PLASMA PROCESSING UPDATE

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Contents

Editor's note

Dr. Balasubramanian cites the study of iron-oxide nanoparticles synthesized by high temperature plasma processing. He throws light on the experiments performed at FCIPT and also discusses about the various analyses performed with different analytic techniques.

Ms. Purvi Kikani, discusses about the development if Gas diffusion barrier coating for packaging polymer by Plasma Enhanced Chemical Vapour Deposition method. She also describes about the initiatives taken at FCIPT to develop SiOx film /coating which has excellent properties and added advantages and will work as an oxygen diffusion barrier for packaging polymers. The experimental setup used for the study and results were also discussed.

Editor: Dr. S. Mukherjee
Co-Editor: P.Vadivel Murugan

Conference/Poster presentations from FCIPT

Name of the author	Topic	Date	Place	Conference
M. Ranjan	Role of contaminent in pattern formation	Nov 2014	CPP-Guwahati	Divertor simulator and plasma material interaction
M.Ranjan	Plasma for plasmonics	Dec 2014	Kottayam , Kerala	PSSI-2014
Vidhi G, G. Ravi	Investigation of Dynamics in a DC Plasma Torch (Poster)	Dec 2014	M.G. University , Kottayam, Kerala	PSSI-2014
Yugesh V, Gavisidayyah Hiremath, G. Ravi, K. Ramachandran	Investigation of the curent- voltage characteristics of a dc non- transfered arc plasma torch using heat balance measurements	Dec 2014	M.G. University , Kottayam, Kerala	PSSI-2014
Anand V, Vishal J, Purvi K	Phasor Voltage Network method for Determining Electrical Model of 13.56MHz RF Plasma and its Matching Network for Low Power Industrial Application	Dec 2014	M.G. University , Kottayam, Kerala	PSSI-2014
Akshay V, Chirayu P, Adam S, Ramkrishna R, Subroto M	Development of Atmospheric Pressure Plasma Torch Array (APPTA) for blood coagulation	Dec, 2014	M.G. University , Kottayam, Kerala	PSSI-2014

ABOUT FCIPT

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This newsletter is designed to update the readers with the latest developments in the important field of plasma processing and plasma based technology development and to look for new industrial opportunities.

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Study of iron-oxide nanoparticles synthesized by high temperature plasma processing

Dr. C. Balasubramanian

Introduction

Materials with dimensions scaled down to the nanometer scale show novel physical and chemical properties that, however, are strongly depended on preparation methods. This behavior is quite general for nano-structures and nanoparticles of metals, compounds and composites [1-3]. Recently, nanoparticles and nanosystems of ferric oxide have attracted large attention because of their magnetic and catalytic applications. The ferric oxide has two major crystalline phases: α-Fe_3O_4 (magnetite) and γ-Fe_2O_3 (maghemite). These spinel-type phases have Fe in different oxidation state in both tetrahedral and octahedral sites. [4]. Indeed, the oxidation affects both structure and properties of a material, especially its magnetic properties. Since oxidation depends strongly on the diffusion of oxygen atoms, the level of oxidation is highly affected by the size of nanoparticles. To a great extent, the nanoparticle size also governs the local order. Therefore, the oxidation level, and hence the properties can be tuned by a different synthesis methods. Various chemical and physical processes have been used to synthesize nanoparticles of α -Fe_3O_4 and γ -Fe_3O_4 [5-7], although, a real challenging issue is how to produce large amount of nanoparticles with both defined size and morphological distribution. Here, we report the use of a high temperature plasma route for the bulk synthesis of α -Fe_3O_4 nanoparticles.

The layout of the plasma route for the synthesis of nanomaterials is outlined in Figure 1. The process involves the evaporation by high temperature, the nucleation and, finally, the condensation of the material. In the high

temperature plasma synthesis, the temperatures in the plasma core could go to thousands of Kelvin depending on the arc current. The high current, apart from increasing the evaporation rate and the particle flux, also results in a higher enthalpy [8] and an increased rate of thermochemical reactions [9]. However, the latter increases the probability of a multicomponent product formation [9]. Apart from the high temperature, during the plasma synthesis route when the products move away from the plasma zone, they also experience a steep temperature gradient of ~10^4 K/cm. This large temperature variation induces a large thermal stress that greatly affects local ordering, stoichiometry and morphology of synthesized nanomaterials. Indeed, the large temperature variation does not provide sufficient time for the particles to grow in a highly symmetrical shape such as spheres or cubes. We have used different plasma current to synthesize iron-based nanoparticles and characterized them for their morphological properties. In addition X-ray absorption spectroscopy has been used to study the local structure and the local order of nanoparticles of different size.

