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Cold Plasma in Research, Development and Deployment

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Abstract: Chemistry and related research, that aims to address and solve myriad challenges, is ultimately evaluated or judged from utilitarian points of view. A successful endeavor therefore not only generates a sense of satisfaction and opens up fresh research directions; it may also substantiate the novelty and apt use of the experimental methodology chosen therein. Diversity in respect of evolving research strategies, aided by simultaneous improvements and availability of associated hardware and software, progressively allow more complex challenges, which seemed beyond reach previously, to be addressed and resolved. Frequently, chemical reactions' commencements necessitate energy input in some form, and thereafter may follow either oxidative or reductive pathway. Various forms of energy employed include heat, ultrasound, light, UV, X-ray, Nuclear Radiations *etc.*, in addition to catalytic and enzymatic supports. In this context, the distinctive and novel reactive energy source of **Cold Atmospheric Plasma** (or **Cold Plasma, CP** in short) offers a simple and frequently superior alternative to a variety of studies that stipulate use of vastly expensive and very complex hardware systems. Though the history of **CP** spans over last 150 years, it remained completely dormant or sparsely researched almost till the 1980s mainly due to ignorance. At present, setting up a **CP** experimental facility or laboratory is an uncomplicated, and generally an *easy-to-finance* proposition. Convenient need based tuning and generation currently makes **CP** technology one of the user-friendliest available for contribution in a variety of *chemistry-inclusive* application areas. Worldwide various laboratories, institutes, and even industries have found its novel and profitable use in diverse areas of application such as pollution control and mitigation, material surface modification, in biology, health and healing, nano materials and fabrications, polymers, improved vehicular engine performance, creating steps towards a cleaner and greener environment *etc.* to name a few. "***Tricks of the CP trade***" in diverse multi-phase, *atypical* and innovative utilitarian studies, including some carried out in our laboratory are presented here to sensitize and motivate researchers about this novel theme open for endless exploration.

Keywords: Free radical; Cold Plasma; Multidisciplinary technology

1.Introduction

Initiations of chemical changes as a general rule necessitate energy input in some form. Various forms of energy available and usually employed comprise of thermal, ultrasound, light, UV, X-ray, Nuclear Radiations *etc.*, in addition to typical catalytic and enzymatic supports. While advancing a laboratory study from a successful R&D effort to pilot scales, and finally into industrial production, the preferred energy utilization scenario and its related process efficiency may however get affected due to factors such as the on-site available energy type and the associated economics. Opportunely, in the last two decades, another unique, quite reactive and scalable source of energy has emerged that now allows

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Author's note: *Though written from a Chemistry based viewpoint, nonetheless this presentation is aimed to popularize Cold Plasma and its inherent utilitarian proffer to a wider group of young and not-so-young researchers in their respective area(s) of learning, including those who enjoy the challenges of multidisciplinary progress in Science, Technology and Health. The examples herein need to be taken as random representations and the interested reader is encouraged to delve into the web and other available literature to get suitably updated on prevailing and freshly emerging directions. Finally, the judgment on "friendliness" is left to the reader's imaginations!*

researchers to take fresh looks into their work approaches. Inventive **Cold Atmospheric Plasma** (or **Cold Plasma**, **CP** in short) offers various unique advantages as a "***chemistry-inclusive initiator***" by virtue of its physical and chemical characteristics. **CP** generation or production is uncomplicated and directly scalable as per demand, in addition to being a highly energy efficient proposition (minimal loss) with *easy-to-finance* prospects relatable to any chosen application. **CP** in research and development is found to be freely exploitable for a variety of purposes, wherein it helps to create appropriate or distinctive reaction environment, and consequently its applications have rapidly gained acceptance all over the world. Readers who are not yet familiar with such exploitations in research and development may find this abridged account of **CP** generation and its functional roles in multidisciplinary environments handy. Herein, some rudimentary details on the **CP** based science and its harmonious amalgamations in variety of domains are discussed, with select working examples to highlight its current as well as future innovative potentials in widening spheres of human activity.

2. *Free Radicals* and the Energy Unit of *Electron Volt*

For effortless perception of the following text it is necessary to get unambiguously acquainted with two simple terms, namely ***Free radical*** and ***electron Volt***. ***Free radicals***, as defined and noted in the ***IUPAC Gold Book*** [1] are atomic or molecular entities that have free or unpaired electron spin. These are represented (with superscript *dot*) as Atom$^{\bullet}$ or Molecule$^{\bullet}$ and may have electric charge, or be neutral. Typical common examples are hydrogen atom, $H^{\bullet}$, mono-nitrogen oxides such as $NO^{\bullet}$, $NO_2^{\bullet}$, methyl radical, $CH_3^{\bullet}$, superoxide anion, $O_2^{\bullet-}$ *etc.* Very familiar hydrated ferric ion $Fe(H_2O)_6^{3+}$ would fall in this category and may be visualized as $Fe(H_2O)_6^{\bullet 3+}$ though in general practice the superscripted $^{\bullet}$ symbol is always omitted. Molecular oxygen needs a special mention here, it being a ***biradical***, $^{\bullet}O_2^{\bullet}$. More importantly though, the chemical reactivity of most ***Free radicals***, especially the small sized ones, fall in the *ultrafast* regime (meaning almost every diffusion controlled collision results in a product formation, therefore such reaction time scales remain in nanoseconds). Some details of ***Free radicals***' chemistry are presented later.

In science, ***Electron Volt*** is a frequently discussed and adopted measure of energy, especially in the field of Photochemistry, Nuclear radiation induced chemistry, **CP** chemistry *etc.* One ***electron Volt*** is the amount of *kinetic energy* gained (in vacuum) by a single unbound electron when accelerated by an electric potential of 1 volt. The numerical value of one ***electron Volt*** (represented as **eV**) is 1.602×10^{-19} Joules (SI unit). Typically, UV photon of 310 nm wavelength energy is 4 eV. (For comparison, one 100 watt incandescent lamp uses 360000 joules or 2.25×10^{24} eV energy.) In the subsequent presentation this unit of energy is used.

Table 1: Assorted Energies in *electron Volts*

Room temperature average thermal energy of a molecule	~ 0.04 eV
CO_2 laser photon (10.6 μm)	~ 0.117 eV
Other photons (a): Visible / 100 nm UV (UV-C)	1.5 - 3.5 eV / 12.4 eV
(b): Hard UV/ X-rays / Nuclear γ-	12.4 - 124 eV / 124 – 124 keV / ~ 1 MeV
Dissociation Energy: $CH_3CH_2\text{-}H \rightarrow CH_3CH_2^{\bullet} + H^{\bullet}$	4.4 eV
Ionization energy of Helium	24.5 eV
Ionization energy of Argon	15.8 eV
Ionization energy of Hydrogen/Oxygen atom	13.6 eV each

In **Table 1** energy of various sources and few physicochemical processes are shown as a handy reference for the discussion below. Extremely high energy content, as in nuclear, X-ray, hard & vac-UV allow each photon to cause multiple electronic excitation, bond dissociation, structural defects, ionization, *etc.* in any target during the course of interaction, including creation of a variety of highly reactive ***Free***

radicals in *ultrafast* timescale of nanoseconds. On the other hand, less energetic visible and IR photons mostly give rise to electronic, vibrational, and rotational excitations, however may even be employed for chemical bond cleavage under favorable conditions (multi-photon events with LASER).

3. Plasma

The oft used word ***plasma*** in Biology and Physics define vastly dissimilar entities or systems; hence its use calls for a description of the area of its existence. Plasma in Biology and Medical Sciences is the fluid fraction of the blood. Although a new physical state was first identified in laboratory by Sir William Crookes in 1879 as "*radiant matter*", half a century later in 1928 Irving Langmuir described this highly energetic physical state of matter as "Plasma" by borrowing the term. When excessive energy gets rapidly pumped into the gaseous atoms or molecules, these consequently lose a fraction of bound electron(s) into free or unbound state, with simultaneous formation of cation(s). The gaseous state then transforms into a new ensemble of ionized entities, as shown in **Fig. 1** for water. It happens with simultaneous formation (high fraction as ***Free radicals***) of variety of cationic, anionic, and other neutral species; their inter-reactions too cause formations of electronically excited species, and new molecules. Diverse physical processes are known to give rise to the plasma state of matter; some of these include use of intense and rapid heating, strong electromagnetic field, electrical potential difference, intense photon density from LASER *etc.* Amongst these, a common and simple method for plasma creation within any gas *at or near atmospheric pressure* is by an *electric discharge*. In a simplified description the essential details are as follows.

