rises rapidly with the current value, which is an abnormal glow discharge, resulting in glow plasma. A large number of active substances, high-energy particles, and ion clusters in the plasma transfer energy to the carrier on the surface of the catalyst under the collision with the surface, and because of the low gas temperature of the plasma, the impact on the internal structure of the catalyst and surface sintering caused by a high temperature are avoided, and so GD has been applied in catalyst preparation and surface treatment widely.

Although, there is a big gap between the principles part and most of the previous ones. Shang et al. [62] utilized an atmospheric-pressure glow discharge (APGD) plasma jet to synthesize a Ni/γ-Al_2O_3 catalyst. The catalyst prepared through this plasma-assisted method demonstrated enhanced activity at low temperatures in the CO_2 reforming of CH_4, compared with that of the conventional preparation approach. Characterization techniques, such as XRD and TEM, revealed that the novel plasma-assisted synthesis resulted in the formation of ultra-small Ni nanoparticles with sizes as small as 5 nm. Furthermore, improved resistance against coke deposition was observed based on TGA, CO_2-TPD, and stability test experiments conducted on the catalyst. The auxiliary function of plasma not only retained a certain reduction effect on the catalyst but also made the particles occupy a narrower width and disperse more evenly on the carrier than the catalyst prepared by thermal roasting. Generally speaking, the treatment effect of GD plasma is higher than other chemical methods and thermal methods at present, such as initial catalytic activity and overall average catalytic activity, and it plays a positive role in the dispersion and reduction performance of catalyst nanoparticles.

2.4. Atmospheric-pressure plasma jet (APPJ)

Plasma catalytic synthesis is a promising technology, as it can provide active metal materials at normal temperature and pressure. Atmospheric-pressure plasma injection is a common catalytic method. Plasma jet technology is one of the emerging cold plasma technologies, which injects plasma into the air under the action of an external electric field and is driven by a stable airflow. APPJ technology has attracted wide attention because of its simple structure, cost lower, and wide application in surface treatment and modification (**Figure 9(a,b)**). APPJ technology finds extensive applications in the fields of materials science and manufacturing, coating deposition, and catalyst surface modification and treatment [63,64].

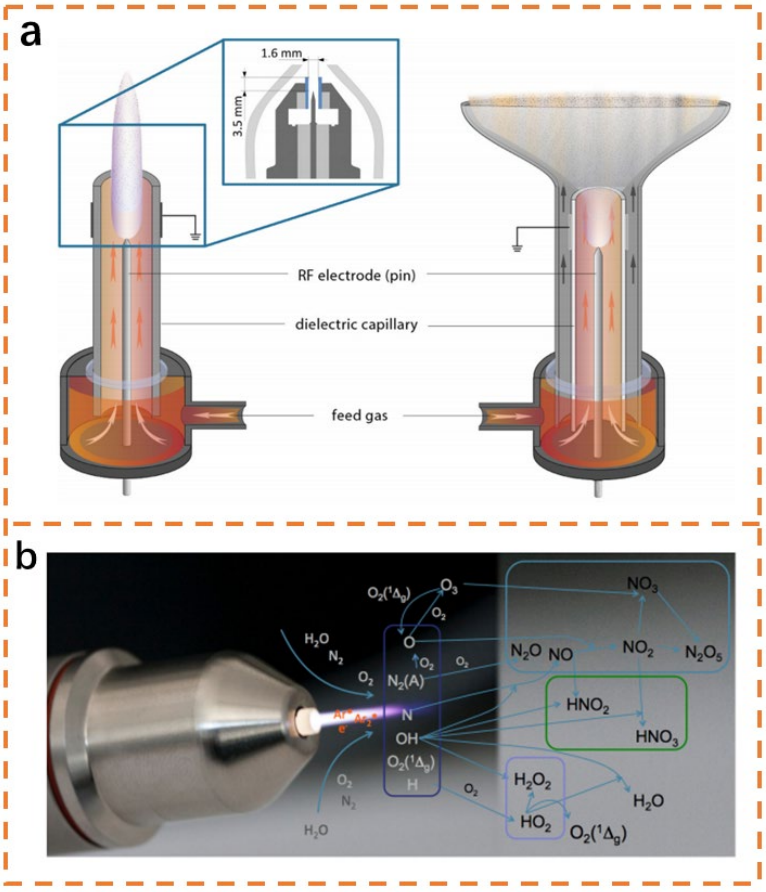

Figure 9. (a) kINPen schematic of pen-like principle and large-area treatment principle. **(b)** kINPen plasma jet induces highly non-equilibrium chemical reactions when atmospheric pressure is manipulated [63,64].