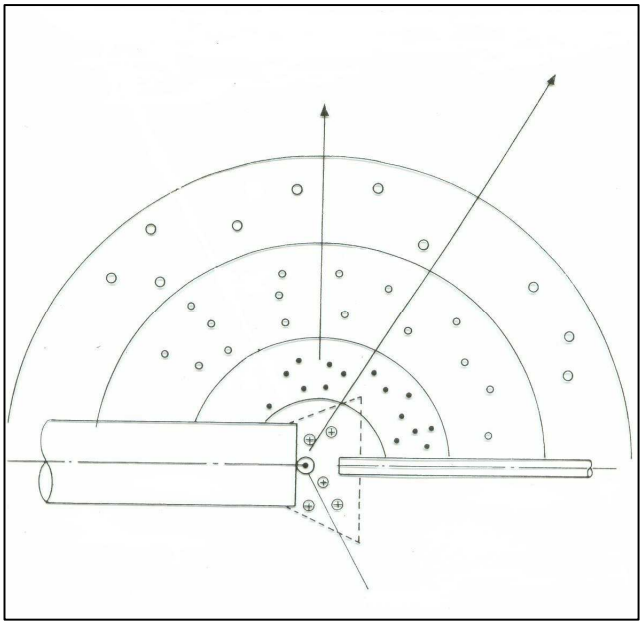

Figure 1: Layout of the arc plasma synthesis process of nanomaterials. The grown and agglomerated nanoparticles are deposited on the substrate holder or walls of the chamber in which electrodes are placed.

Experimental

A DC arc plasma has been used to generate oxide nanoparticles of iron. The electric arc was struck between the anode made with an iron metal block of diameter 40 mm and the cathode made with an iron rod of 10 mm diameter. A multi-port, double walled stainless steel chamber water-cooled housed the electrode assembly. The cathode was a movable electrode. A constant current DC power supply was connected to the electrodes and an arc struck between them by bringing the electrodes in contact and immediately withdrawing it. The arc generated provides a high enthalpy, which in turn vaporises the electrode material. The iron metal vapours react with the oxygen in the surrounding air to form oxide. As the reacted molecules move away from the plasma zone, nucleation and cluster growth occur and the synthesized nanoparticles adhere to the inner walls of the chamber. After particles fully settle on the chamber walls, it was collected for the analysis without any post synthesis treatments. Experiments were carried out for different arc currents. We compare here materials obtained with 32 A and 65 A. The crystallinity analysis was carried out using an X-ray diffractometer (Philips, PW-1710, Cu-K_α radiation). The morphology was studied using a 200 keV JEOL transmission electron microscope (JEM-1200 EX). The local atomic order and the electronic properties were characterized using the x-ray absorption spectroscopy (XAS) at the Fe K-edge. The XAS measurements were made at the XAFS beamline of the Elettra synchrotron radiation facility at Trieste, where the synchrotron radiation emitted by a bending magnet source (energy of 2.4 GeV and with a maximum current of 140 mA). About 8 mg of the powder samples of nanoparticles were mixed uniformly in a boron nitride matrix and pressed into pellets of diameter ~8 mm, for obtaining a unit Fe K-edge step jump. The measurements were made at 300 K in the transmission mode using three ionization chambers for simultaneous measurements on the sample and on a reference (a thin Fe foil in our case). As a routine experimental approach, several X-ray absorption

scans were collected to ensure the reproducibility of the spectra, in addition to ensure a high signal to noise ratio. The XAS data were processed using standard procedures [10] to obtain normalized x-ray absorption near edge structure (XANES) spectra and extended x-ray absorption fine structure (EXAFS) data.