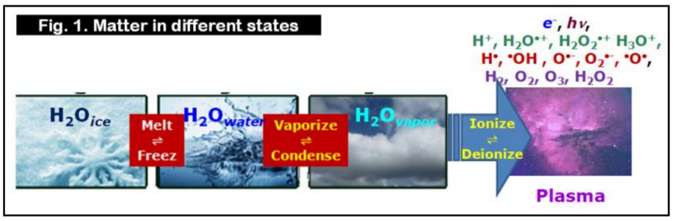


Fig. 1. Matter in different states

4. Plasma near Atmospheric Pressure

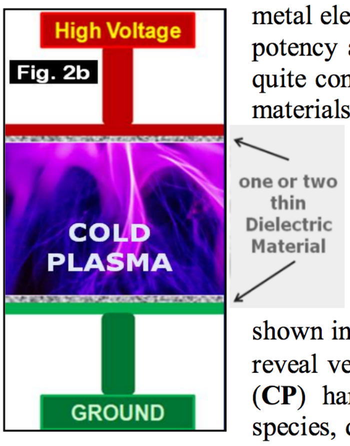
It needs to be noted that the background cosmic rays and natural radioactivity *continuously* and *randomly* generate of ion pairs (freed $\boldsymbol{e^-}$ and $Cat^{\bullet+}$) in our surrounding atmosphere or in any other gaseous medium. Typically, the steady-state concentration of such ion pair is a very low, ~ $10^3 - 10^4$ m^{-3}; as older ion-pairs get neutralized or trapped and lost, simultaneously new ones are generated independent of the previous events. In this scenario, as presented in **Fig. 2a**, if appropriate magnitude potential difference (few kV mm^{-1}) is applied between two separated points or surfaces inside a gaseous medium, the freed $\boldsymbol{e^-}$ being very light as compared to any $Cat^{\bullet+}$ generated, gets suitably accelerated towards the anode (+*ve* charged electrode surface), and may gain sufficient energy during its flight to ionize more intervening atoms or molecules on collision, producing $\boldsymbol{e^-}$ multiplication or an avalanche within 10^{-12} - 10^{-9} s time scale (Townsend multiplication). Under supportive conditions the avalanches sustain to create a visible electric discharge. Parameters that play crucial role include the *Prevailing Gas Pressure* (*near atmospheric pressure as discussed here*), Magnitude of *Applied High Voltage*, Inter-electrode *gap*, Electrode *shape* (curvature), Nature *of Gas etc.* Thus, continuous current flow (for time scale 10^{-9} s and slower, and persist for the period the potential difference exists) may ensue between the two electrode surfaces.


Fig. 2a

Subtle differences in *electrical breakdown* of gases differ due to: (*i*) Dissimilar electron-impact ionization processes in Atoms or Molecules due to Internal Energy Partition dynamics, defined by the constituent atom *Electronegativity*, *Ionization Potential etc.* (*ii*) At atmospheric pressure lower than normal, fewer ionizations per unit volume happen due to longer *mean-free-path*, causing insufficient multiplication. On the other hand, at higher pressure the *mean-free-path* gets shorter, but more frequent collisions cause a loss of high fraction of kinetic energy in thermal processes (as sufficient energy to cause next ionization may not be gained by the accelerated $\boldsymbol{e^-}$ before its premature collision). In effect, in either case higher breakdown voltage may be mandatory. Typical breakdown voltage values *at atmospheric pressure* for various common gaseous media are: **Ar 1.73 (kV mm^{-1}), He 1.56, N_2 2.51, H_2 2.73, Air 3.4, N_2O 4.2, CO_2 4.3, O_2 4.5**. In addition to the physical mode of electron multiplication mentioned above, a fraction of the freed electrons (and small fraction of cations) chemically interact with neutral or other ionic species present and produce electronic excited species, atomic clusters (both charged or neutral), anions (by electron capture, mostly if strong electronegative atoms such as oxygen, fluorine are present), and may also cause fragmentation of some molecules present (*typically organic*). Some of the electronic excited species created inside the ensemble decay in ultrafast time scale emitting copious amounts of *em*-radiation covering the range of IR to UV-C, always giving the plasma an intensely bright appearance. Well known examples of such plasma are (a) lightning bolts we observe during thunder storm and rain, (b) a welding job, (c) an electric spark near live wire, *etc*. Thus, following breakdown of medium resistance as described above, free and rapidly increasing flow of current occurs as long as the potential difference holds, and an arc-like random electric discharge may develop. The medium may break down completely, allowing uncontrolled and very high current flow (reaching 10^n ampere) within the plasma zone, causing ionic density to rapidly approach very high fraction. The plasma thermal condition inside may reach extremely high degree Kelvin (billions of degrees inside stellar innards, few hundred thousand inside lightning bolts, few thousand degrees within welding arcs), creating the well known condition of **Hot Plasma**. The average *electron temperature*, $\boldsymbol{e_T}$ ($\gg 10^{3+}$ K) in **Hot Plasma** almost equals other *ion temperatures*, $\boldsymbol{i_T}$ (and also equals constituent *gas temperature*, gas$_T$ and boundary or *contact surface temperature*, cs$_T$; the subscript $_T$ refers to the respective ***kinetic temperature***, *e.g.* 1 eV value of $\boldsymbol{e_T}$ = 11604.5 K (from the relation 1.602×10^{-19} J / 1.381×10^{-23} J/K, taking into account the Boltzman constant, $\boldsymbol{k_B} = 1.381 \times 10^{-23}$ J/K). Thus, Hot Plasma is frequently referred to as "**Equilibrium Plasma**" due to the thermal equilibrium amongst various constituents. However, unlike Physicists and Engineers, for researchers aiming for chemical and biological applications, **Hot Plasma** is not a preferred direct energy source, as material identities may get lost and particles like electrons, protons, cations *etc.* may prevail within. *Therefore, is it possible to tinker with and manipulate such an energetic environment, and tone down to conditions conducive for Chemistry and Biology?*

5. Storyline of Cold Plasma

In the context of high voltage driven electric discharge discussed in **Fig. 2a**, it was beneficially observed that when one or two thin layer(s) of any ***dielectric material*** is/are interposed between the two metal electrodes, the resulting current flow, and consequently the electric discharge potency are significantly reduced to mild levels, and the resulting effect emerges quite conducive for carrying out controlled chemical reactions. Standard dielectric materials include glass, quartz, mica, alumina *etc.* The applied high voltage now charges the exposed surface area of dielectric attached on metal electrode to an *almost equal* magnitude. It may be noted that within the dielectric material its constituting molecules only get electrically polarized, and free passage for electric current through its bulk material gets barred. As a result, the overall circuit current flow gets restricted to the μA to mA range, and only very mild and controlled electric discharge occurs. As shown in **Fig. 2b**, the plasma thus created remained "**Cold**", and its characteristics reveal very low extent of contents' ionization ($\leq 2\%$). The resulting **Cold Plasma** (**CP**) harbors various types of oxidizing and reducing atomic and molecular species, due to occurrence of large number of reactions within (described below in detail). It may be vital to note that various **CP** constituents do not attain thermal equilibrium, and only the



electron temperature, e_T attains high levels (> 10^{3+} K). On the contrary for bulk constituents, *i.e.* the $i_T \approx gas_T \approx cs_T$ (~ 10^2 K) remain << e_T. Thus, **CP** is also known as ***Non-equilibrium Plasma***, ***Atmospheric Pressure plasma, Dielectric Barrier Discharge Plasma*** etc. (*Although* ***Cold Plasma*** *generation is also possible employing very different technology of radio frequency and microwaves, such set ups need pertinent generation facilities, frequently limiting their common or ready accessibility and applicability for interdisciplinary and in specific basic research use. Therefore, these plasma generation methodologies are not discussed here*)

Table 2: Typical **CP** constituents produced in various gases near atmospheric pressure

