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NBP/NPD A new air stable Solid organic semiconductor UV Photocathode

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Abstract: A new air stable organic semiconductor Polymer NBP/NPD was investigated as solid UV photocathode for use in gaseous UV photon detedctors. QE was measured as a function of photon wavelength in spectral region 190-250nm and shows cut off near 240nm. Although, its quantum efficiency (QE) is very low as compared to CsI but being air stabile solid and preparation of photocathodes with large surface area it can be suitable potential photocathode in plasma diagnositic, barium flouride scintilation based calorimetry and very high photon flux experiments.

Keywords: (Organic semiconductor polymers, photon flux, UV gaseous Photon detectors, Solid Photocathodes, MWPC (Multiwire proportional chamber), GEM (Gas Electron Multiplier) and Thick GEM)

1. INTRODUCTION

Gas filled Multiwire proportional chambers (MWPcs) were made suitable for the detection of UV photons with introduction of UV sensitive Vapours simultaneously (Séguinot, 1988). (Bogomolov, *et al.*, 1978) The vapor phase photocathodes have a number of advantages: gas flow and temperature can be used to control light absorption length on the other hand continuous renewal of photosensitive material prevents it from ageing (Vasileiadis, *et al.*, 1996). A large number photosensitive Vapours such as TMA, TEA, EF, TMAE etc (Biteman 2001) (Peskov, 1981). were investigated for use as photocathode in gaseous UV photon detectors with simple parallel plate geometry. Among all Photosensitive vapors TMAE has highest QE for detection of fast component of barium fluoride which reaches up to 10% at λ=230 nm and in spectral 160-190 nm reaches to 30-40%. (Holroyd, *et al.*, 1987). Use of quartz as entrance window for radiation in detectors active volume makes it more robust. Since it is cheaper and safer to handle in comparison to previously used CaF_2 and BaF_2 windows that are costly as well as fragile. It is used in many high energy experiments largest ever built RICH detectors such as:(OMEGA RICH), (DELPHI RICH), (TPC RICH) and (SLD CRID) etc (Siebert 1994)". (Va'Vra *et al.*, 1999) However, TMAE has some disadvantages: at room temperature its vapor pressure is low, so a long gas gap is required for phot coverage which in turn results in bad time resolution, to overcome this detector has to be operated at high temperatures i.e., (40^0-50^0) which severely damages the rubber seals and pipes used in gas flow system of detector. On the other hand, it is highly chemically reactive and therefore, imposes restriction on choice of materials used in construction of detector. Ions are formed during the avalanche process, Detectors containing TMAE as photocathode, are subject to polymerization on the surface of anode wires and the end result is wire ageing (Va'Vra, 1987). In later years attempts were made to search compounds that show a comparable quantum efficiency (QE) and easy handling (Dangendorf, *et al.*, 1991) (Laghari 2014) (Halepoto, *et al.*, 2019). (Simons, *et al.*, 1985) ". The focus was on the solid phase photosensitive materials because a solid photocathode favours the fast timing good position resolution as all the photoelectrons are emitted from a smooth surface(Laghari 2014) (Halepoto, *et al.*, 2019). (Simons, *et al.*, 1985) CsI is the Centre of attention since then because its QE is highest of all the solid photocathodes investigated yet. However, its QE is lower than that of TMAE by more than a factor of 2 at wavelengths larger than 190 nm. It is used in a number experiments in combination to MWPC, such as: NA44 at CERN, STAR at HALA-A, HADES at GSI, COMPASS at CERN etc However, short exposure to humid air can degrade the CsI photocathode because of its hygroscopic nature (Heroux, *et al.*, 1966).". A detailed ageing studies of CsI photocathode revealed that even a few mC/cm^2 , of charge collection at photocathode surface resulted in severe decrease of QE[26]. The ageing of CsI was due to two reasons, firstly, high photon flux impinging on the photocathode surface caused damage to it. Secondly, during avalanche process ions were created due to ionization of fill gas in the active volume of detector that travelled back to the photocathode surface (ion back flow IBF). These ions got deposited at the photocathode

