Chapter 24

Characterization of a Newly Developed 13.56 MHz Non-Thermal Plasma Torch and Its Applications

- N. Tiwari, V. C. Misra, S. N. Sahasrabudhe & S. Ghorui

24.1 Introduction

Plasma torch is a device that converts electrical energy into concentrated jet of plasma. Based on equilibrium of species, it is classified as thermal and non-thermal plasma torches. In thermal plasma, electron temperature and ion temperature are equal. Temperature and velocity of this type of plasma torch are very high. Applications of this type of torch is through heat and momentum transfer. Thermal plasma torches are further classified as non-transferred arc and transferred arc plasma torches. In transferred arc plasma torch, arc between cathode and anode is transferred to job. This type of torch has been used for single wire arc spray coating and arc welding. In non-transferred arc plasma torch, arc stays within the device. This type of plasma torch has been used in L&PTD for plasma spray coating, plasma gasification, plasma nano-synthesis and UF_6 to UF_4 conversion. In non-thermal plasma torch, electron temperature (2-4 eV) is much higher than ion temperature (30-100 ℃). Since gas temperature is low, it is called as cold plasma also. Due to various reactive species present at low gas temperature, this type of plasma is useful for various biomedical [243–245] and industrial applications [246, 247]. Applications of this type of plasma is mainly through chemical reaction of species generated in the plasma and the applicant. In this chapter, design, characterization and applications of a newly developed 13.56 MHz, non-thermal plasma torch are presented. Species generated in the plasma are identified. Gas temperature, electron temperature and number density are determined experimentally. Based on characteristics of the plasma jet, few applications like synthesis of H_2O_2, NO_2, NO_3 and applications like nitrogen functionalization and optics cleaning are explored.

24.2 Experimental Setup

Photograph and schematic of portable 13.56 MHz non-thermal atmospheric pressure plasma source developed in-house are shown in Fig. 24.1. System consists of APPJ torch, 13.56 MHz, 1 kW RF power supply, Automatic matching network and gas supply unit. APPJ torch is heart of the system. It consists a central electrode surrounded by a double wall water cooled outer electrode. A nozzle cap is fitted on the outer electrode. Design of the torch is made such that gap between central electrode and nozzle cap can be adjusted from 1 mm to 2 mm. Material of construction is Aluminium. The gap between central electrode and outer electrode is kept larger to avoid plasma discharge in the upper part. Discharge will take place in the annular area between central electrode and nozzle. Nozzle cap with diameter (3 mm, 4 mm, and 5 mm) were used to generate different volume of the plasma jet specific to particular applications. Argon is used as main plasma forming gas. A small amount of (0.2 lpm to 0.8 lpm) Nitrogen or Oxygen is mixed with Argon to get oxidative and nitrosative environment in the plasma through a mixer unit. For plasma generation, Argon