Gas →	**CP constituents**
He	$h\nu$, e^-, He^*, He_2^*, He^{**}, $(He)_n^{\bullet+/*}$
Ar	$h\nu$, e^-, Ar^*, Ar_2^*, Ar_3^*, $(Ar)_n^{\bullet+/*}$
N_2	$h\nu$, e^-, $N^\bullet$, $N_2^{*/**}$, $N_2^{\bullet+}$, $N_2^{\bullet+*/**}$, $N_3^\bullet$
O_2	$h\nu$, e^-, O, $O^{\bullet-}$, $O_2^{\bullet-}$, O_2, O_3
Dry air **99%** $N_2 + O_2$	**Primary** = $h\nu$, e^-, O, $N^\bullet$, $N_2^{*/**}/O_2^{*/**}$, $N_2^{\bullet+}/O_2^{\bullet+}$, $O_2^{\bullet+*/**}/N_2^{\bullet+*/**}$ **Secondary** = $O^{\bullet-}$, $O_2^{\bullet-}$, N_xO_y, O_3
Humid Air **99%** $N_2 + O_2 + H_2O$	**Secondary** = H_2O_2, $HO_2^\bullet$, $O_2^{\bullet-}$, HN_xO_y ***etc.*** in addition to some of the above
CO_2 in moist air, **99%** $N_2 + O_2 + CO_2 + H_2O$	**Secondary** = C_xO_y, HCHO, C_2N_2 ***etc.*** in addition to some of the above
Few % H_2O_v in > 90% He or Ar	**Secondary** = $H^\bullet$, H_2, $H_2^{\bullet+}$, $H_2O^{\bullet+}$, $^\bullet OH$, O, O_2, O_3, $O^{\bullet-}$, $O_2^{\bullet-}$ in addition to primary He or Ar related some species as above

Table 2 lists typical **CP** major constituents in various gases. Notice subtle difference related to the nature of species generated in the specific gas employed, mainly due to inherent differences in physical characters discussed previously. The characteristic wavelengths of the light thus emitted also differ amongst different gases used due to the specific and dissimilar de-excitation pathways for various atoms, ions, and neutral entities respectively created. The emitted light wavelengths measured by Optical Emission Spectroscopy (OES) conveniently reveal the emitters' characteristics even in any mixed soup, and help identify the related species present within. Thus, it is quite obvious that utilization of different gases and even mixtures of varying fractions can give rise to numerous possibilities in respect of creation of reaction conditions, either to mimic ones that prevail elsewhere, or explore novel ones. Since He is an expensive gas, relatively cheaper and freely available Ar is frequently preferred in most studies.

Some randomly selected **CP** reactions and respective *timescales of occurrence* are shown in **Fig. 3**. It may be noted here that various time events substantially match the time events observed in the case of pulsed nuclear radiation and LASER light use, and likewise very potent and reactive soup of ***Free Radical*** and non radical species get created. It may be noted that in open atmosphere various primary **CP** constituents from another gas may generate secondary oxygen and nitrogen (**ROS** and **RNS**) species in significant amounts. Therefore, in most cases the subsequent practical **CP** Chemistry falls within the domain of ***Free Radical*** induced and

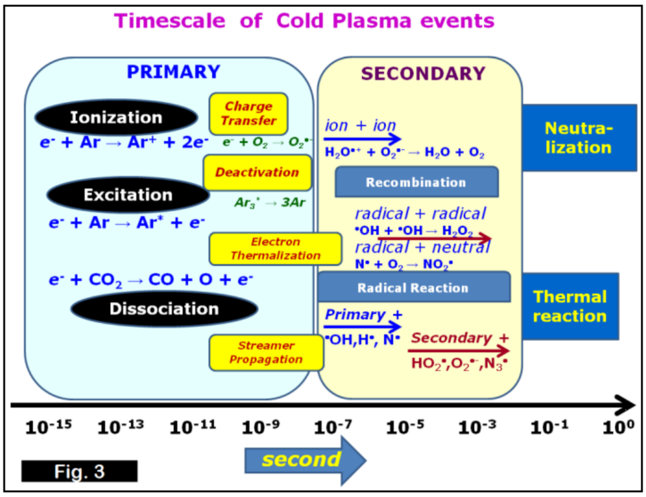


Fig. 3

ROS/RNS mediated changes, and the "***Trick of the Trade***" boils down to appropriate exploitation of the reaction parameters in any intended direction. However, before specific examples are presented, it is necessary to have a detailed look into the experimental **CP** generation tactics, specific design details, and typical associated hardware necessary for successful endeavors. *It may be worthwhile to record here that use of high voltage mandates appropriate insulation of all exposed and conducting points and surfaces, and use of suitable protection gears. Excellent earth line connection is part of the system design that must never be ignored.*

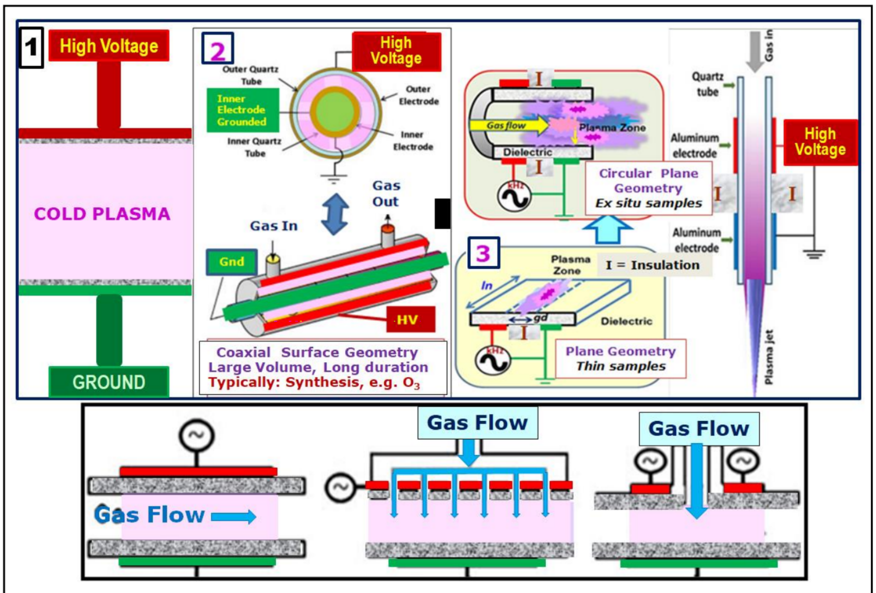


Fig. 4 Experimental Cold Plasma Generation Protocols

In **Fig. 4**, some selected CP reactor designs are presented. **No. 1** is the most common parallel dielectric plate geometry, already discussed in **Fig. 2b**. Note that the dielectric plates are thin, 1 mm or thicker. The dielectric plate plasma active surface area equals its shared opposite surface area with the metal electrode, attached contiguously without any gap on the back side. The linear gas-gap between the plate surfaces may be less than 1 mm to few cm, and necessitate use of proportional high voltage for medium breakdown. Any kind of sample, such as a flowing gas, or liquid in a container, or solid sample may be arranged or positioned inside this gap for direct exposure from **CP** contents. Design **No. 2** relates to a coaxial or cylindrical surface geometry of the dielectric plates in use, wherein the reactant(s) in a flowing gas passes between the two dielectric surfaces (inner surface of the outside metal coated dielectric and outer surface of the inner metal coated dielectric). While liquid samples would need special protocols to handle, solid samples are conveniently accommodated within the gap. Typical use of this generator geometry is found in ozone production (for almost last one and half century, presented later). Design **No. 3** highlights utilization of a single dielectric plate. In this plane geometry two electrically separated and parallel strips of metal are coated or fixed on one side (bottom as shown) of the dielectric plate, and the gap between the strips is adequately insulated (**I**). One of these strips is connected to the high voltage supply, and the other is grounded as shown. Plasma generation on the intervening area on the top of the dielectric surface allows sample treatment. Furthermore, if the flat dielectric plate is imagined to be rolled into a tubular shape, then the **CP** gets created and contained inside the tube volume as shown. For treatment, samples may be placed within the active plasma zone. However, if need arises then the active plasma may be carried out of the tube and into the open with subtle design modifications, and by maintaining adequate gas velocity. Then sample exposure with the released **CP** jet (alternately called pen, brush, wand *etc.*) is possible at some distance from the active creation zone. This is currently a convenient and oft employed CP source design.

