ChemFET sensor: Repercussion of Swift Heavy Ion irradiation on nanorods of nickel-based (NRs-Ni3HHTP2) Metal-Organic framework

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Abstract:

Repercussion of Swift Heavy Ion (SHI) irradiation on nickel-based nanorods of Metal-Organic Framework (NRs-Ni3HHTP2-MOF) for enhancement in the properties of ChemFET based gas sensor has been investigated. Nanorods of Ni3HHTP2-MOF were synthesized by chemical method and exposed to C\textsuperscript{12+} ions irradiation with fluence 1\times10\textsuperscript{11} ion/cm\textsuperscript{2} and 1\times10\textsuperscript{12} ion/cm\textsuperscript{2}. The structural, spectroscopic morphological and optical characterizations were carried out using x-ray diffraction (XRD), fourier transfer infrared spectroscopy (FTIR), atomic force microscopy (AFM) with scanning electron microscopy (SEM) and UV-visible spectroscopy were studied respectively. Whereas the bandgap was calculated from Tauc's plot. The synthesized nanorods of Ni3HHTP2 MOF were drop-casted on gold coated microelectrodes on silicon/silicon dioxide (Si/SiO\textsubscript{2}) substrate, where silicon layer serves as a gate and gold microelectrodes on silicon/silicon dioxide (Si/SiO\textsubscript{2}) substrate as a source and drain. The transmutations in material properties due to SHI irradiations were serviceable for enhancing field-effect transistor (transfer and output) properties.

Keywords: Swift Heavy Ion (SHI), Metal-Organic Framework (MOF), Sensing, ChemFET study

1. Introduction

In the last few years, the Metal-organic framework (MOF) is one of the focusing materials in the research world due to its tunable properties. MOFs are ultra-high porous, large surface area, highly crystalline, high stability material and importantly it can be tunable by altering central metal or organic ligands[1-3]. MOFs are helpful in various applications like gas storage, sensor, chemical separations, biomedical imaging, catalysis and drug delivery as precursors for cooking graphite and metal oxides materials [1, 2, 4].

The most critical problem in front of modern society is a continuous increment in pollutions in terms of air, water, sound etc[5-7]. Among these air pollution absorbed through the respiratory system. Above permissible exposure limit (PEL), hazardous gases responsible for immediately life-threatening[8]. Sulfur dioxide is one of the responsible gases for increasing cardiorespiratory mortality and morbidity in human beings as well as the creation of corrosion in nonliving things [8, 9]. Therefore, researchers have been focusing on enhancing sensing properties of detectors for detection various gases including SO\textsubscript{2} [10-12]. Since last few years, MOF has been one of the mostly explored materials for detection various gases including SO\textsubscript{2}. M. Tchalala[13] et al. reported fluorinated metal-organic frameworks (MOFs) used for the selective removal and
sensing of SO₂ analytes. Therefore, screening of new materials and their modification for enhancing sensing properties are continuous process in the research area.

Since the last few decenniums, sundry materials have been modified extensively by high energy particles (electron, proton) of heavy ions[14-17]. The irradiation of energetic ion beams were engenders several types of defects in materials like chain scission, ionization or excitation and ion track formation etc. The SHI irradiation is one of the promising implements for material modifications and workable for enhancing electrical properties[18, 19]. Zhang et al.[19] studied the performance of SHI irradiated MoSe₂ material. The electrical changes were observed by using TMDC-channel field-effect transistors (FETs). Zeng et al.[20] explored the effects of electrical properties in graphene devices by exposing it to energetic ion beam irradiation where graphene was irradiated by 1.79 GeV Ta ions. It was observed that SHI irradiated graphene at lower fluence exhibited optimized field-effect transistors performance, whereas, at higher fluence, devices were significantly depreciated electrical properties after the irradiation process. Also, Manikanthababu et al.[21] reported electrical characterization of vertical Schottky barrier diodes (SBDs) based on Ag ion irradiated Ni/β-Ga₂O₃ materials with 120 MeV.