Studies have also examined the process of species formation in electron cyclotron resonance (ECR) plasma and on a catalyst surface. The characteristics of the catalytic surface influence both the generation and adsorption of plasma-activated atomic species. Sajjadl et al. [65] used glow plasma and the sol-gel method to study a CoW−$NiAl_2O_4$ catalyst (**Figure 10(a)**). After being treated with glow plasma for 45 min, the catalyst obtained a higher specific surface area and smaller particle size. At present, GD plasma is mainly used to prepare various metal catalysts. Shimizu et al. [66] used Ar/O_2 as the process gas to modify the surface of dye-sensitized solid solar

cells (DSSSCs) by an APPJ to improve their working efficiency (**Figure 10(b)**). After being treated with active substances and free radicals generated by the atmospheric-pressure plasma jet for 15 min, the current density increased and the solar energy conversion efficiency of DSSSCs was about 22.5% higher than before plasma treatment. It cannot be ignored that Chang et al. [67] directly prepared crystalline $Li_4Ti_5O_{12}$ (LTO) particles from a salt solution by an atmospheric-pressure plasma jet. The salt solution containing titanium and lithium ions was atomized by ultrasonic wave as the precursor and then transported to the APPJ by a gas carrier. By controlling the preheater, the composition and concentration of the precursor solution, and the flow rate of the carrier gas, particles with various shapes with particle sizes ranging from 1 nm to 100 nm were obtained (**Figure 10(c)**). When the plasma jet was used to fabricate the electrode, the specific capacity of the $Li_4Ti_5O_{12}$ powder produced at 50 °C exceeded 100 mAh/g. This study demonstrates the utilization of atmospheric-pressure plasma as an alternative technology for effectively eliminating toluene. A TiO_2 colloidal solution prepared using an improved sol-gel method was coated onto glass beads to facilitate the decomposition process of toluene. The catalyst film exhibited particle sizes ranging from 50–100 nm and possessed an anatase structure after being calcined at 500 °C for 1 h. Notably, in the presence of the TiO_2/O_2 plasma system, the conversion rate significantly increased and reached 70% when subjected to a pulse voltage of 13 kV over a duration of 120 min. This outcome is particularly remarkable compared with that achieved in photocatalytic systems, which yielded a conversion rate of below 40% [68].