In **Fig. 4**, various gas flow arrangements are also shown, which are self explanatory. In some cases the complete **CP** generation system is housed in an enclosure for convenience or safety (especially if some obnoxious product needs to be isolated or handled separately, or for isolating the system from open atmosphere). Since high voltage is an integral part of the set up, appropriate supplies include DC, AC 50/60 Hz, Pulsed DC, High frequency AC *etc.* types as per need or application. Each type offers different **CP** characteristics suitable for design of specific set ups. While a number of these high voltage supplies are freely available commercially as compact table-top units, frequently these are designed and fabricated in-house if such technical expertise is available. During **CP** experiments in our laboratory, at times we found *em*-interference from such devices onto other electronic measuring instruments or computer placed nearby. To overcome this serious quandary, we designed and developed a portable, table-top **CP Flexible Brush** system (with its dedicated inbuilt power supply) wherein the primary **CP** was locally generated in a quartz tube, then it was "*temporarily extinguished*", but with its "*information of creation*" was carried over a safe distance (6 - 10 feet) through a Teflon tube via a thin copper wire, and made to reignite as a secondary *ex situ* **CP** *plume* on any sample, thus enhancing the device flexibility and its consequent adaptability [2]. Similar complete basic ready-to-use systems may be fabricated or purchased for ₹50 – 100k. In this context, the reader may note that the familiar kitchen gas-lighter enfolds a piezo-electric transducer inside, which on application of pressure produces a spark that ignites the cooking gas over a stove. The spark appears as the transducer generates required level of high electric voltages (kV), sufficient to cause air+gas electrical breakdown. With appropriate modifications, the same transducer has shown its ability for very convenient CP generation in small local volume [3], especially in many handheld, immensely utilitarian devices now available commercially [4].

An example of Argon **CP** plume is presented in **Fig. 5**, to assist readers visualize its physical characteristics and get acquainted with the chemically transforming ensemble over its exposed length. As the narrow and laminar plasma zone exits into the open air from left to right (*e.g.* from a tube as discussed in **Fig. 4, part 3**), it carries primary mono-, di-, and trimeric Argon radical cationic, neutral, and excited species (with some e^-) out of the tip. Upon exit, the surrounding air continuously gets sucked and mixed within the **CP** plume due to high speed of Ar flow (cm to m s^{-1}, at L min^{-1} volumetric flow rate exiting narrow diameter orifice). The **CP** plume contents get transformed (in μs – ms time scale) as chemical and physical interactions generate secondary oxygen, nitrogen, water related atoms, non-radicals, and ***Free Radicals*** (neutral, cationic and anionic nature) partially in excited states. With forward flow, the plume further changes its chemical and physical characters; its shape gets into a turbulent mode and widens considerably. Diminishing plume visibility also suggests that the fraction of light emitting (*electronically excited molecular and atomic*) species survive only for few milliseconds outside the tube. In experiments with large gaps, light emission dies down within a certain distance from the exit tip, and a dark afterglow region results. The chemical nature of the constituents continues to change further as de-excited and uncharged reactive atomic and molecular species, and other ***Free radicals*** are created within. Finally some of these "*chemical contents*" reach any sample placed downstream. Thus, it is quite apparent that factors such as the primary gas flow rate, plasma tube orifice diameter, distance of sample from tube exit, surrounding air composition *etc.* allow the user to design and carry out experiments to employ diverse primary, secondary, or even tertiary chemical initiators of varying reactivity. It may also be noted that replacing the surrounding air (using a suitable enclosure) with chemically different environment help to change the nature and type of secondary species. For example, adding a monomer vapor in argon matrix allow controlled and exclusive polymer coating over a sample surface. The user may even plan sequential or mixed coatings for creating innovative alterations, making this simple arrangement throw up novel ideas and applications. Even by avoiding all extraneous chemicals, in a closed chamber, one may conveniently achieve progressive surface cleaning, otherwise controlled etching, chemical modification,

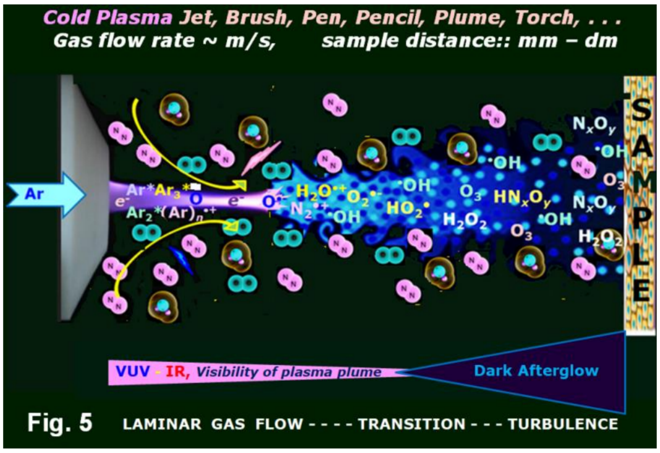


Fig. 5

append alternate *redox* effects, *etc*. Thus, the possibilities are truly endless. Lastly, presence of intense vac-UV and visible radiation of energy 1.5 - 10 eV in the **CP** also allows users to exploit this energy for myriad applications. Following randomly selected studies emphasize the versatility and utilitarian potential of ***Cold Plasma***.

6. CP in Biology and Health

A purist may suggest that molecular level changes in biological contexts are relatable to basic chemical and physical steps. Thus, one may wonder if **CP** *Physics & Chemistry* may have any relevance in biology domain. The classic book "**Plasma Medicine**" by *Fridman and Friedman* published in **2013** (Wiley) amply provides wide ranging answers, all in the affirmative. More recently, a review suggest that continuing basic research remains essential to improve, optimize, and enlarge the spectrum of safe medical applications of **CP**, and also monitor and control plasma treatment and its effects [5].

Humans face seven most common biological enemies in everyday life which are sources of variable trouble. These include **virus, bacteria, mold, pollen, various chemical pollutants, dust mites and pet dander**. We are already aware that **CP** is able to continuously provide **ROS, RNS** and other types of ***Free Radicals*** and intense UV-vis light at the flick of a switch. In this scenario, some recent examples below are intended to motivate readers to further explore, seek answers, and realize the true potential of **CP**, or even contribute actively to find new cures in this ever changing world.

Currently the most discussed virus, SARS-CoV-2 in its various avatars has put the world in a topsy-turvy mode. Thus, the prime search is for a suitable **CP** counter action to tackle this situation. The answer is YES, and seemingly quite potent! For example, the UCLA group has recently demonstrated that the virus is killed with **30 seconds** of CP assisted disinfection treatments on various types of surfaces, **including plastic, metal, cardboard, cotton from facemasks,** and even rough and wrinkled **leather surface** on basketball, football and baseball [6]. Similarly, the Max-Planck Soc. in Germany in collaboration with Terra-Plasma Medical has modified a previously developed hand-held device for chronic wound treatment into a direct application **CP** mechanical ventilator for ***SARS-CoV-2*** *patients* [7]. On another front, next generation of protective masks are under development at the University of Michigan, which aims to harness the power of CP into a small **headset that both blocks and neutralizes airborne pathogens** (including virus) thus allowing free movement of the wearer [8]. Researchers at the University of South Australia have demonstrated that an "*Enhanced* ***Cold Plasma*** *protocol*" that otherwise helps to eradicate antimicrobial-resistant bacterial infections in diabetic foot ulcers, *also* ***significantly reduces SARS-CoV-2 viral load*** [9]. Their strategy to utilize **CP** based "on-demand" amplified antimicrobial formulation comprises of a rich mixture of highly oxidizing molecules: peracetic acid, hydrogen peroxide, and other reactive species such as Tetraacetylethylenediamine and Pentaacetateglucose as antimicrobial precursor acetyl donors, which amplify the antimicrobial effects of **CP**. Thus, not only the targeted virus, but a host of other bio-active enemies can be quickly and effectively neutralized with innovative on site production and utilization of **CP**. With such success **CP** has opened up vast arena for research on its all round antimicrobial potency and creation of more future technologies for exploitation. *A large number of publications await like thinking readers perusal*!