To date, researchers have explored SHI irradiation for modification of properties of various materials like Conducting Polymers (CPs), Single-Walled Carbon Nanotubes (SWNTs), Graphene (Gr), Metal Oxides (MOs) etc by using various SHI and fluence rate[22-25]. Researchers have also explored SHI irradiation on various MOF materials. R. Dutta et al.[26] have reported SHI irradiation on NiBTC MOF using 100 MeV O⁷⁺, which exhibited enhancement in electrochemical sensing properties. Recently P. Sayyad et al.[27] studied the effect of Au ion with 100 MeV at fluence 1×10¹¹ ion/cm² and 1×10¹² ion/cm² irradiation on FeBTC MOF. They observed drastic changes for higher ion fluence rate. Moreover, decrease in crystallite size, increase of energy bandgap, decrease in average surface roughness and new functional group (C–H) was observed after SHI irradiation at a higher fluence 1×10¹² ion/cm².

Recently, we have explored nickel-based NRs-Ni₃HHTP₂ MOF for detection sulfur dioxide (SO₂) using ChemFET modality [28]. However, to the best of our knowledge the influence SHI irradiation for enhancing properties of materials for ChemFET sensing has not been explored so far. In the present work, SHI irradiation has been explored to enhance the ChemFET sensing properties of NRs-Ni₃HHTP₂ MOF using C¹²⁺ ion with fluence rate 1x10¹¹ and 1x10¹² ion/cm² irradiations. The influence of irradiation on the NRs-Ni₃HHTP₂ MOF was investigated by using structural analysis, surface morphological, electrical and optical properties.

2. Experimental details

2.1. Fabrication of Microelectrode

The device platform was prepared by using a typical photolithography process as reported earlier[29]. Highly boron (B) doped silicon (Si) substrate having p-type nature with thickness 525µm performed as a back gate terminal in FET measurement. A 100 nm thick SiO₂ layer was deposited on the Si substrate by low pressure chemical vapor deposition. It is followed by deposition Cr layer (20 nm) and Au layer (120 nm) by e-beam evaporator and standard lift-off technique. The width of Au micro electrodes was 200µm and the gap between two micro
electrodes was 3μm. Later micropatterned substrates were immersed in piranha solution (70% concentration H₂SO₄/30%H₂O₂) followed by rinsing and drying under N₂ flow before use.

2.2. Synthesis of NRs-Ni₃HHTP₂ MOF

Nickel (II) acetate (tetrahydrate) (99.99%, purchased from Sigma Aldrich) was used without further purification along with 2,3,6,7,10,11-Hexahydroxytriphenylene Hydrate (HHTP) (98%, purchased from TCI). The chemical method followed for synthesis of NRs-Ni₃HHTP₂ MOF. Before mixing both chemicals, 2.63 mmol nickel (II) acetate (tetrahydrate) was continuously stirred with 4ml deionized water. Further addition of 1.31 mmol HHTP in continuously stirred chemical with continuous heating at 90°C for 8hrs was provided. The chemically synthesized NRs-Ni₃HHTP₂ solution was drop casted between two gold microelectrodes which was dried in room atmospheric conditions.

2.3. SHI irradiation

The SHI irradiation was carried out by using material science beamline, 15UD Pelletron tandem accelerators at the Inter-University Accelerator Center, New Delhi, India. The scanning area of ion irradiation was 1 × 1cm² of devices riding on a ladder which was placed in the irradiated vacuum chamber under 10⁻⁶ mbar pressure. The targeted material irradiated with C¹²⁺ ion with 50MeV at 1pnA for fluence 1 × 10¹ⁱ ion/cm² and 1 × 10¹² ion/cm².

The value electronic stopping, nuclear stopping and range of ions in NRs-Ni₃HHTP₂ were calculated by using the SRIM simulator program. The calculated values were 1647 eV/ Å, 10.84 eV/ Å and 10.25 μm respectively.