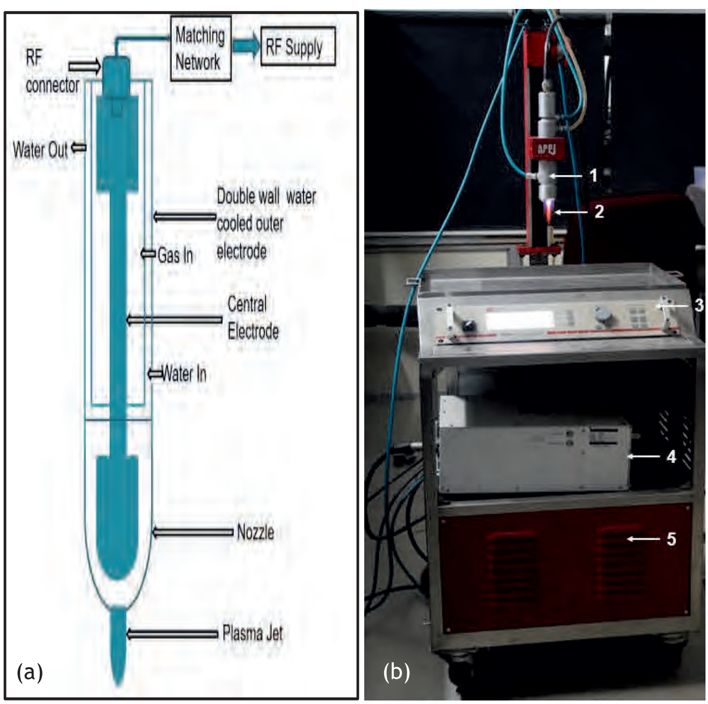

Figure 24.1: a) Schematic of the source, and b) Portable APPJ unit developed in BARC: 1 - Plasma device, 2 - Plasma jet, 3 - RF power supply, 4 - Automatic matching network, and 5 - Water tank.

of 30 lpm is passed through annular region between central electrode and outer electrode. 3 lpm of water is fed to the outer electrode. Initially RF of 100 watt is applied to central electrode and matching is done through matching unit and plasma is formed and a jet comes out. Experimental setup for plasma jet characterization through emission spectroscopy is shown in Fig. 24.2. Setup consists of spectrograph attached with CCD, convex lens of 10 cm focal length, XYZ movement setup, optical fiber, spectrograph software and computer. One to one image of the plasma jet is formed on the image plane of the fiber. This is achieved by keeping the distance 20 cm from the object to lens and lens to fiber.

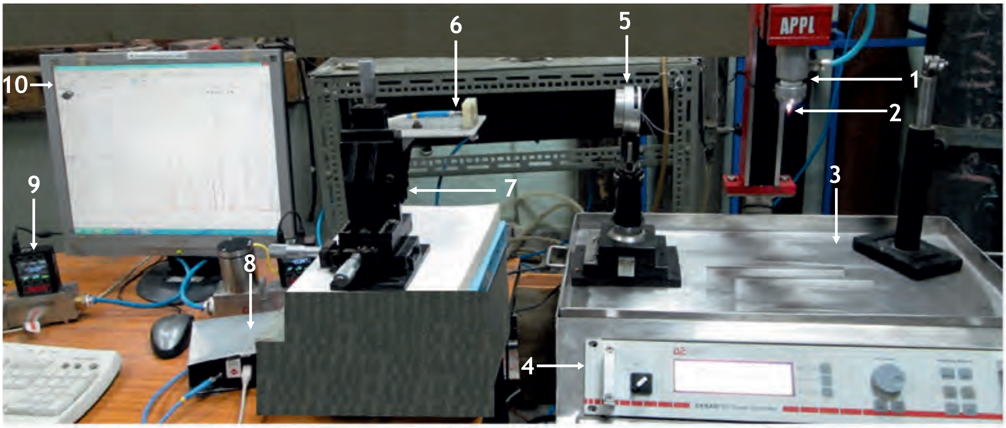

Figure 24.2: Experimental setup for optical emission spectroscopy: 1- Plasma Torch, 2 - Plasma Jet, 3 - Application tray, 4 - RF power supply, 5 - Optical lens, 6 - Optical fiber, 7 - X-Y mounting stage, 8 – Spectrograph, 9 - Mass Flow Controller, and 10 - Data acquisition.

24.3 Characterization of the Plasma

24.3.1 Emission spectra of Argon plasma

Emission spectra captured covering range from 200 nm to 800 nm is shown in the following Fig. 24.3. It is clear from the figure that intensity of the Argon lines in red region is very high (∼20000 times) that compared to blue region. So, it is very difficult to resolve full wavelength range in single scan. To resolve spectra for desired argon species, oxidative and

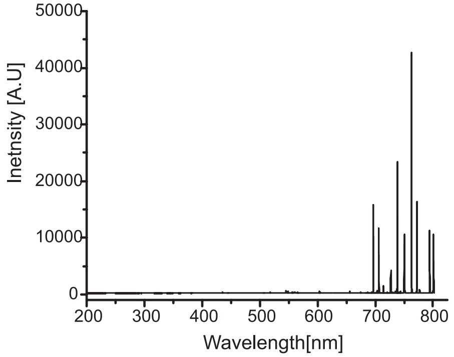

Figure 24.3: Emission spectrum of Argon plasma.