The major health concern otherwise for many decades has been Cancer in its various forms. In this context, Nuclear Radiation sourced from either ^{60}Co radiotherapy machines, *e.g.* **"Bhabhatron"** developed in our country, or dedicated accelerator based devices for targeted treatments, and also from use of specific radioisotopes is well known. It is therefore pertinent to inquire if **CP** can mimic and contribute likewise in a complementary mode. On an affirmative note, more than a decade ago in 2011 pioneers in this ***field*** revealed the "***possibility of a paradigm shift in cancer therapy***" with **CP** [10]. Research carried out then found enormous potential to transform and enhance the available treatment technologies by deploying dedicated **CP** devices. Thereafter, in 2013 the Max-Planck Institute for Extraterrestrial Physics in Germany reported synergistic effect of **CP** with Chemotherapy on aggressive **brain tumor (glioblastoma) cells**, hailing the combination treatment as a new hope [11]. (*The same institute has also developed a number of table-top and hand-held* ***CP*** *devices to treat and cure Cuts,* *Wounds, Nail fungus, Ulcers, Bacterial and Fungal Infections*). In 2015 it was revealed that the assortment of **ROS** and **RNS** type ***Free radicals*** were readily participating as potent weapons against Cancer, thus emphasizing their role and importance of appropriate physical exploitation of chosen chemical processes at nano-micro levels on site [12]. In 2019 an exciting and long anticipated development from Purdue University thrilled the world, probably ending any skepticism and waiting [13]. It revealed a "**New CP apparatus to Kill Cancer Cells in the Colon**". The "*Caandy Helois* ***CP*** *Scalpel*™" to remove microscopic cancer tumors remaining from surgery has been approved by the US FDA for first-ever use in a clinical trial. Further research in this direction continues [14], and it is hoped that the above short account would motivate readers to further explore, and may be participate and exploit, to achieve more such excitements with **CP** applications.

Hand sanitization activity prior to 2020 was habitually limited to frontline medical workers and some others in specific jobs. It was mostly ignored by the common populace worldwide. However, in the last two years this activity holds new found importance and necessity. Previously, typical hand sanitizers contained chosen chemicals like ***Triclosan, Benzalkonium Chloride, Providone Iodine*** *etc*. It is not unknown though that these non-alcoholic concoctions are not entirely friendly in long time application and use, and are linked to problems like dermal irritation, allergy, and toxicity of various types. With the advent of and late preference for alcoholic sanitizers, especially in the last two years, other types of warnings have simultaneously appeared from FDA as well as researchers [15]. These include symptoms such as headache, nausea, and dizziness after frequent use, especially in closed environs. Suggestions include soap and water being superior to sanitizer; preferably **hand washing if available** needs to be followed, as was a common past practice. In this context however, it is quite revealing to note that **CP** based compact hand dryer cum sterilizer is commercially available since 2013, with the claim of 93 - 99% kill rate against a variety of pathogens tested, within a very short time [16]. Some of other commercially available products for similar usage are presented later. An immense potential to research and develop stand-alone or portable commercial devices for common or targeted use awaits the interested researchers in S&T.

Within the last few decades mobile phones and allied devices have become our inseparable friends. Following wide variety of user activities these are constantly exposed to biological entities released in user proximity, and also by close contact with other surfaces *etc*. as the user travels and rests. Even presence of fecal contaminants is not unknown. No wonder it is believed that "*The mobile phone not only remembers telephone numbers but also lack of personal hygiene and types and history of physical contacts*". More recently it is believed to be a forgotten or ignored *carrier-source* of ***SARS-CoV-2*** virus [17]. **CP** once more has proved to be quite usable in this regard, and back in 2015 an efficient "**mobile sanitizer**" was successfully researched, which revealed a 10 min treatment with very potent $^{\bullet}$OH radical laden **CP** environ was sufficient, without affecting normal phone operation in any manner [18]. Further efforts in future are expected to turn out pocket-friendly units, *ca.* a mobile case with added piezo-electric based **CP** generation as per specific user need.

Other related developments include creation of **CP** devices and machines for applications in Dentistry to carry out Restoration, Treat Oral Infections, Teeth Whitening *etc* [19]. The active Free Radicals and other species in such use are reported to be $\mathbf{^{\bullet}OH, {}^{1}O_2, O, O_2^{\bullet -}, NO^{\bullet}}$**.** These are currently awaiting FDA clearance. In the author's laboratory a simple Ar gas based handheld **CP** Electroporator was developed in 2015 for selective introduction of extraneous matter (DNA or drugs) into cell through partially opened cell walls, followed by its self repair. It was observed that the same arrangement could be profitably employed to kill *E coli* if so desired.

Thus, inactivation of microorganisms within a short time by non-reversible chemical destruction of cellular macromolecules including DNA has been the "*trade-trick"* in Sterilization, Treatment and Healing of infected and chronic wounds, ulcers and burns, Increased coagulation of blood, Biocompatibilization of surfaces, Aesthetic and ophthalmology applications, Selective inactivation of cancer cells and healthy cell regeneration. It is vital to note that unlike Nuclear Radiation treatment, the patient is never exposed to any radiation. Additionally, during **CP** treatment electricity does not flow through the skin or body. The operators of such devices or machines also do not face any risk for health.

Other hallmarks of simple and controlled **CP** usage are low cost of installation and process management, markedly reduced treatment times, and absence of chemicals. The world over R&D scenario currently reveals a healthy effort in all round development in this area.

7. CP in Chemistry research

Researchers who choose to remain engaged in pure Chemistry domain may be encouraged by the following randomly selected examples. Herein divergent possibilities for adoption of **CP** in their daily work are highlighted: (a) Production of 10 - 100 nm sized *iron nano particles* from ferrocene in alcohol solution at minimal cost and effort was achieved in a reductive environment offered by pure Ar **CP** jet, for products' potential applications in water purification, special magnetic micro- and nano-electronics usage [20]. (b) Graphene-supported *palladium nano-catalyst* (~ 50 nm) was conveniently made with **CP** for hydrodesulfurization of carbonyl sulfide (COS) in coal gas [21]. Almost 25 times enhanced catalytic activity was observed compared to Pd supported on activated carbon or Graphene-supported palladium composite prepared by conventional reduction process. (c) Creation of High-performance *Platinum nanoparticle* embedded TiO_2 photocatalyst for dye degradation [22]. The process involves simple steps like mixing H_2PtCl_6 solution with nano TiO_2 suspension for 24 h, followed by drying at 100 °C for 2h, and sample treatment in reducing **CP** of Ar and H_2 mixture. The TEM of 1.5 wt% Pt/TiO_2 suggests formation of ~ 100 nm sized catalyst, and almost 25 times enhancement in its activity. (d) First time report from author's lab of a simple and efficient *one-step conversion* of few thousand ppm aromatic *benzene* to exclusive *aliphatic compounds* such as *(i)* methane (~ 50% without catalyst, and exclusive generation with added H_2) or *(ii)* ethylene (with packed TiO_2 coated catalyst within the **CP** generator, **type-2** in **Figure 4**), both in moderately flowing Ar gas [23]. (e) On-line transformation of abundantly available *C1 to C4 light hydrocarbons* (mostly methane) into usable liquid fossil fuel (*petrol or gasoline*, C5 to C12, and *diesel*, C12 to C20) was achieved in a single step with **CP** in combination with **Solid Oxide Electrochemical Cell** [24]. The latter assisted in minimizing radical recombination reactions, eliminating formation of undesirable products. The other byproduct was water (no CO or CO_2 formed). A web search for similar exploitable and novel **CP** use and applications in the field of Chemical science and technology reveals a rapidly exploding number of studies, with significant simplification of reaction designs with reduced number of steps, dip in energy usage, avoidance of unnecessary chemicals and solvents in specific cases as is preferred or desirable for a "green technology".

8. CP for Improvements in Environments' Quality

Presentations so far amply suggest that the **CP** approach has the ability to contribute significantly in cleaning up of our environments, that have been irrationally and uncontrollably been allowed to degrade with time. In this section the current scenario is reviewed.

Fig. 6 summarizes the various reactive cleaning steps and process offered by **CP** presence. All unacceptable entities are taken care of by one or more of the four distinct steps, not necessarily in any particular order or sequence. Random studies, processes and products are summarized below for a closer look at the level of development over the years.