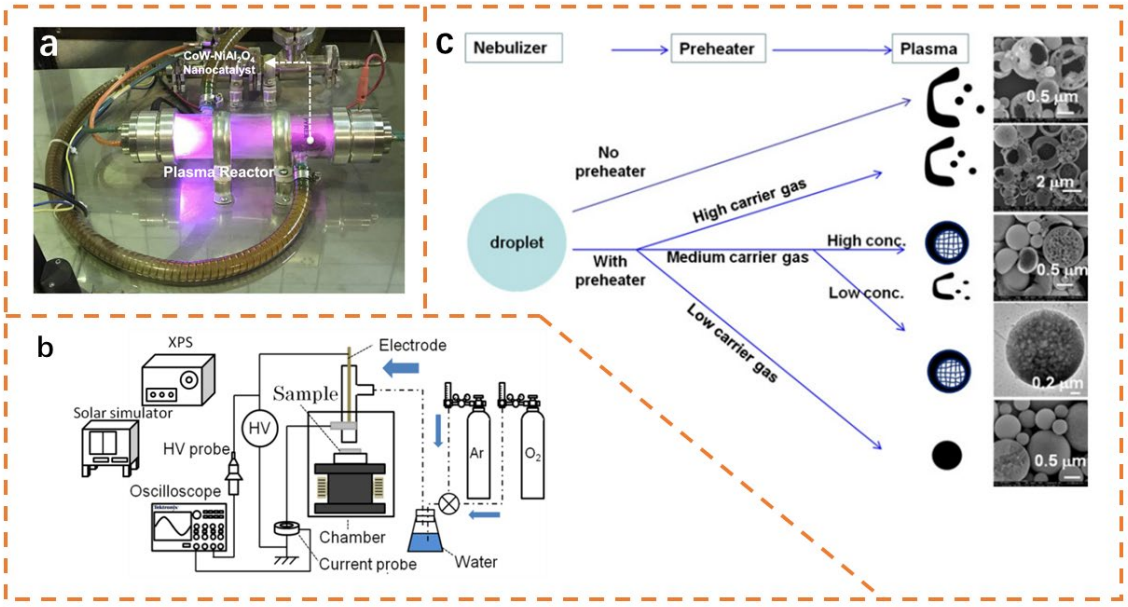

Figure 10. (a) Experimental setup for TiO_2 surface modification by atmospheric-pressure plasma jet. **(b)** Sol-gel-plasma mixing experiment of NiO-Al_2O_3 solid solution nano-catalysts. **(c)** Schematic diagram of formation of particles under various operating conditions [65–67].

In view of different application fields, researchers of the plasma jet technology have carried out in-depth and detailed research work around the interaction process between plasma and materials and solved the core technical problems related to the

structural design of plasma generator, working medium selection, complex interface process control, plasma effect optimization, and so on in specific application fields. They have also developed a practical and systematic plasma process system, accelerated the popularization and the large-scale and efficient application of atmospheric-pressure discharge plasma science and technology, and deeply and systematically understood the complex physical and chemical processes in plasma.

2.5. Radio frequency discharge

Radio frequency discharge plasma is a plasma formed by the breakdown of low-pressure gas under the alternating action of an external electric field. However, as there is no electrode in the discharge area, therefore there are no problems of electrode corrosion and material pollution. Radio frequency plasma technology has unique advantages in the fields of catalyst preparation, membrane synthesis process, material surface treatment, and so on.

Many research works have been carried out by relevant experimenters according to the theoretical basis. Rahemi et al. [69] prepared a Ni/Al_2O_3-ZrO_2 nano-catalyst through the plasma impregnation method. After plasma treatment, the catalyst showed characteristics of a high specific surface area and high dispersion and there was a strong interaction between the catalyst and the carrier; hence, the catalytic activity was higher than that of the traditional catalyst, and the stability and carbon deposition resistance of the catalyst in various processes significantly improved. Hofmann et al. [70] utilized silane as the Si source and gold as the catalyst to cultivate silicon nanowires at temperatures below 400 ℃ through PECVD. The growth rate was significantly enhanced by a radio frequency plasma, which activated the plasma and allowed for further reduction in the deposition temperature. Additionally, the Si nanowires exhibited a pure crystalline silicon core that was enveloped by an oxide sheath measuring only 2 nm thick. Li [71] used argon corona discharge plasma to treat a nickel-based catalyst at normal temperature and pressure and measured the catalytic activity and stability of the catalyst in the process of methane partial oxidation before and after plasma treatment. The results showed that the conversion of CH_4 increased by about 10% after the plasma treatment and the carbon deposition on the surface of the Ni catalyst was prevented after the argon plasma treatment, thus improving the stability of the catalyst.

An RF plasma source is a novel category of atmospheric-pressure cold plasma generator. For cold plasma to be used widely, it is necessary to study the structural design and discharge characteristics of a large-area and uniform RF plasma generator, which can generate and maintain a variety of working gases, and to study the gas temperature, velocity and concentration distribution of active particles in the discharge area and the jet area under different working gas types, flow rates, power frequency values, and input power values.

2.6. Corona discharge (CD)

Corona discharge plasma is produced by the breakdown of gas in an inhomogeneous strong electric field at atmospheric pressure and with the low relative current of the plasma. In order to generate this uneven strong electric field, point or

line discharge electrodes are needed. Although there are not many research works and experiments on CD plasma under the influence of PECVD and DBD, the unique plasma generation mode and characteristics are still very obvious. Due to the insulation damage following gas breakdown, the internal resistance decreases. Consequently, during the discharge process from the Townsend discharge rapidly passing through the self-sustaining discharge region, there will be a reduction in the electrode voltage and the appearance of bright light around the electrode, known as the corona discharge. Gas corona discharge is a localized self-sustaining plasma discharge.