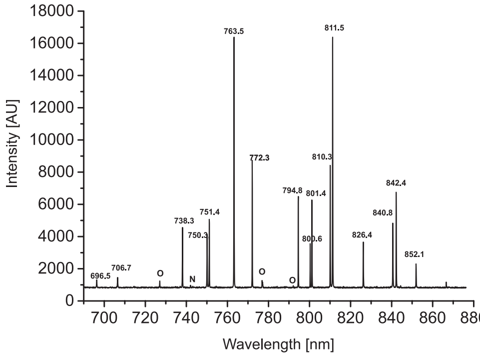

Figure 24.4: Emission spectra of Argon plasma in the range 690 nm to 880 nm.

nitrosative species, emission spectra for desired wavelength range were recorded separately. Emission spectra for Argon plasma in the red region of wavelength is shown in Fig. 24.4. Emission spectra of Argon plasma shows presence of atomic oxygen. It means that energetic electrons in the plasma is able to break oxygen molecule present in the air. This feature is very favourable for mild oxidative environment. Wavelength 696.5 nm, 706.7 nm, 738.3 nm, 750.3 nm, 751.4 nm, 763.5 nm, 772.3 nm, 794.8 nm, 800.6 nm, 801.4 nm, 810.3 nm, 811.5 nm, 826.4 nm, 840.8 nm, 842.4 nm, 852.1 nm shows argon atomic lines.

Emission spectra of Nitrogen band:

Molecules of N_2 also forms ions of N_2^* and N_2^- in the Ar-N_2 plasma. Band spectra for these molecular ions were recorded in the wavelength range 300-405 nm using high resolution spectrograph. N_2 Second positive system and N_2 First negative system were observed in the emission spectra of the plasma jet as shown in Fig. 24.5.

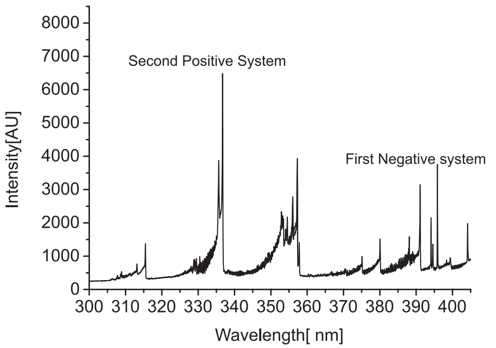

Figure 24.5: Second positive and First negative system of N_2.

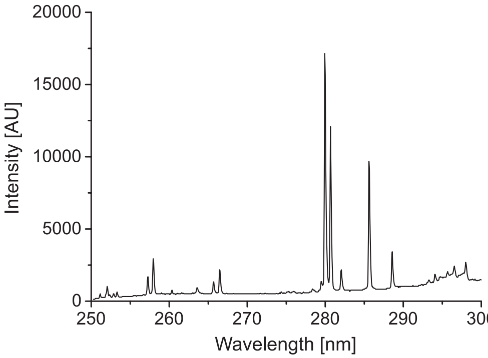

Figure 24.6: Emission spectra of Series of NO band.

Series of NO band:

NO radicals are very important for various medical applications like physiological and pathological biochemistry [248]. It is formed by recombination of atomic nitrogen and oxygen species when a small fraction of nitrogen is mixed with argon APPJ discharges in air. Emission of NO spectra is shown in Fig. 24.6.

OH Band:

OH radicals are short lived and highly reactive. It is very useful for various industrial applications as well as medical applications like synthesis of hydrogen peroxide, killing pathogens. OH is formed by breaking the H-OH bond in the water by energetic electrons present in the plasma. In this setup, OH is formed by interacting plasma jet with water. Water is diffused in the plasma and breaks in H_2O in OH and H. Emission spectra for OH band (A-X) is shown in following Fig. 24.7.