(a) **Indoor CP deployments:** In

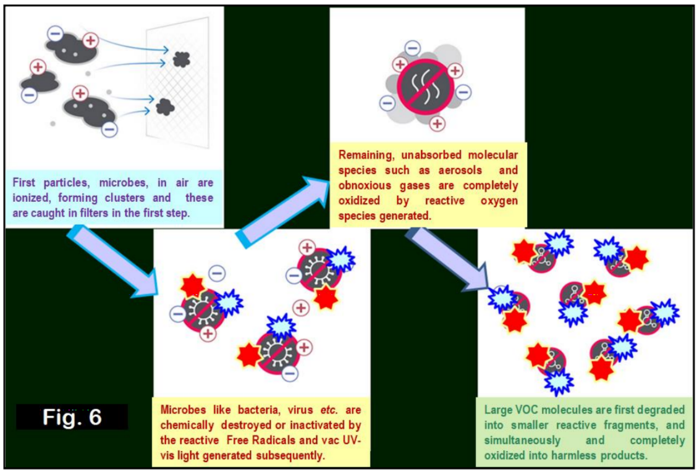


Fig. 6

First particles, microbes, in air are ionized, forming clusters and these are caught in filters in the first step.

Remaining, unabsorbed molecular species such as aerosols and obnoxious gases are completely oxidized by reactive oxygen species generated.

Microbes like bacteria, virus *etc.* are chemically destroyed or inactivated by the reactive Free Radicals and vac UV-vis light generated subsequently.

Large VOC molecules are first degraded into smaller reactive fragments, and simultaneously and completely oxidized into harmless products.

a recent study, inactivation of indoor airborne viruses is reported with use of a glass bead packed bed **CP** reactor (type-**1** in **Fig. 4**) [25]. A disposable filter near the exit removes all leftover particulate material. At a high air flow rate of 270 Lpm, the device works continuously to purify air by 3 orders of magnitude. Imagine such devices placed in your laboratory at strategic locations; mountain fresh air may be available to you with just the flick of a switch! Of course, more than one commercial product is already available in the international market, including India for suitable purification of indoor environments; these also include small portable ones for travelers for use in cars as well as hotel rooms, to larger model for fixed use in larger homes, rooms, schools, hospitals *etc* [26].

(b) Typical examples for **outdoor CP deployment** (very large capacity systems) presented below were researched and developed for specific purposes. (*i*) A 510 MW_{elec} coal-fired thermal power plant in USA is reported to utilize a three-stage process that includes a **CP** reactor, followed by a combination ammonia scrubber and absorber unit to neutralize and absorb the various acids formed; and finally, a wet electrostatic precipitator to remove the mists and aerosols [27]. Consequent reduction achieved for various species are as follows: SO_2 - 98 %, NO_x - 90 %, total Particulate - 99.9 %; Fine Particulate - 95 %; Mercury - 80 -90 %. (*ii*) A patented Gas Phase Cold Plasma (GPCP) reactor was designed and developed at the Pacific National Laboratory, USA as a cost-effective and environmentally friendly alternative to the prevailing thermal removal of lethal pollutants and volatile organic contaminants (VOCs) from gas streams [28]. Reported destruction efficiency therein of various hazardous air pollutants as well as *chemical and biological warfare agents* are as follows: Trichloroethylene > 99.9%; Perchloroethylene > 99.9%; Benzene 97.85%; Naphthalene > 99.9%; GD nerve agent > 99.8%; Hydrogen cyanide > 99.4%; Cyanogen > 99.8%; Methyl cyanide 98%; Phosgene > 99.84%; Methane > 97%; Freon14 ~ 70%; Phosphonofluoridic acid > 99.8%; and Dimethyl methyl phosphonate > 99%.

(c) **Potable or safe and clean water** is already a luxury at various locations and countries on our blue planet earth, mainly due to rampant exploitation of pristine natural resources and additional pollution from numerable sources. **CP** based solution in this direction is constantly getting modernized. In the distant past Chlorine was the gas of choice for water treatment. However, it was realized that Cl_2 gas is less powerful for micro-organisms, useless against chemical contaminants, and in presence of certain polluting chemicals may form carcinogenic trichloromethanes and chlorinated phenols. Thus, its deployment was eventually replaced by ozone, O_3 generated onsite from air or oxygen. The reactor design **Fig. 4**, no **2** has been the mainstay for **CP** based O_3 generation, which is safe, cheap, and one-step process controlled by the flick of a switch, and needs only minimal human intervention in the form of maintenance. No wonder, world over the current estimate of O_3 production for water purification may be higher than 10^{12} ton yr^{-1} (~ 32×10^3 ton s^{-1}). Ozone destroys bacteria, viruses, spores, mold and algae, also oxidizes most harmful chemicals such as dyes, insecticides *etc*. It is well known that excess O_3 quickly decomposes into O_2 in air and as H_2O_2 in water, and finally into H_2O and O_2. Various small and portable table-top O_3 generators are commercially available for vegetable, fruit cleaning at home and elsewhere. In such cases the dissolved O_3 itself, or its daughter product in water, mainly the ***Free Radical*** $^{\bullet}OH$ efficiently completes the intended clean-up job. (*All users of ozonizers need to note that ozone at ppm level is harmful, hence its release inside a closed room needs to be strictly avoided. Instead, such use may be practiced only outside in open air, away from human activity.)* More recently however, it has been reported that stubbornly resilient and toxic Poly- and perfluoroalkyl (PFAS) compounds, sometimes found in contaminated drinking water (*from over use of Teflon type coatings on kitchenware followed by its slow degradation*) are not decomposed and removed by O_3. For hassle free and successful removal of such chemicals, another innovative **CP** technology has been successfully researched [29]. It utilizes a ***semi-hot*** **Plasma**, first created is flowing air, that is directly injected into the contaminated water inside a reaction chamber. The suitably transformed **CP** with its "*afterglow reactive chemicals*" (Refer to **Fig. 5**) destroy all the *otherwise impossible to destroy species* present. Very recently, a commercial water purification product has appeared in the market that claims a paradigm shift in "*oxidative water treatment*" [30].

Thus, **Cold Plasma S&T** allows Environmental Remediation at low cost, with on-site usability, and is capable of running on solar energy, with minimal equipment complexity, is immensely exploitable and locally modifiable for chemical degradation and total removal of pollutants such as: *VOC*s (volatile organic compounds including carcinogens, hazardous gases, harmful coloring agents and chemicals, bacteria and allergens (in humid and aquatic waste), particulates (such as aerosols), obnoxious odor (emanating due to presence of aldehydes, ketones *etc.*, H_2S (sewage or industrial), NO_x and SO_x (fossil fuels' burning and other industrial sources), and dust mites frequently found indoors. **CP** thus appears to have endless abilities!

9. CP in Material Surface Changes and Improvements

Cold Plasma being a surface-active contrivance, its convenient exploitation on solid samples and materials as per specific requirements has been wide spread. In **Fig. 7** various modes of **CP** assisted surface treatment are shown, which are self descriptive. Some random studies covering a wide range of aims and objectives are discussed below. In the domain of "New or extra *functionalization* of **Textiles**' Surface(s)" diverse range of materials were treated to add explicit surface properties. For example wool, nylon, polyester fabric surfaces were altered to *hydrophobic* (water repelling) type from *hydrophilic* (water attracting) type with precursors such as styrene, butadiene, and dodecylacrylate put in **CP** created from different gases [31]. Similarly, properties like absolute hydrophobicity, color-latching, superior appearance and feel with crease control, fire resistance, controlled porosity, anti-microbial character *etc.* were incorporated by treating fabrics with **CP** of air, O_2, Ar, F_2, He, CO_2 or mixtures. Quite interestingly the **CP** technology could be employed to manufacture "dual functionality" fabric, *hydrophobic* on one side and *hydrophilic* on the reverse [32]. Creation of *self-cleaning* cloth may get a boost with the use of **CP** technology.

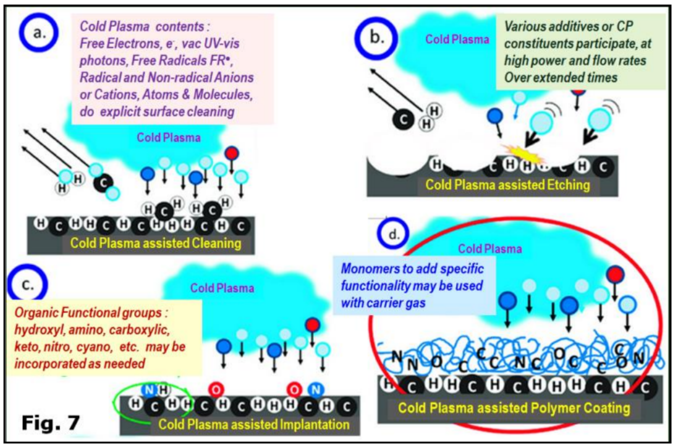


Fig. 7

Wood, with complex organic nature, is similarly amenable for surface chemical modifications. It is no wonder that the **CP** treatments have been extensively used to chemically modify wood and derived timber surface [33]. Superior finish and facile adhesion of surface polymer composite layer (wood-plastic combo) was thus achieved. This treatment method minimizes fungi growth and termite attacks, and also helps to incorporate surface water and scratch resistance characters. A clean wood sample, *e.g.* a finished bathroom door, moving on rollers, is sprayed with a chosen liquid monomer and immediately exposed to **CP** at 360° geometry. The results are instantaneous and long lasting. (*Similar results had also been achieved employing Nuclear Radiation; thus **CP** acts as a mimic, but comparatively at token strain on resources and pocket*).