2.4. Material characterizations

The X-Ray diffraction (XRD) was carried out using Bruker D8 Advance having potential difference 40kV and current 40kA with source CuKα (wavelength 1.5406Å). The FTIR spectrum was recorded using Bruker Alpha ATR. For surface morphology, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were carried out by Tescan MIRA 3 LMH and Park XE-7 instruments respectively and UV-Vis spectroscopy done by using Jasco V-750. FET measurements were carried out using Keithley 4200A semiconductor parameter analyzer (SPA).

Sensing measurements were performed using indigenously developed dynamic gas sensing setup which was attached with corrosive and non-corrosive mass flow controllers (MFCs) and data performance was recorded using Keithley 4200A. Tedlar bags were used to get the desired concentration of gas analyte.

3. Results and discussion

3.1 Structural Characterization

The structural analysis of pristine and SHI irradiated NRs-Ni₃HHTP₂ MOF was carried out using X-ray diffraction (XRD) shown in figure 1-a. In pristine NRs-Ni₃HHTP₂ (figure 1-a) (black) exhibits 2θ peaks at 5° and 9.4° and matches with reported data [26] which is consistent to (100) and (020) Miller indices respectively. The percentage of crystallinity for pristine NRs-Ni₃HHTP₂ is 48%. After C¹²⁺ ion irradiation, 20 angle peak intensity decreases with increasing
fluence rate. The resultant distinct 2θ peaks were observed after irradiation materials at 46° and 48°. The percentage of crystallinity after C12+ irradiation for fluence rate 1x10^{11} (figure 1-a (red)) and 1x10^{12} ion/cm^2 (figure 1-a (blue)) was 23% and 20% respectively. This result confirms the crystal structure collapse with increase in amorphous phase after SHI irradiation.

Besides giving crystalline structure information, the peaks of the diffraction pattern provide valuable information in other aspects of the material. The crystalline size of pristine and SHI irradiated NRs-Ni3HHTP2 was calculated by using the Debye–Scherrer's formula in equation (I) at 2θ angle 4.515°.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

where as D is crystallite size, \( \lambda \) is the wavelength of x-ray source radiation i.e. CuKα wavelength is 1.5406Å, \( \beta \) is full width at half maxima (FWHM) calculated from Gauss fitting and \( \theta \) is the Braggs angle of diffraction. Also, the dislocation density (\( \delta \)) (equation II), distortion parameter (g) (equation III), and inter-chain separation (R) (equation IV) were shown in table 1. The crystallite size of pristine NRs-Ni3HHTP2 was 705.2 Å decreased 658.3 Å and 615.6 Å with fluence rate 1x10^{11} and 1x10^{12} ion/cm^2 respectively. Also, it is interesting to see that the micro-strain increases with increasing fluence rate.

\[ \delta = \frac{1}{D^2} \]  

\[ g = \frac{\beta}{\tan \theta} \]  

\[ R = \frac{5\lambda}{\delta \sin \theta} \]

| Materials                  | 2θ ° | FWHM | Crystallite size D (Å) | Micro strain (\( \varepsilon \)) | dislocation density (\( \delta \)) (X10^{21}) | distortion parameter (g) | interchain separation (R) |
|---------------------------|------|------|------------------------|-------------------------------|---------------------------------|-------------------------|--------------------------|
| NRs-Ni3HHTP2             | 4.515| 0.346| 705.2                  | 0.0862232                     | 1.537                           | 4.381965552              | 12.2316438               |
| 1x10^{11} ion/cm^2       | 4.515| 0.406| 658.3                  | 0.1011752                     | 2.11                            | 5.141843972              | 12.2316438               |
| 1x10^{12} ion/cm^2       | 4.515| 0.420| 615.6                  | 0.104664                      | 2.257                           | 5.319148936              | 12.2316438               |

Table 1: XRD parameter calculated for pristine and irradiated NRs-Ni3HHTP2 MOF materials.