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surface and damaged it. In order to protect CsI photocathode surface from bombardment of these positive ions, Sauli invented gas electron multiplier (GEM) in 1996. First generation of GEM based gaseous photon detectors contained semitransparent solid photocathodes (Buzulutskov, *et al.,* 2000). As efficiency of reflective photocathodes is high as compared to semitransparent (Charpak, *et al.,* 1991) thus, a multi GEM structure with CsI thin layer on surface of upper GEM was successfully employed in PHENIX-HBD (Anderson 2011), GEM based gaseous UV photon detectors were fast enough devices with time response $> 2\,ns$. (Mörmann, *et al.,* 2003). This technique helped to suppressed the ion back flow and protected the CsI photocathode surface from bombardment of positive ions. Semitransparent (Bondar, *et al.,* 2003) and reflective UV photocathodes combined with triple GEM structures resulted in reduction of IBF from 2-10% respectively. At low value of electric field, IBF can be reduced to 1% without changing the gain[34]. Investigations have showed that this condition is not favorable for reflective UV photocathodes because at low values of electric field, photoelectron extraction efficiency of CsI surface is too low. The micro hole strip plate (MHSP) is the modified version of GEM structures, enhanced avalanche or suppressed IBF to $3x10^{-4}$ with multiple MHSPs in reverse biased mode in Ar/CH_4 at a gain of 10^5. Extremely low IBF (less than 10^{-3}) was obtained with a specially designed (MHSP), COBRA. A gain around 10^5, obtained with multi-GEM structures, in laboratory conditions can not be sustained in large tracking experiments below or around 10^4. Derived from the GEM design were thick-GEMs (THGEMs). As compared to the typical GEMs, the material budget for THGEMs is too large. The position resolution is also about 1mm.Moreover, effective electron transport and collection along with large gain were reported. GEM COBRA analog is the THICOBRA and blind -THGEM also called WELL. Typical multi-THGEM with CsI layer coating on upper surface of first THGEM were designed, constructed and run with Ar and Ne based gas mixtures. An effective gas gain of the order of 10^5-10^6 and a time resolution of 10ns [39]was obtained with similar triple THGEM in the laboratory. IBF study with typical triple THGEM revealed that it reduced to 30%. The discussion shows that development and use of GEM and GEM-based technologies for protection of CsI photocathode surface from the degradation resulted from IBF is departure from simple and cost-effective parallel plate geometry to a complex costly technology. It seems that use of these developments is departure from the main target i.e., cost-effectiveness, large surface area coverage, air stability with room condition operation of gaseous UV photon detectors. Thus, there is still strong need to search new air stable UV photosensitive materials that can be potential candidates for replacement of CsI in future. In this context systematic investigation of quantum efficiency of NPB/NPD, a new organic semiconductor UV sensitive material is presented in this paper.

2. MEASUREMENT PROCEDURE

The experimental arrangement used was same as used in. The photocathode samples were prepared by depositing a thin layer of NBP on a copper substrate made from a clean piece of PCB sheet. A piece of PCB sheet measuring 2.3 cm x 2.9 cm was cut and cleaned with abrasion. For further cleaning grease, it was boiled in a solution of DECON 90 for 10 minutes, rinsed with double distilled water again boiled in pure DD and finally rinsed with organic solvent acetone, dried under dust free conditions to be ready for layer deposition. Since NBP is a sublime grade organic semiconductor polymer so, the different samples of NBP photocathodes were prepared by sublimation of NBP using local made and calibrated joule heater, maintain different layer thickness of different samples, exposure time was varied. Four different samples for exposure time of 2,4,6 and 8 minutes were prepared as under. Each time a weighed amount of NBP was taken in a steel boat fitted in joule heater. A freshly prepared substrate was placed inverted above the steel boat in such a way that a strip measuring 2.3 cm x3 mm was left masked for the purpose of electrical contact. The volage of joule heater was set from calibration curves so that the temperature of steel boat reached to the sublimation point of NBP and maintained steady for required time with a digital temperature meter. Each time a fresh sample was prepared and loaded in quick change over test chamber, it required 3-5 minutes approximately. The chamber was then evacuated with a turbo molecular pump system to a vacuum of 2.4 x 10^{-4} Torr. and scanned with double beam UV-visible spectrophotometer (UV-1601) Shimadzu Japan in a wavelength range 190-240 nm- The photocurrent resulting from the test chamber was measured using a Keithley electrometer (6517A). The beam flux was monitored in situ using a standard 10 x 10 mm^2 reverse biased photodiode Hamamatsu (S1723-05). Another Keithley Electrometer was used for recording current from standard photodiode. A guard ring arrangement was used in test chamber assembly to reduce the leakage current. Measurements were made in vacuum at a bias voltage of 25 volts.