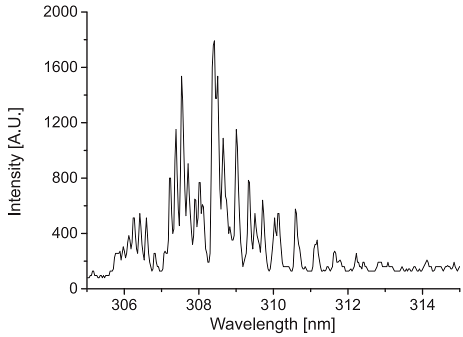

Figure 24.7: Emission spectra of OH band.

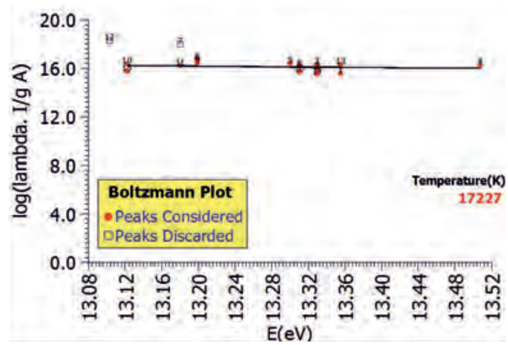

Figure 24.8: Boltzmann plot.

24.3.2 Plasma parameters

Electron temperature:

Electron energy plays important role for all biological as well industrial applications. Electron temperature is basically average kinetic energy of the electron. Boltzmann plot technique is used considering the plasma is in partial local thermal equilibrium [249]. Relation of intensity and electron temperature is given by [250]:

$$ln\left(\frac{I_{ul}\lambda_{ul}}{g_u A_{ul}}\right) = ln\left(\frac{Lhn_0}{4\pi Q}\right) - \frac{E_u}{kT} \tag{24.1}$$

where I_{ul} is the intensity of the line radiation, A_{ul} is the transition probability from E_u to E_l, n_0 is the population density in ground state, λ_{ul} is the wavelength of the radiation emitted, h is Planck's constant, L is the size of the plasma, Q is the partition function, and g is statistical weight. Slope of the line gives the electron temperature as shown in Fig. 24.8. Sixteen argon atomic lines 696.5 nm, 706.7 nm, 738.3 nm, 750.3 nm, 751.4 nm, 763.5 nm, 772.3 nm, 794.8 nm, 800.6 nm, 801.4 nm, 810.3 nm, 811.5 nm, 826.4 nm, 840.8 nm, 842.4 nm, 852.1 nm as shown in the emission spectra of Argon in Fig. 24.4 were used for Boltzmann plot. Typical electron temperature at the nozzle exit is of the order of 1-2 eV.

Plasma Gas temperature:

Plasma gas temperature was measured using thermometer as well as thermocouple. It was observed that plasma gas temperature is less than 100 ℃ at the nozzle exit. Axial plasma gas temperature varies from 65 ℃ (Nozzle exit) to 38 ℃ (15 mm from nozzle exit).

Plasma Density:

Plasma density was measured using stark broadening of Hα line. Relationship between full width at half maximum ($\Delta\lambda$) with density (N_e) is given by [251]:

$$\Delta\lambda_{H\alpha}(nm) = 1.78\left(\frac{N_e}{10^{23}}\right)^{0.67965} \tag{24.2}$$

Emission spectra for captured Hα line is shown in Fig. 24.9. Estimated electron density at the nozzle exit is of the order of 2-3 $\times$ $10^{21}/m^3$.