Results and Discussion

(a) TEM analysis

Nanoparticles of both samples were dispersed on a 400 mesh copper grid and studied under a 200 keV transmission electron microscope (TEM). Figures 2 (a) and (b) present the transmission electron micrographs for the 32 A and 65 A samples, respectively showing the morphology and particle size distribution. Although, the particle shapes are slightly different, the observed variation in the particle size distribution for both samples is characteristic of high temperature plasma synthesis processes [5]. For samples prepared with the lower current, the average particle size is ~ 34± 12 nm being a mixture of particles with spherical or almost octagonal shapes. For samples prepared with the arc current of 65 A, the average size of the particles is 48± 21 nm while shapes are mainly distorted octagons. The size distribution (not presented here) has been calculated from different TEM micrographs in addition to those shown here.

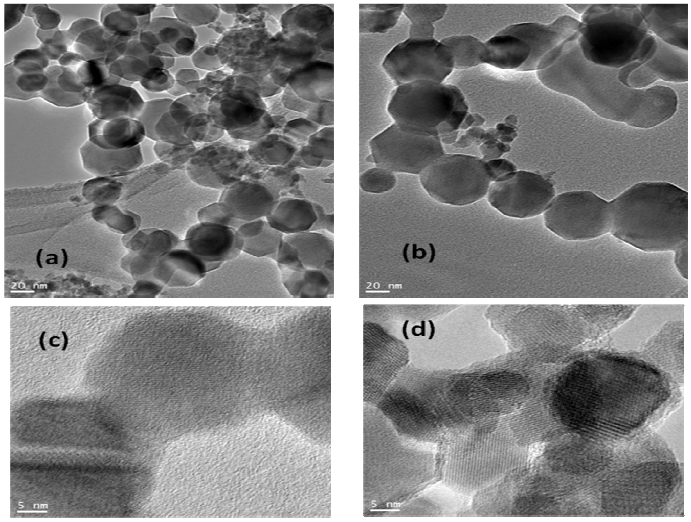

Figure 2: TEM micrographs of the nanoparticles synthesised with arc currents 32 A (panels a, c) and 65 A (panels b, d).

(b) XRD analysis

The crystallinity of the samples was analysed by powder X-ray diffraction. XRD spectra of 32 A samples as well as 65 A samples are shown in Fig. 3. There are no major differences between the two spectra except for the peak at 33.2° corresponding to the Fe_2O_3 (hematite), which appears better in the 65 A sample. The spectra have been compared with the standard XRD spectra for Fe_2O_3 (hematite) as given in the JCPDS data. This contribution points out the possibility of a possible multi-component product formation at higher energies. Thermodynamically, various thermo-chemical reactions are possible depending on the enthalpy available and, higher the enthalpy higher is also the probability to tune reactions and products formation. A multiphase product formation has been already reported working at high arc current with a higher enthalpy [9]. However, the XRD analysis clearly indicates high crystalline phases while the "*d*" values point out the presence of both Fe_3O_4 and γ-Fe_2O_3. The *d* values as calculated from standard XRD spectra for Fe_3O_4 is given in JCPDS data. The uncertainty is mainly due to the fact that the *d* values of both phases are very close to each other and requires the use of a powerful local structural probe such as the XAS for the identification of the chemical phase.

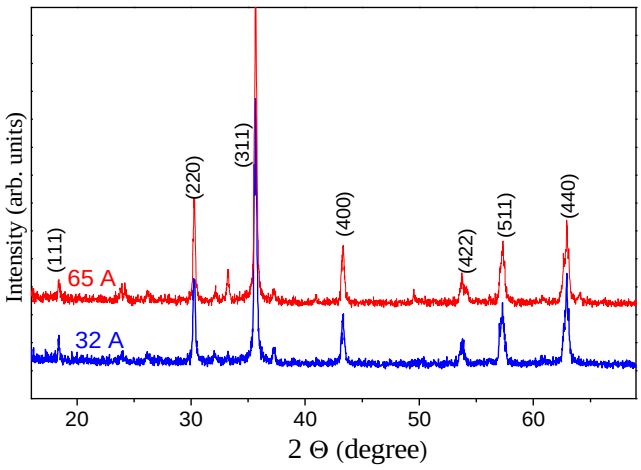

Figure 3: XRD spectra of iron oxide nanoparticles synthesised under arc currents of 32 A and 65 A.