Innovating according to the theoretical basis, Jiang et al. [72] applied plasma and a V_2O_5-WO_3/TiO_2 catalyst to convert nitrogen oxides (NO_x) in smoke into N_2 and H_2O in a wide temperature range (**Figure 11(a)**). The use of plasma improved the catalytic activity of V_2O_5-WO_3/TiO_2 and the removal efficiency of nitrogen oxides. Lu et al. [73] explored the feasibility of CD plasma combined with a supported catalyst for the remediation of soil contaminated by polycyclic aromatic hydrocarbons-phenanthrene and studied the actual effect of the degradation of polycyclic aromatic hydrocarbon phenanthrene after the use of the catalyst (**Figure 11(b)**). The results showed that the synergistic effect of corona plasma and the catalyst effectively improved the degradation effect of polycyclic aromatic hydrocarbon phenanthrene. The experiments showed that the catalytic effect and repeatability of the MnO_2/γ-Al_2O_3 catalyst were the best, and the degradation rate of polycyclic aromatic hydrocarbon phenanthrene improved to about 67% after five consecutive uses. Zhang et al. [74] used CD plasma technology to degrade dimethyl phthalate in water under the synergistic effect of bismuth tungstate and synthesized a vortex nano-material catalyst of γ-Bi_2WO_6 with high purity and high crystallinity by the hydrothermal method. Under the synergistic effect of CD plasma and the bismuth tungstate photocatalyst, the removal rate of dimethyl phthalate reached about 90% after half an hour and bismuth tungstate had good adsorption resistance, good sedimentation, and a good reuse effect on dimethyl phthalate. Zhao et al. [75] proposed a new method to convert CO_2 and H_2O into ethanol with the help of negative CD plasma using a Cu/ZnO/Al_2O_3 catalyst (**Figure 11(c)**). The combination of plasma and the catalyst effectively improved the low-temperature yield and selectivity of ethanol. The synergistic effect of partial copper oxide and plasma promoted the dissociation of methanol to produce ethanol, thus making ethanol have high selectivity.

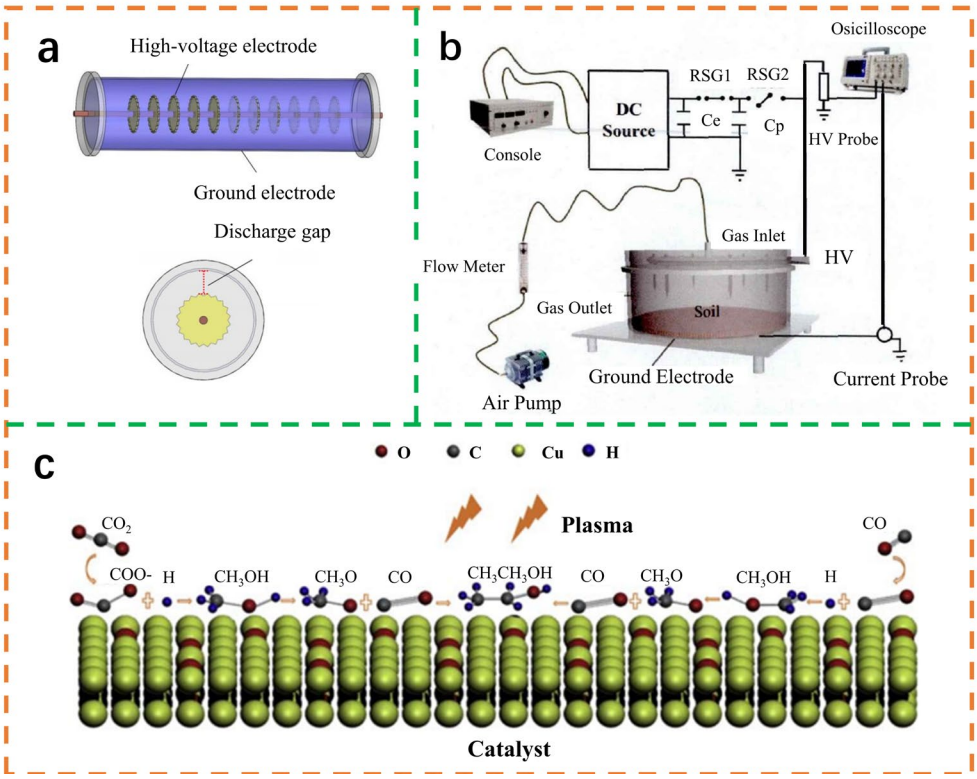

Figure 11. (a) Schematic of multitooth wheel-cylinder CD reactor. **(b)** Schematic of experimental system. **(c)** Synthesis mechanism of ethanol on Cu/ZnO/Al_2O_3 catalyst with assistance of plasma [72,73,75].