3. RESULTS AND DISCUSSION

General properties of NBP

N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine NPD/NPB is an organic semiconductor polymer with molecular formula $C_{22}\,H_{14}\,N_2\,O$. It is a sublime grade solid at room temperature with melting point 279-283 ^{0}C. It is air and thermally stable non-toxic molecule. It was purchased from Tokyo Chemical industry Co., LTD (TCI) and used as it is without fuether purification. The chemical structure of NPB/ NPD Is shown in **(Fig.1)**

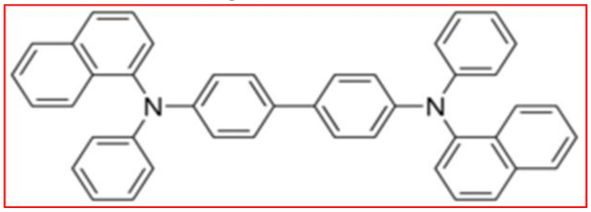

Fig.1 chemical Structure of NBP/NPD

2.QE of NBP/NPD Photocathode.

(Fig.2) shows the QE result of NBP/NPD photocathode. Since NBP/NPD is a sublime grade organic semiconductor polymer so, photocathode samples were prepared using sublimation technique. Four different photocathode samples were prepared in order to study effect of thickness on the quantum efficiency. The thickness of the photocathode could not be measured using this technique. However, it could be approximated by varying exposure time. Four samples for exposure time 2,4,6 and 8 minutes were prepared one by one and their QE was measured as function incident photon wavelength in wavelength range 190 nm- 240nm. Each sample showed maximum QE at 190 nm and cut off at 240 nm. The shape of curve was similar for all four samples. The sample with exposure time 6 minutes showed maximum QE **(Fig.2)**.

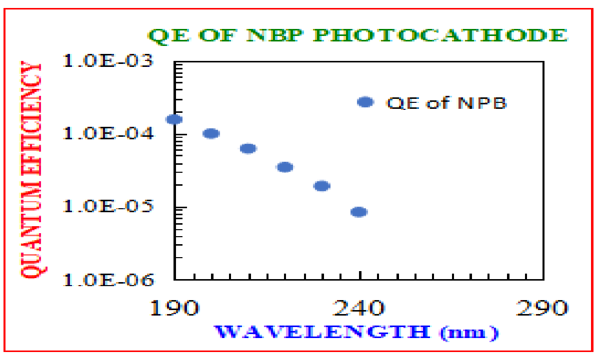

Fig. 2. QE of NBP/NPD Photocathode

In order to investigate the effect of the layer of NBP/NPD on the QE. The quantum efficiency curve for NBP/NPD photocathode with the QE curve of bare copper cathode. **(Fig.3.)** shows comparison of QE of NBP/NPD photocathode with bare copper cathode on log linear graph as function of incident photon wavelength.