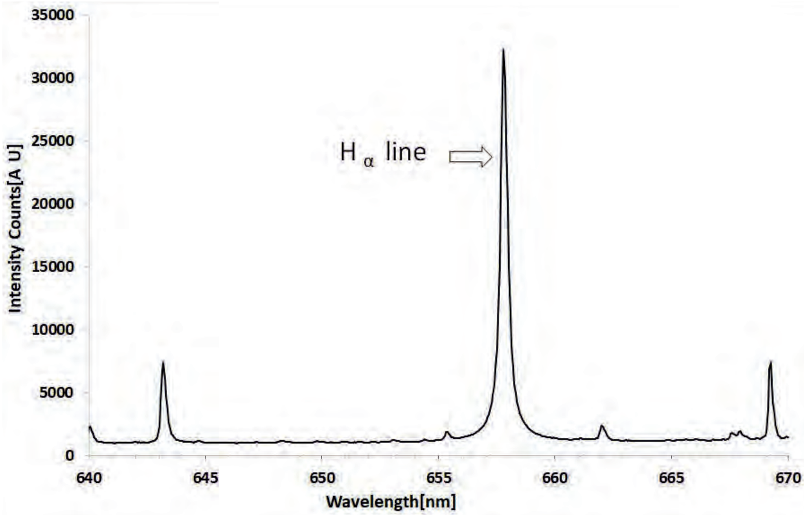

Figure 24.9: Emission spectra for H_α line.

24.4 Applications

After knowing the features of the plasma torch, it has been utilized for following applications:

24.4.1 H_2O_2 generation

Hydrogen peroxide is the simplest peroxide primarily used as an oxidizer, a bleaching reagent and antiseptic. It is highly effective disinfectant for virus. Commercial synthesis of hydrogen peroxide follows complex wet route which uses high energy, costly equipment's, large set up space and requires substantial time to start and end the process. Non-thermal atmospheric plasma torch is an excellent alternative for synthesis of H_2O_2, as it is fast and single step process. Hydrogen peroxide was synthesized by exposing distilled water to plasma at a distance 2 mm from the nozzle exit. 50 ml water poured in an open container was used for synthesis. Formation of H_2O_2 in plasma treated water as a function of time was measured. Standard H_2O_2 test stick (Quantofix peroxide 100) was used to measure the concentration.

Mechanism Involved:

There are two possible mechanisms involved in the synthesis of hydrogen peroxide using cold plasma.

A) **First mechanism:** Hydrogen peroxide is formed by interaction of highly reactive atomic oxygen species with water molecule.

B) **Second Mechanism:** H-OH bond is broken by high energy electrons and forming atomic hydrogen and OH radicals. Hydrogen atoms combines with other hydrogen atom and form molecular hydrogen gas. OH radicals combines with other OH radicals and H_2O_2 is formed.

It was observed that concentration increases slowly initially, and eventually increases exponentially with time and reaches 100 ppm in 20 minutes. Decay of concentration of H_2O_2 was also measured with time and it was found that synthesized H_2O_2 is stable for 48 hours.

24.4.2 Nitrogen and Oxygen functionalization

The functionalization is necessary to enhance the wettability of multiwalled carbon nanotubes (CNT) and reduce their sedimentation in aqueous dispersion to meet various process needs. Conventional multistep chemical routes used for the purpose are time consuming as well as generates large amount of acid and other effluents. Non-thermal atmospheric plasma torch is an excellent alternative for nitrogen functionalization [252, 253]. This torch has been used for functionalization of carbon nano-tubes (CNT). Argon (35 lpm) mixed with 0.3 lpm nitrogen was used for this purpose. Figure 24.10 shows the process of nitrogen functionalization on CNT in controlled environment and open environment. Same setup was used for oxygen functionalization of carbon nanotube by mixing oxygen in place of nitrogen.

Possible mechanism:

Ar/N_2 plasma effectively replace carbon atom to N atom in the CNT lattice within few minutes. Possible mechanism of MWCNT oxidation by Ar/O_2 MW-SWP are generation of:

(A) C-O bonds;

(B) C=O bonds;

(C) O-C-O bonds.