A series of innovative experiments have opened the door for the future of this plasma technology. Zhang et al. [76] investigated the oxidative dehydrogenation of ethane into ethylene and acetylene with carbon dioxide at ambient temperature and atmospheric pressure by pulse corona plasma over various catalysts. The selectivity towards ethylene was significantly enhanced when utilizing the Pd/Al_2O_3 metal catalyst. The ideal ratio of C_2H_6 to CO_2 in the feed during the plasma catalytic oxidative dehydrogenation of ethane was 1:1. Additionally, as the energy density of plasma increased, there was an observed enhancement in the conversion of ethane and a higher yield of ethylene and acetylene. Saud et al. [77] used needle CD coupled with a Pd/ZSM-5 catalyst to adsorb dilute ethylene and plasma catalytic oxidation. The catalyst's ability to adsorb ethylene was enhanced through the implementation of plasma catalytic oxidation in a circulating manner. The utilization of cyclic adsorption and plasma catalytic oxidation for ethylene not only facilitated a low-temperature oxidation procedure but also effectively minimized energy consumption. When the input power was half that of normal operation, the adsorption efficiency and conversion rate remained unchanged (**Figure 12(a)**). Chao [78] demonstrated an economical reforming process that combined arc plasma with catalysts in series for hydrogen production. Granular Ni catalysts were packed in the post-plasma zone and generated hydrogen by means of partial oxidation of methane. The elevated temperature was maintained both by the hot gases from the plasma region and by the heat of the reforming reaction itself without extra energy. In addition, the experimental data agreed well with the thermodynamic results, indicating that high thermal

efficiency was achieved with the plasma-assisted catalysis process. Yu et al. [79] used needle-plate DC corona discharge plasma combined with a Mn-based catalyst to degrade acetate waste gas (**Figure 12(b)**). The CD coupling catalytic mode was a two-stage system. When MnO_x with a load of 15 wt% was placed in the system, the degradation effect of ethyl acetate was the best, and the mixture of ethyl acetate and butyl acetate was degraded in a two-stage system with degradation efficiency values of 91.49% and 90.16%. Aziznia et al. [80] investigated the impact of CD plasma on the mixing process with a Ni catalyst supported by γ-Al_2O_3 in methane CO_2 reforming. Additionally, they examined how discharge power and the composition of the Ni/γ-Al_2O_3 catalyst influenced the performance of the catalyst. The conversion of methane and carbon dioxide obviously increased after corona plasma was used. When the Ni catalyst was used in the plasma reaction, the ratio of H_2/CO in the product changed and the selectivity of CO increased, resulting in fewer by-products, such as hydrocarbons and oxygen compounds. Chavadej et al. [81] used CD plasma and TiO_2 catalyst to remove volatile organic compounds. The findings from the experiment indicated that the energy generated by the plasma activated TiO_2, which led to enhanced CO oxidation. The increase in voltage and in the number of stages in the plasma reactor improved benzene conversion and CO_2 selectivity. The presence of the catalyst had little effect on benzene conversion but significantly improved CO_2 selectivity. Marafee et al. [82] took advantage of a Sr/La_2O_3 catalyst to study CD plasma. Compared with the catalytic process without plasma, the application of CD plasma improved methane conversion by almost five times and the selectivity to C_2 by more than eight times, and catalytic stability also greatly improved.