Similarly, chemical creations of new and exotic surfaces were also achieved. In a study to design photocatalytic, self-cleaning, and anti-staining *Super-hydrophobic* surface, a required ***nano particle*** + ***nano composite*** combo surface coating could be effortlessly achieved using a dispersed aerosol of oleate-capped ZnO in n-C_8H_{18} in flowing He gas **CP** [34]. The coating combined the chemical characteristics of both the NPs and the organic component, which originated from the plasma polymerization of *n*-octane. In another study, **CP** assisted liquid deposition of -CF_2-CF_2- group on various substrates such as cotton, polyester, polypropylene, nylon *etc.* using liquid aerosols helped to create an oil, water and alcohol repellent (~100%) surface coat [35]. Similarly, powder deposition technology has been patented that employs **CP** in combination with dispersed nano powder to create a nano-porous nano-structured ceramic surface coating of 10 nm – 10 μm thickness [36]. In author's laboratory, a simplified surface cleaning process was developed for *Silicon Surface Barrier Detector* prior to its fabrication (*for use in **Nuclear***

***Radiation** detection*), with use of 90% Argon and 10% air based **CP** for 3 min [37]. The methodology helped to reduce detector operational leakage current substantially, as compared to the ones fabricated following conventional methods. Thus, the approach of surface cleaning and modification with **CP** for few min in various application areas is not only quite innovative, but also quick, cost-effective and eco-friendly. In summary, some of its salient features include (1) Mostly in a Single-step, solvent free approach; (2) Deposition of organic, inorganic, nano-composite, nano particle coating possible (e.g. polymer, silica-like coating, anti-scratch films, ceramics *etc.*); (3) Typically polymeric package materials may be suitably modified by increasing the surface energy to facilitate gluing and to improve printability, avoiding the need of using a primer, and promoting coloring (dyeing); (4) Improvement of mechanical properties, added *hydrophilicity* or *hydrophobicity*, reduced shrinkage, *etc*.; and (5) Surface or Interface cleaning. *In this context, it may therefore be a logical and appealing proposition to try and test if diamonds' surface get colored from application of controlled surface defects by **CP**, and thus mimic Nuclear Radiation**,** which is currently in use for creation of artificial (bulk volume) color in high-demand commercial diamonds.*

10. CP in Food Technology and Related Applications

It needs to be stated that in our country (and elsewhere) for many decades Nuclear Radiation technology is being widely and effectively employed in *Radiation Processing of Food Items* [38]. Consequently, the treated food items become pathogen and parasite free and gain shelf life, which frequently allow mere chilling in place of deep freezing during storage, and thus help save energy usage. For example, export of local fruits such as mangoes (*to USA*) has become possible. However, a high construction cost, other factors associated with such large treatment facilities, including adherence to stringent safety norms have restricted its universal small and medium-scale appeal.

In the context of **Food Items' Processing and Preservation**, it may be noted that the harmful pathogens, parasites, and pesticides reside mainly on or near the item surface. Hence, **CP** applications, with its rich contents of **ROS/RNS** discussed previously have a direct bearing on such elimination. Examples on use of **CP** treatments include ongoing research in various countries, which provide convincing reports of its local success. Research in the Glasgow University in Scotland in 2013 revealed that various items inside a sealed package or non-metallic container without any additives could be exposed with **CP** [39]. Ozone produced within the package (**CP** type **1** in **Fig. 4**) efficiently destroyed or inhibited bacteria or virus growth that occurred otherwise, thereby sterilizing the contents' surface area uniformly, and helped to extend product shelf-life. Few examples of such treatment include: reduction of pathogens in poultry, healthy bread and muffins. Similarly, in another study revealed that with few min of **CP** treatment, strawberries could be freed of microorganisms [40]. A study from Purdue University revealed similar **CP** treatment helped to extend shelf life of tomatoes by 4 weeks [41]. In 2016 the New South Wales Department of Primary Industries and the Australian Government initiated research studies with **CP** deployment to benefit the growers, processers, packers and consumers of fruits (apple, blueberry, citrus, strawberry), nuts (macadamia, almonds), vegetables (spinach, lettuce, fresh-cuts), aiming to mitigate the food safety risks [42]. In 2018, the Vietnam Institute of Technology has initiated research on the use of environment friendly **CP** technology for decontamination of agricultural products and fresh food and vegetables [43]. Thus, incorporation of **CP** treatments in Food Industry and Technology, as also projected by a currently available commercial system [44a], describes achievable benefits world over such as (a) Increased germination and yields; (b) reduced bacterial levels at harvest, especially with use of **CP** generated nitrate fertilizer; (c) Degradation of various types of pesticides before storage and consumption; (d) Pest and mytotoxin removal; (e) Pasturization and sterilization; and (f) most significantly, anticipated reduction of food wastage [44b].

A recent monograph written and edited by experts in the field, aims at academic researchers, food scientists, and government officials working on disinfection of food products [45]. It unequivocally states that **Cold Plasma**, one of the newest and novel technologies for food preservation, is promising and affordable, waterless, waste-free, and leaves no chemical residue on the products, works as a disinfectant of food products and packaging materials while maximizing microbial and spore inactivation. Finally, this section would remain incomplete without the following anecdote, from space. In 2001, experiments were funded by **The European Space Agency** to eliminate **"***The foul exhaust air from cooking* ***French Fries*** *within the* ***International Space Station*****". CP** did not fail to provide the most appropriate response to this demand. A suitable device was installed that works by using electrons and ***Free radicals*** within the **CP** disc to neutralize odors. The **CP** breaks up the offending molecules into harmless components that do not smell and do not need to be extracted afterwards. The cleaning was found to be almost thousand times faster than the traditional existing chemical method [46] that was replaced.

11. CP in Travel and Transportation

In the modern day fossil-fuel driven transportation, a *random* comparison of two passenger car models (of two-door range) made over a gap of almost 113 years, one finds the petrol mileage has barely improved, from reported ***mpg*** of about 24 or 10 km L^{-1} in 1908 to just 30 or 12 km L^{-1} today. Of course, the overall improved getup and looks have never failed to impress. Similar mileages are also ascribed to other makes and models. To realize the prevailing scientific premise, or may be lack of it leading to this conundrum, one needs to peek into various chemical steps that drive the internal combustion engines (ICE), and take a astute look into various transformations.

The fossil fuels employed in ICEs include either Petrol/Gasoline (C_5-C_8 hydrocarbons) or Diesel (C_{10}-C_{21}) with ~ 86% C & 14% H contents. Taking the typical example of petrol, for its complete (theoretical) combustion, *ca.* $\mathbf{2C_8H_{18} + 25\ O_2 \rightarrow 18H_2O + 16CO_2}$, each C_8H_{18} molecule needs 12.5 O_2 molecules to produce 9 H_2O and 8 CO_2 molecules. The existent picture regarding the combustion products are however quite different. The variety of products in tail pipe exhaust, in addition to N_2, CO_2 and H_2O, include: *CO, NO_x, NH_3, SO_x, RH, RR'H, C_6H_6, ROH, HCHO, RCHO, RCOOH, RCOR', RNH_2, $ArNH_x$, PAHs, VOCs, H_xNO_y, $PM_{2.5\ \&\ 10}$, Metals, etc* [47], which suggests the oxidation reaction above remains nearly a fantasy, and occurrence of large number of other unneeded chemical reactions, seriously affecting the anticipated mileage. (*In a related concern, it is no secret that fossil fuel usage contributes towards global warming, and in persistence of localized harsh environmental pollution world over* [48].) A *back of the envelop* random analysis for a car (*with 4 cylinders, capacity 1 L each, with 2 fillings for 1 crankshaft revolution, running at 2400 rpm, at 50 kmph speed and top mileage of 10 km L^{-1}*) reveals an duration of just over 10 ms available for the fuel oxidation, which never allows the reaction to get to completion. Moreover, since HC fuel oxidation needs only oxygen (just 21% of the air), the major 78% N_2 plays no role in it. No wonder, finally all are waking up to this grim realization, and seeking better alternatives. However, it is anticipated that fossil fuel usage may continue for a long and indefinite period, thus appropriate correction in the fuel usage steps have become mandatory, forcing intensive $\boldsymbol{D^4}$ *(design, development, demonstration, deployment)* in various directions. **CP** is found to play an active role in these applications too, and the following account throws some light on its utilitarian roles.