(c) XAS analysis

X-ray absorption spectroscopy is a site-specific local probe [10] well suited for studying disordered systems and also nanoparticles [11, 12] While the x-ray absorption near edge structure (XANES) spectra provides information on the higher order atomic correlations, the extended x-ray absorption fine structure (EXAFS) probes first order atomic correlations. XANES spectra of both iron oxide samples are shown in Figure 4. A comparison between the two spectra reveals that spectral features are close to the spectra of Fe_3O_4 [13, 14]. Therefore, together the XANES and the XRD data suggest that the thermal plasma-arc synthesized oxide nanoparticles of iron are mainly crystalline Fe_3O_4 type. Moreover, a closer inspection of the XANES spectra points out clear differences in the spectral weights of the near-edge features. This can be better appreciated from the difference spectra as shown in the lower panel of Fig. 4.

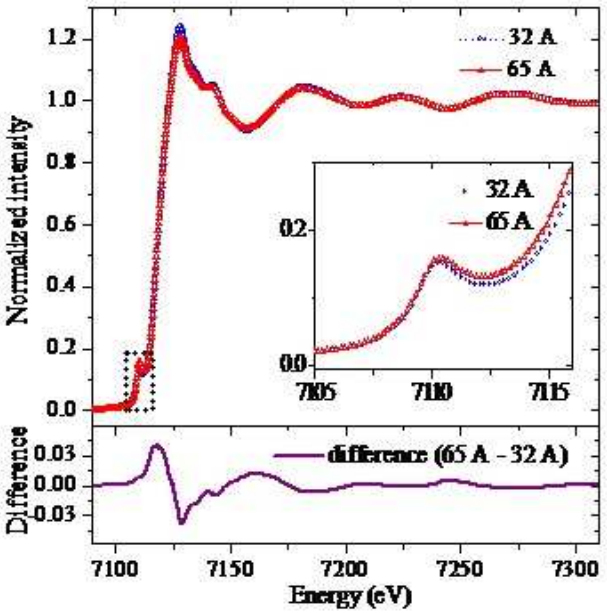

Figure 4: Main panel: Fe K-edge x-ray absorption near edge structure (XANES) spectra for the 32 A (circles) and 65 A (triangles) samples. Inset here shows a magnified pre-edge region marked with dotted square in the main panel. Lower panel provides the difference XANES spectra revealing clear changes in the pre-edge and near-edge regions.

In particular, the pre-edge intensity is higher for the 65 A case (see inset in Fig. 4). X-ray absorption is a local process in which a core electron is excited in an unoccupied electronic state via the dipole selection rule (□l = ±1). With increasing oxidation state the position of the pre-edge peak shifts to higher energy, reflecting the crystal field splitting of 3*d* orbital sub-bands. On the other hand, intensities of the Fe K-edge pre-peak features are sensitive to the local oxygen coordination geometry. In addition, the Fe K-edge XANES pre-edge peak intensity is a measure of the local disorder [15], in general increasing with increasing local disorder. In the present case, the Fe K-edge pre-edge intensity indicates a reduced local order in the 65 A sample.

Conclusion

In conclusion, we report the successful synthesis of magnetite (Fe_3O_4) nanoparticles by a high temperature plasma process. Data show that the plasma current affects the morphology, composition and local order of oxide nanoparticles of iron. The plasma produced particles are highly crystalline as evidenced by the x-ray diffraction results. Fe K-edge x-ray absorption spectra clearly identify the stochiometry of the produced particle to be close to Fe_3O_4. Transmission electron microscopy studies reveal that with increasing the plasma current, the morphology of the produced nanoparticles changes from a symmetric spherical shape to a lower symmetry hexagonal shape. The X-ray absorption results show a relatively large local disorder in sample with larger plasma current where the average particle size is larger. This could be a consequence of the large temperature gradient occurring at higher plasma currents.