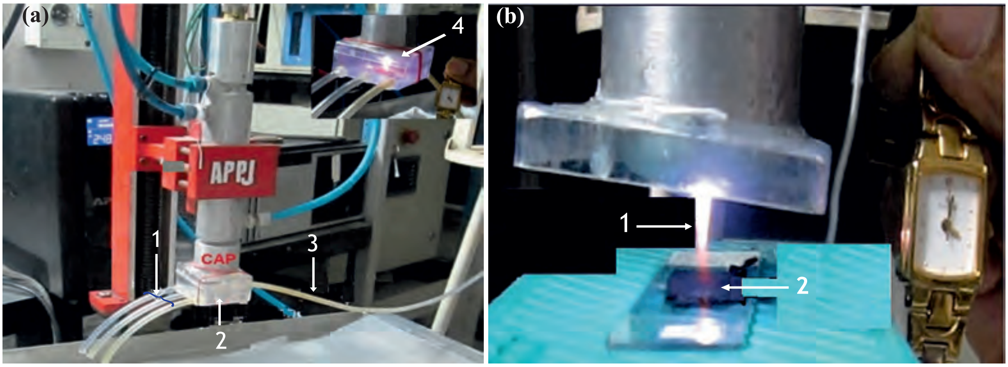

Figure 24.10: Nitrogen functionalization on CNT. (a) Controlled environment: 1- Gas exit lines, 2 - environment control, 3 - gas purging lines, and 4 - CNT treatment; (b) Air environment: 1- Plasma Jet and 2 - CNT sample.

It was observed that the surface was changed from hydrophobic to hydrophilic after plasma treatment but there is no change in morphology of CNT network after treatment.

24.4.3 Optics cleaning

Deposition of carbon layer on optical elements is a serious problem as it deteriorates the performance of various optics like gratings, mirrors, lens and prism and these optics needs to be refurbished. In order to remove the contamination layer from optics surface, various methods like UV based cleaning, laser cleaning and plasma cleaning are used. Non thermal atmospheric pressure plasma jet is an excellent tool for cleaning of optics due to fast carbon removing rate without destroying the optical surface.

Possible Mechanism:

Nascent oxygen formed in the plasma reacts with carbon atom and forms CO which further reacts with O forms CO_2 and cleaned optical surface is obtained. The device is tested for cleaning carbon contaminated optics. Flow rate of argon and oxygen was 40 lpm and a small fraction of oxygen (0.5 lpm) was mixed. Figure 24.11 shows the glass sample before and after cleaning.

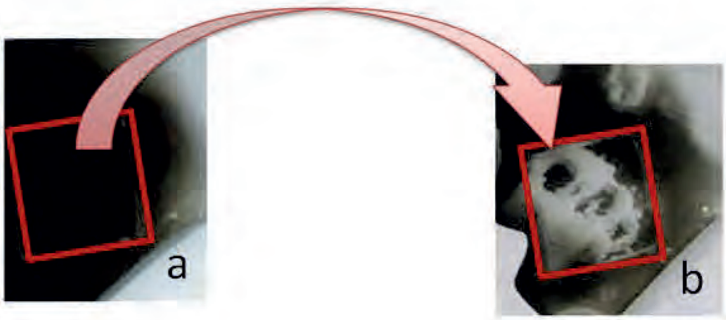

Figure 24.11: The glass samples: (a) Before cleaning, and (b) After cleaning.

24.4.4 Plasma nitriding

Nitriding is a method of surface hardening. In conventional gas nitriding, several cleaning processes like wet blasting, pickling and chemical reduction are required. Non thermal plasma provides a better alternative due to presence of high energy electron and radicals. The device is tested for plasma nitriding of titanium sample. Samples were polished using silicon carbide paste of coarse medium and fine size. Prepared sample is treated with Argon gas of flow rate 40 lpm mixed with small fraction of nitrogen (0.5 lpm). Figure 24.12 shows the process of nitriding.

Figure 24.12: Process of plasma nitriding on titanium sample.

Possible Mechanism:

Plasma nitriding is a heat treating process that diffuses nitrogen into surface of a metal to create a case hardened surface.

$$N_2 \longrightarrow N + N \tag{24.3}$$

$$Ti + N \longrightarrow TiN \tag{24.4}$$

Frequently Asked Questions

Q1. What is plasma torch? What are the gases used for plasma generation?

Q2. What are the difference between thermal and non-thermal plasma torches?

Q3. How temperature of the plasma is determined? What is typical electron and ion temperature in non- thermal plasma?

Q4. How density of the plasma is determined? What is typical value of electron number density in non- thermal plasma torch?

Q5. What are different applications of plasma torches? Write down mechanism of any two applications of non-thermal plasma torch.