In the year 2007, research in the **Los Alamos National Laboratory, USA** found that **CP** assisted fuel combustion (CPAC) is indeed a fertile area for R&D. An atomized fuel (RH) stream prior to combustion when passed through a **CP** zone attached downstream to an existing fuel injector, randomly broke down the long chains of hydrocarbons into smaller fragments (*typically at energy input of < 10 eV, each molecules produced neutral Free radicals,* $R^{\bullet}/H^{\bullet}$, *while at > 10 eV various ionic Free radicals,* $R'^{\bullet+}/R''H^{\bullet+}$ *were formed*). Consequently, not only the combustion was observed to be stabilized, the fuel burning efficiency also enhanced to raise ***mpg*** and reduce pollution [49]. In a related research in 2018, the **Eindhoven University of Technology, Netherlands** in their research dealing with ***Cold Plasma Flame Diagnostic & Modeling*** revealed that the unique nature of Cold Plasma makes fossil fuel combustion leaner and cleaner, and simultaneously minimizes greenhouse gas emissions [50]. In their study a new CP based burner geometry allowed thorough experimental and theoretical investigations of the basic mechanisms, and revealed further optimization was necessary for the complex physicochemical parameters of **CP** flames in varied scales in space and time. Interestingly, at the same time in **Japan** an engine attachment, Plasma Direct™ unit was commercialized and is available for various models of motor cycles, passenger car and SUV engines running on petrol/gasoline [51]. Placed upstream, it creates variety of ***Free radicals*** in the air-fuel mixture inside the ICE, which modified the combustion to reach all corners of the ICE, producing improved ignition and higher ***mpg*** values, in addition to being environment friendly. In the last few years, **Transient Plasma Systems** in **USA** has developed a number of **CP** based products, including a *Nanosecond Pulsed Power Ignition System*, which allows a number of desired fuel ignition benefits [52]. In summary, **CP** assisted Fuel Reformation and Ignition helps to break down the long chains of hydrocarbons in fuel into smaller fragments, thus reducing the fuel ignition/oxidation time, improving the engine performance by ~ 20%, in addition to the reduced presence of unburned and undesirable combustion products such as CO, NO and NO_2 while utilizing less power than conventional *Spark Plug*. Simultaneous progress in the field of electronics allowed matched generation of nanosecond pulse DC voltage with compact and portable hardware.

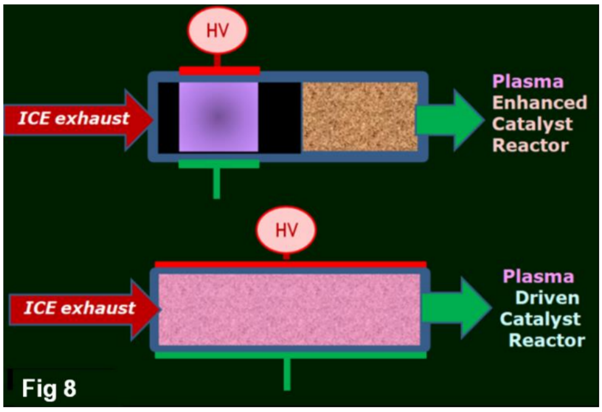


Fig 8

The adventure of **CP** use in transportation sector however is not over yet. Keeping in view the world-over demands for a cleaner environment, purification of ICE exhausts with **CP** are also being researched, with appreciable success, and more are on the way. Typically, as shown in the **Fig. 8**, the exhaust gas mixture is treated in a catalytic reactor (CR) chamber placed downstream to the ICE for treatment. Such deployment of **CP** in either of the two arrangements is possible: (i) Plasma Enhanced CR, wherein **CP** generation is sustained in the exhaust gas mixture to chemically activate it prior to the CR, or (ii) Plasma Driven CR, wherein **CP is** generated within the CR volume. For almost two decades, various studies had revealed the benefits of such **CP** use in variety of combinations, configurations, and constant and suitable modifications are in progress [53]. The key benefits achieved so far with CP based ICE exhaust gas treatment include (*i*) Oxidation of leftover or unburnt fuel and consequent reduction of its atmospheric release; (*ii*) Efficient and improved NO_x / NH_3 transformations, mainly to N_2; (*iii*) Applicability to the full range of Diesel and Petrol engines; (*iv*) Efficiency not being affected by sulfur content in fuel; (*v*) Various gaseous species released are N_2 H_2O, O_2, CO_2 even at low temperature operation (cold start), with Plasma system power consumption ~1 kW *vis-à-vis* typical engine power of 60 kW (< 2%). Thus, from fuel input to tail pipe exhaust, **CP** is able to play varied roles, and contribute in multiplicity of improvements in vehicle performance and the surrounding environment.

12. CP Elsewhere and Conclusions

The above presentation reveals various features of ***Free Radical*** mediated science that occur within, and highlight the related ease of system design, handling, use, and applications in a myriad of human activities, directly and indirectly. The story of its *Friendly* nature however would remain incomplete if some other related applications are not highlighted here. These include (a) Sterilization of medical devices on site, which otherwise need to be autoclaved or N_2O treated. The medical devices are sealed into a bag or tray, and placed inside the **CP** device [54]. The device generates O_3 inside the bag to sterilize the device. The sealed packet may be stored prior to use later. Excess ozone quickly decays back to oxygen, preventing any exposure of the user. (b) Printing of μm sized structures using nano inks by combining high-resolution plasma printing with rotogravure printing [55]. (c) Mercury free Fluorescent Light, produced efficiently employing the reaction $Xe \xrightarrow{CP} Xe^{*/\bullet+} — Xe \rightarrow Xe_2^{*} + Xe_2^{\bullet+}$, wherein xenon (in neon) discharge emission at $\lambda = 147$ & 172nm gets converted to white light with phosphor coating [56]. (d) Similarly, Plasma TV utilizes Xe (in Neon) **CP**, and the three primary colors Red/Blue/Green in pixels are generated with different phosphors [57]. (e) Plasma Clean Room Air

Conditioner, working on the principle of air sterilization and cleaning discussed in the previous section **C** [58]. (f) A new Barrier Ionic Discharge (BID) detector in Gas Chromatograph employs a **CP** in He gas for highly sensitive and hassle free universal detection and analysis of trace organic and inorganic compounds [59]. (g) For effective and quick removal of unpleasant odors from textiles, a portable and small handheld device offers style and comfort at home and during travel, as it instantly refreshes the cloth without washing or deodorants [60]. In essence, the **CP** science and technology has conclusively proved that it quite powerful, versatile, and is able to participate as a ***standalone multidisciplinary approach*** with multitude of roles and applications**.** *Finally, this presentation would be missing the element of fun and wonder without a mention of the* ***multihued, transcendental, ethereal*** *phenomena of* ***Aurora*** *observed in our sky near the poles (Aurora Borealis near North Pole, and Aurora Australis near South Pole). The vivid colors therein are generated by de-excitation of excited oxygen atom (emitting mainly green, some brownish red, yellow photons) and nitrogen atom (blue, red, violet photons) whenever a* ***Giga-scaled CP*** *forms due to ionization of earth's upper atmosphere by charged particles released periodically within the solar wind* [61].

Cold Plasma science and **Cold Plasma**-enabled technologies have significantly revolutionized the modern society lifestyle, and enabled our understanding way beyond the innate processes that dominate the solar activities and the interstellar medium. It is anticipated that with continued stewardship, apt awareness about its universal applicability would bring in further innovative R&D world over, and simultaneously translate into *pan-India* societal benefits and broaden its *friendliness*.

Declaration

This presentation is an updated and focused summarization of the more elaborate talk delivered in December 2021 at the 35th annual conference of the Orissa Chemical Society.

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