Acknowledgements:

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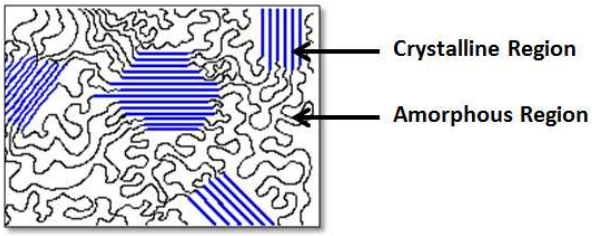
Development of Gas Diffusion Barrier Coating for Packaging Polymer by PECVD Method

Ms. Purvi Kikani

Gas diffusion barrier coating on polymeric substrate is an essential part of modern packaging for protection of food and pharmaceutical products against outside environment. For the past few decades the trend of replacing traditional materials such as glass, metals and paper by polymeric materials has been growing continually in the field of packaging. Cold Plasma Technology is an emerging, green process offering many potential applications for food and pharmaceutical packaging as well as for flexible electronics. [1-2]. Most high performance semiconducting organic compounds show degraded performance when they are exposed to environmental oxygen and moisture. Thus gas diffusion barrier coating is again unavoidable part of such devices [3-4]. Molecular structure of thin polymer film (polymer packaging web) is found in the form of chains oriented like networks. This structure possesses certain porosity as well as gaps through which gas molecules can easily pass through and reach the packed product. Plasma surface modification such as crosslinking, coating etc. on top of it reduces such pores and gaps by forming an even, smooth and almost impermeable layer and thus prevent gas molecules reaching the packed product. Plasma deposited inorganic coating on polymer substrates have been exploited in recent years as an alternative to metalized polymer for packing applications due to their transparency, recyclability, microwave use and excellent barrier properties [5, 6].

At present multilayer (i.e. 5-11layers) high barrier polymer films are used in market for packaging various food products. Multiple polymer materials (i.e. PE, PP, Nylon, EVOH

etc.) are used in multilayer film structures for producing package, which increases its cost multi-fold and also makes it difficult to recycle. The equipment cost for producing multilayer films is also of high value. Hence, the development of surface modification technologies to improve barrier properties of 1-3 layer PE films would be of great help to food processing industries in producing low cost environment friendly packages. In general packaging polymers are semi crystalline in nature as shown in figure below.



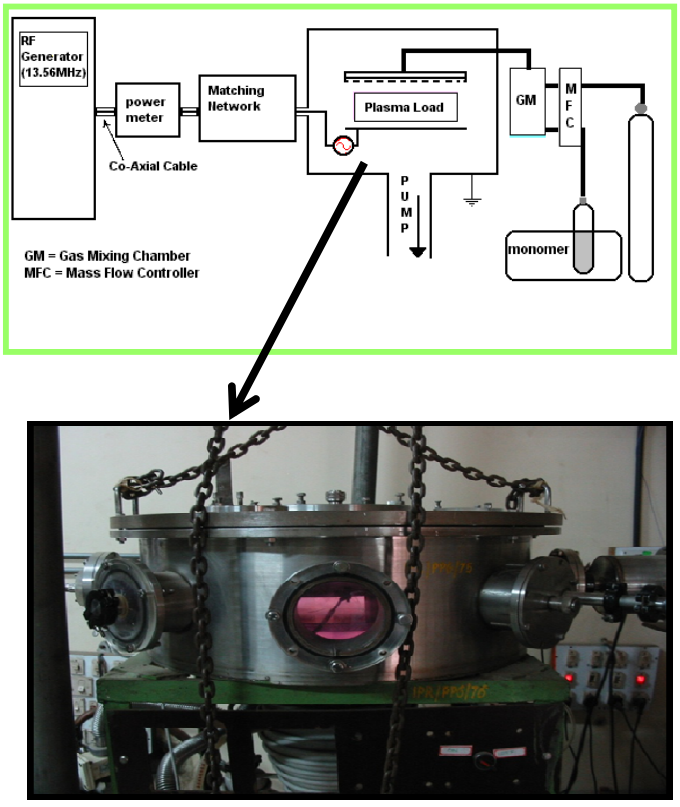
Such semi-crystalline polymers have both amorphous and crystalline regions as shown in fig. The presence of crystallites in the amorphous matrix leads to the different gas / vapour transport properties of the semi crystalline polymers compared to amorphous polymers [3-6]. Crystallites are considered to be impenetrable. Penetrant molecules generally enter through the free volume available in amorphous interlayer separating two crystallites due to segmental mobilities in amorphous region.

At FCIPT, we have attempted to develop SiO_x film/coating which works as an oxygen diffusion barrier for packaging polymers.