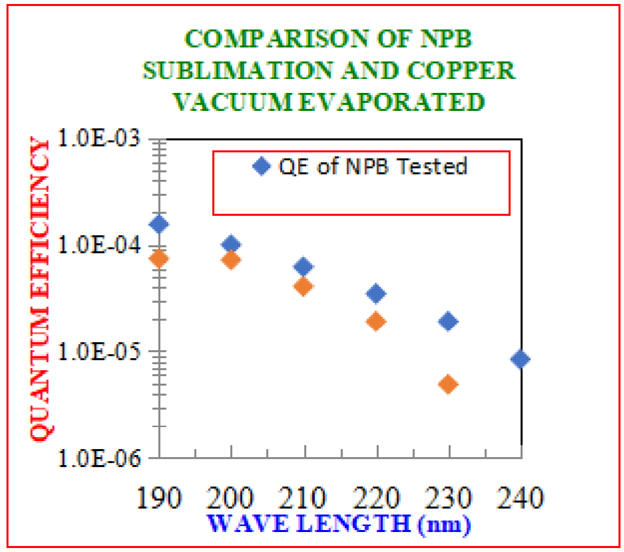

Fig. 3. QE comparison of NBP/NPD with bare copper

The layer effect is visible from **(Fig.3)**. When vacuum evaporation technique was used for preparation of photocathodes from such materials, a shift in QE was noticed in general. This is because, the surface of the photocathode is highly smooth when prepared using vacuum evaporation technique, this minimizes the scattering of both the incident photons as well as photoelectrons, thus the QE is highly improved. This technique also helps to improve the exact measurement of layer thickness. Since, there was some technical issue with Auto 306 coating system of our research lab, thus, the development of photocathodes using this technique was not possible at present. However, a shift in QE of this photosensitive material can be predicted on the basis of earlier work by our group with similar materials (Ahmed 2014). (Rajpar, *et al.*, 2014) ". An expected shift in QE of NBP/NPD photocathode, when developed using vacuum evaporation technique in comparison to photocathode prepared using sublimation technique is illustrated in **(Fig.4)**.

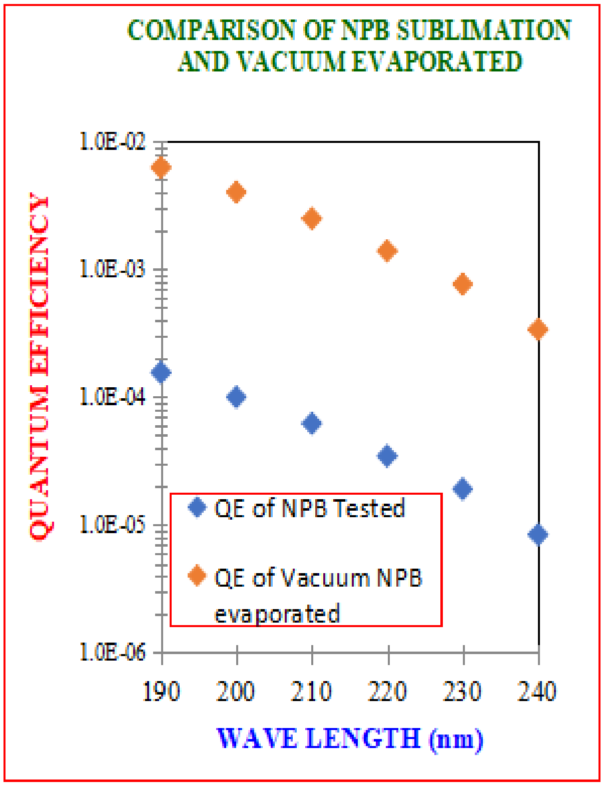

Fig.4. Expected shift in QE of NBP/NPD

it is apparent from the **(Fig.4)** the QE of NBP/NPD photocathode is lower than the QE of best known solid photocathode CsI by a factor of 40.However, ease of preparation of a photocathode with large surface area and air stability makes it suitable for use in some applications gaseous UV photon detectors where photon flux is high.

4. CONCLUSION

QE of NBP/NPD, an organic semiconductor was measured using sublimation technique as a function of incident photon wavelength in spectral region 190-240 nm in vacuum. A photocathode sample for exposure time 6 minutes showed maximum QE at 190 nm and cut off at 240, an expected shift in QE for vacuum evaporation technique was also estimated. It was observed that application of the layer of NBP/NPD enhanced the sensitivity of the metal surface, but the absolute value of QE is too low, however, it may possibly be used in barium-fluoride based high energy calorimetry and plasma diagnostic. Furthermore, it is unreactive to oxygen, easy preparation of large surface are photocathodes and thermal stability make it attractive. Also, its cut off value is at 240 nm whereas CsI shows cut off at 220 nm only. It is suggested that expected QE shift for vacuum evaporation technique should be confirmed. It is also expected that application of a protective layer on the surface of CsI may enhance its spectral sensitivity and increase it QE value.

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