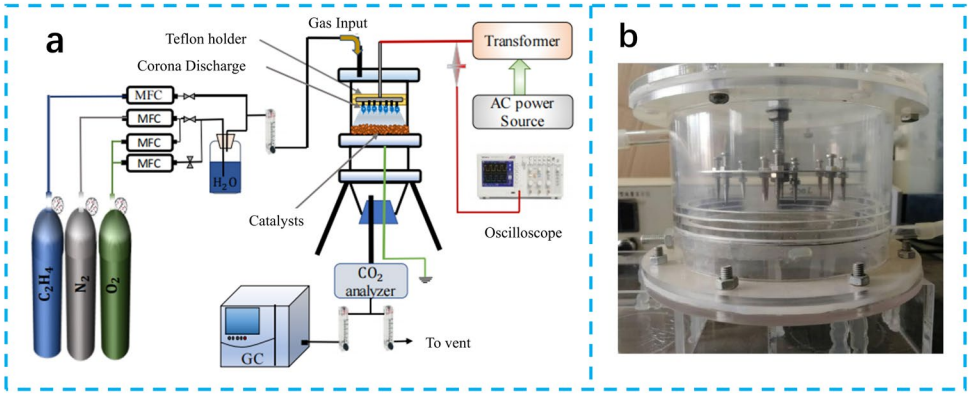

Figure 12. (a) Schematic diagram of the CD-coupled catalytic reactor (CDCCR) system for removal of C_2H_4. **(b)** Experimental reactors and flow chart [77,79].

CD plasma appears in the phenomenon of local free discharge of a gas medium in an uneven electric field, and the high electric field intensity generally appears near the tip of the electrode with a large curvature radius, and so this narrows the space for treating a catalyst in the device generating the corona plasma, which leads to insufficient catalyst treatment area, and hence the expected effect cannot be obtained. Moreover, because CD plasma has an uneven distribution of electric field intensity when used for treating various catalysts, leading to far less sample uniformity than those of other plasmas, the practical application of CD plasma in catalyst preparation

and surface modification is not as good as that of other plasmas, and it has not been applied to mass production at present.

2.7. Solution plasma processing (SPP)

Solution plasma is generated by discharge in a solution environment, which is similar to plasma generated in a gas-phase environment and contains a lot of high-energy substances and high-activity substances. Solution plasma is mainly generated by an aqueous solution (**Figure 13(a)**), and it includes pulse discharge, microwave discharge, glow discharge, pulse and ultrasonic cavitation combined discharge, and so on [83]. The main research direction of solution plasma is gradually developing from pulse discharge and glow discharge to a comprehensive discharge treatment of many processes, and it is applied to the preparation of nano-catalysts and other materials.