Silicon oxide possesses excellent physical and chemical properties, such as transparency from ultraviolet to infrared, good thermal stability and conductivity, chemical inertness, and wear and corrosion resistance. Moreover, SiOx is harmless to both human beings and the environment and is abundant in nature.

Experimental Setup & Plasma Production

For these PECVD experiments stainless steel process chamber was used with 60 cm diameter and 30 cm height. Oxygen and Hexa-methyl-di-siloxane (HMDSO) gas mixture was introduced via multipoint gas feeding shower head. Plasma was generated between two parallel plate electrodes using radio frequency (13.56 MHz) power source. Experiments were conducted with different oxygen gas concentration in the above said gas mixture in order to get the desired film chemistry. Experimental set-up is as shown in the figure below.

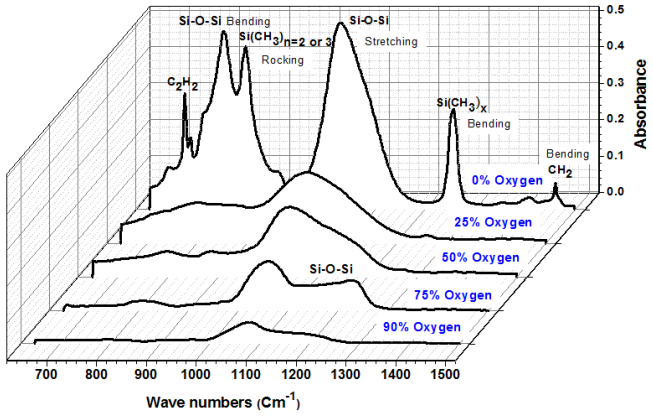


Results

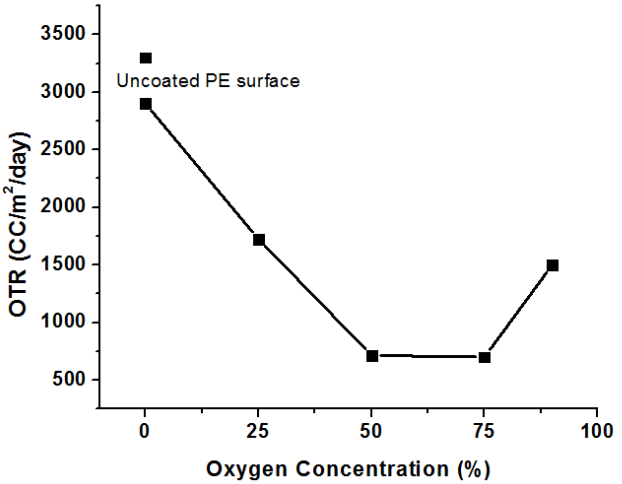
In these experiments at constant total pressure P_t = 0.06 mbar, oxygen partial pressure was varied in oxygen / HMDSO gas mixture for deposition of SiOx like films on PE and one side polished silicon wafer substrates.

SiOx film chemistry was recorded by ATR-FTIR spectroscopy for films deposited at different oxygen concentration in oxygen/HMDSO gas mixture. In the case of 0% oxygen concentration, spectra represents the surface chemistry of plasma polymerized (pp) HMDSO film which shows different modes such as rocking and bending of $Si-CH_3$ vibrations at840.52 and 1257.21 cm^{-1} respectively. Spectra also show Si-O-Si stretching and bending vibration at 1031.01 and 800cm^{-1} respectively. It is observed that as we go on increasing oxygen concentration in the gas mixture, existence of $Si-CH_3$ bonds reduces

gradually and film nature becomes more inorganic type. This is clearly evident in fig. below.



Oxygen Transmission Rate (OTR) was measured for virgin PE and for SiOx deposited PE film. OTR value obtained for virgin PE film is 3300 cc/m^2/day. OTR values found to decrease when oxygen concentration was increased. Minimum OTR value was obtained for 75 % oxygen concentration is 700 cc/m^2/day. OTR values found increased at 90% oxygen concentration. This is shown in fig. below.



This application is still under development and the target OTR value at present is 150 cc/m^2/day for edible oil pouches.

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OTHER NEWS

Plasma Pyrolysis system for disposing solvents and solid waste

FCIPT has delivered the plasma pyrolysis system to **CSIR-CSMCRI** for disposing solvents and solid waste generated at their lab. The system will be installed and commissioned shortly.

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