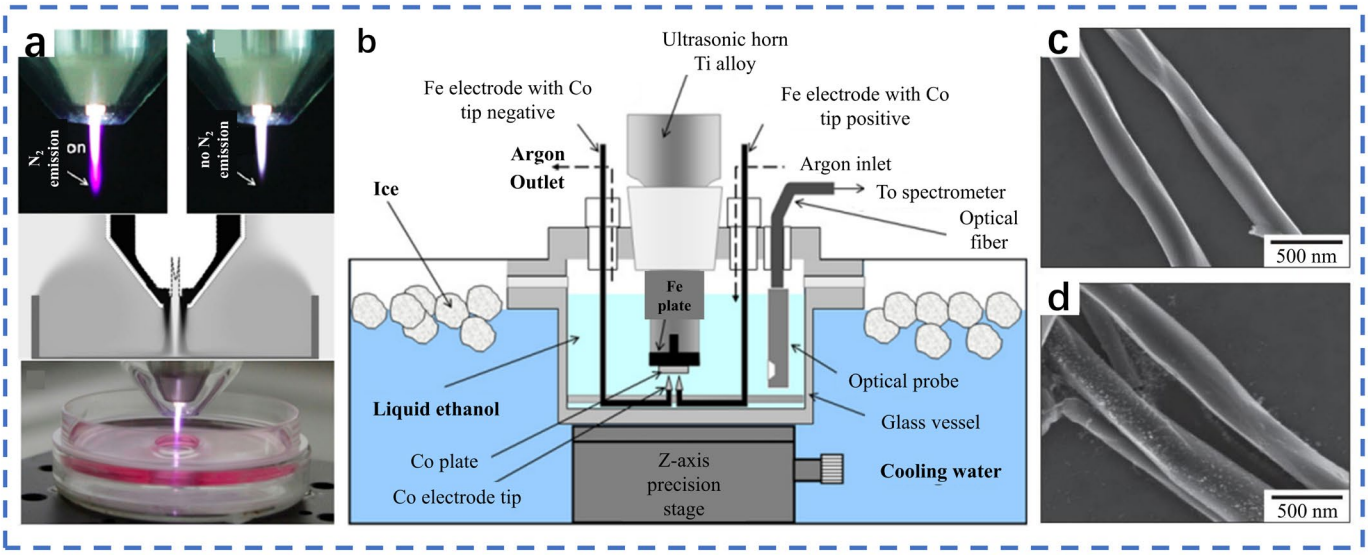

Figure 13. (a) Plasma jet diagram. **(b)** Schematic diagram of experimental apparatus. **(c)** SEM images of CNTs before and **(d)** after in-liquid plasma process [83–85].

Sergiienko et al. [84] used the combined action of a regulated DC power supply and ultrasonic cavitation to generate plasma in an ethanol solution to synthesize nano-graphite flakes (**Figure 13(b)**). The thickness of the obtained graphite layer was about 8.8 to 30 nm, and the transverse dimension varied from several hundred nanometers to more than ten microns. Show et al. [85] dispersed nano-platinum particles on CNTs in water by means of plasma (**Figure 13(c,d)**) and used a platinum catalyst, which was applied to proton-exchange-membrane fuel cells. The platinum catalyst's particles prepared in this way were about 10 nm, and the maximum electric power of the fuel cell made of the platinum catalyst assembled by this method was 108 mW/cm^2. Bulychev et al. [86] prepared nanoparticles by the liquid-phase plasma method under cavitation conditions. During discharge, plasma was generated on both sides of the metal plate, and corresponding metal oxide particles were formed in the liquid-phase environment on the side where the plasma was generated. Under this condition, the size of oxide particles was kept within 50 nm. Hattori et al. [87] used metals, which were W, Ag, and Au, as electrode materials and used plasma to corrode and disperse

the electrode in a liquid-phase environment to obtain nano-sized gold oxide, silver, and tungsten particles, and their general shapes were more spherical and rectangular. With unremitting research, this field has made great progress.

Solution plasma technology provides a possible way for the preparation of nanomaterials and the synthesis of catalysts. The temperature, the corrosion rate of the electrode, the crystal form, and the growth rate of the target product can be accurately controlled by controlling parameters, such as discharge power or substrate spacing, and this technology can be slightly improved and applied to the direction of preparing catalysts from other materials. However, whether the catalyst obtained in this way can be used for a long time, whether the catalyst is stable, and whether the strength of the material can meet the application standards are all urgent problems to be solved [88,89].

3. Conclusion

The recent advancements in the discussed areas indicate that plasma catalysis is a rapidly evolving field of research, offering not only numerous exciting scientific discoveries but also the potential for new technologies and industrial applications. Chemical catalysis relying on nanoparticles and other nanomaterials has already found various established uses, such as converting natural gas into syngas or facilitating the growth of inorganic nanowires and nanotubes. As highlighted by several examples in this review, the interaction between catalysts and cold nonequilibrium plasma can result in synergistic effects. These effects have the potential to enhance process outcomes, including conversion efficiency, energy utilization, and selectivity, and even achieve results that are typically unattainable through traditional approaches using either catalytic or plasma-only methods. Theoretical and practical studies have demonstrated that the activity of a solid-phase catalyst is closely correlated with its crystalline phase structure and specific surface area. Ultrafine catalytic materials exhibit excellent catalytic activity due to their large surface area, imperfect lattice, and abundance of defects. In recent years, plasma technology has emerged as a prominent research focus for the preparation of ultrafine particles. The cold plasma preparation process operates at low temperatures and high speeds, preventing metal nanoparticles from agglomerating or crystallizing fully, resulting in a partially crystallized state. In addition, cold plasma generates a strong electric field on the surface of the catalytic material, facilitating robust metal-carrier interactions. Surface metal-support interaction (SMSI) typically involves embedding metal nanoparticles onto the carrier material. This embedding effect enhances stability by establishing a more secure contact between metal nanoparticles and carriers, while also promoting synergistic reactions between metals and carriers that can alter reaction activity and selectivity. Furthermore, SMSI can modify the electronic properties of metals and regulate the adsorption capacity of active metal species towards gas molecules and intermediates, thereby enhancing both the activity and stability of catalytic materials.

As the fourth state of matter, cold plasma has unique physical and chemical characteristics, such as high reactivity, a large number of high-energy particles and ions, and low molecular temperature, which give it unique advantages in catalyst preparation and modification and make it widely used in chemical synthesis, catalyst

surface modification, material surface treatment, and other fields. Different cold plasmas have similar effects on catalysts, but their effects are different in specific application processes. Plasma chemical vapor deposition is more suitable for the synthesis of membrane catalysts, forming a dense nano-particle film on the surface of the carrier. Compared with other methods, DBD plasma has more advantages in assisting the synthesis of granular catalysts. GD plasma can reduce the particle size and improve the particle dispersion of catalysts after being used in the synthesis process, and it can improve the sintering resistance and chemical stability of various catalysts. A plasma jet sprays the catalyst carried by the plasma onto the surface of a carrier, which can be widely used in coating deposition and surface treatment and modification. Solution plasma substitutes plasma into a solution to complete the functions of dispersing and precipitating the catalyst to be dispersed in the liquid and dispersing or comprehensively utilizing one or more plasmas in the solution for higher work efficiency and effect.

In the application of plasma to prepare catalysts, the high-energy characteristics can be used to shorten the preparation period, avoid the agglomeration phenomenon in the catalyst preparation process, ensure the uniform distribution of grain growth and the formation of the crystal structure, reduce the occurrence of the carbon phenomenon on the catalyst surface, and avoid the sintering of the catalyst and the carrier surface caused by traditional high-temperature roasting. In the process of preparing a catalyst, the high-energy particles or ionic groups in cold plasma mainly change the surface morphology and improve the grain structure under the collision with the catalyst and generate more active sites for the functional groups on the surface of the catalyst to attach so that the catalyst has a nano-catalytic morphology that is more suitable for various substances.

4. Prospects

Plasma, a rapidly advancing catalytic treatment technology, has garnered considerable attention in recent years among scientists and industry professionals. Nonthermal plasma offers exciting prospects for modifying surfaces and creating new materials with specific properties. It is evident that the interaction between plasma and catalysts is intricate, often resulting in outcomes that cannot be attributed to a single process. While certain factors may dominate, such as the impact of packing in DBDs on the electric field distribution and the overall effect on plasma-catalytic processes, other factors have yet to receive thorough consideration. In this paper, several such factors that could significantly influence the process were discussed. Compared with traditional physical and chemical treatment methods, plasma treatment technology can not only simplify the operation process of traditional catalyst preparation and shorten the preparation time but also shows the advantages of a high degree of plasma ionization and decomposition without a pollution source. And the safety factor is high, which shows a unique aspect that is not possessed by chemical and thermodynamic methods.

At present, some strategies and principles of plasma catalytic treatment deserve further in-depth research with the development of plasma. First, plasma has been proven to control catalyst surface morphology, such as topography, roughness of the

pores, microstructure, and so on. However, in the process of plasma treatment, some uncontrollable factors often lead to the failure to obtain the expected effect on the catalyst surface. In view of this situation, the plasma generation mode can be changed, the catalyst can be pretreated, and the plasma bombardment time can be reasonably arranged. Second, the interplay between diverse catalysts and cold plasma is intricate, and frequently the outcome of their combination cannot be ascribed to a singular, specific process. In the case of improper single treatment, improper handling of cold plasma treatment may lead to the initiation of thermodynamic reactions. Therefore, it is crucial to utilize reactive species, such as atomic oxygen and hydrogen, in order to assist the synthesis of various functional groups and optimize the redox properties of catalysts. Third, the introduction of defects in the catalyst can serve as anchoring points for metal particles on the support surface. This effectively prevents the aggregation of metal particles, thereby enhancing the interaction between the catalyst and its support. The plasma modification process is significantly influenced by various discharge conditions, such as the gas environment, energy input, treatment duration, and reactor setup. Thorough investigation and analysis of these factors are essential for the successful implementation of plasma treatment. Moreover, it is crucial to prioritize the design of a suitable plasma reactor that ensures both discharge uniformity and stability.

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Availability of data and material: The manuscript includes data and materials from previous studies.

Data availability: Data will be made available on request.

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