3.2 Spectroscopy analysis

Fourier Transfer Infrared spectroscopy (FTIR) spectrums were recorded for pristine and irradiated NRs-Ni3HHTP2 MOF materials in ZnSe window having range 4000-500 cm\(^{-1}\) shown in the figure 1-b. The bands 700-900 cm\(^{-1}\) shows continuous stretching containing CH3-metal group due to CH2 rocking vibration present in NRs-Ni3HHTP2 MOF. C=C stretching vibration bonds represent in between 1500-1580 cm\(^{-1}\). Whereas O-H stretching vibration present in the 3200-3700 cm\(^{-1}\) range. In the case of irradiated NRs-Ni3HHTP2 MOF materials, some of the bands become narrow and intensity decreases, these change are attributed to the scissoring and
crosslinking of material by ion beam irradiation[30]. This fact might be responsible for the amorphous nature of NRs-Ni₃HHTP₂ MOF materials after irradiation.

Figure 1: a) XRD patterns and b) FTIR spectrum of pristine (black) and C¹²⁺ ion irradiation with fluence rate 1x10¹¹ ion/cm² (red) and 1x10¹² ion/cm² (blue) on NRs-Ni₃HHTP₂ MOF materials.

3.3 Morphological studies

Scanning electron microscopy (SEM) images were recorded before and after C⁺¹² ion with fluence rate of 1x10¹¹ and 1x10¹² ion/cm² irradiation on NRs-Ni₃HHTP₂ MOF shown in figure 2 (a, b and c) respectively. This confirms the presence of nano-rods in synthesized Ni₃HHTP₂ MOF. The average size of nano-rods (pristine Ni₃HHTP₂, 38nm) decreases with fluence rate i.e. C¹²⁺ with fluence rate 1x10¹¹ and 1x10¹² ion/cm², 35nm and 28nm respectively. This was done due to the high energetic ion passed through materials which loses electronic energy and creates defects [23]. An increased influence rate shows more clusters which are attributed to scissoring and crosslinking of material and is in good agreement with XRD and FTIR results.

Atomic force microscopy (AFM) was carried out (shown in figure 2 (d, e and f)) for determination of roughness (shown in figure 2 (g, h and i)) of pristine and SHI irradiated C¹²⁺ with fluence rate 1x10¹¹ and 1x10¹² ion/cm² on NRs-Ni₃HHTP₂ MOF respectively. The roughness was calculated by XEI image processing software. The roughness of pristine NRs-Ni₃HHTP₂ MOF was 32.518nm and roughness after C¹²⁺ ion irradiated sample was 20.053 nm and 19.475nm with fluence rate 1x10¹¹ and 1x10¹² ion/cm² respectively. The decrease in surface roughness is due to discontinuous tracks and the creation of defects after irradiation of high energetic ion. Higher fluence creates more clusters in material which reduces the surface roughness as compared to lower fluence.
Figure 2: SEM images (a, b and c) and AFM images (d, e and f) with surface roughness (g, h and i) for pristine (black) and C\textsuperscript{12+} ion irradiation with fluence rate 1x10\textsuperscript{11} ion/cm\textsuperscript{2} (red) and 1x10\textsuperscript{12} ion/cm\textsuperscript{2} (blue) on NRs-Ni\textsubscript{3}HHTP\textsubscript{2} MOF materials respectively.

3.4 Optical Studies

The optical absorbance spectra of pristine (black) and C\textsuperscript{12+} irradiated with fluence rate 1x10\textsuperscript{11} ion/cm\textsuperscript{2} (red) and 1x10\textsuperscript{12} ion/cm\textsuperscript{2} (blue) on NRs-Ni\textsubscript{3}HHTP\textsubscript{2} MOF shown in figure 3. It was observed that the pristine NR-Ni\textsubscript{3}HHTP\textsubscript{2} and irradiated materials absorbance peaks are in the 400-550 nm visible wavelength range. The intensity reduction was observed in irradiated materials. The bands at 450–500 nm have been frequently associated with defect absorption[31]. This was due to the creation of free radicals and ions form by irradiation on NRs-Ni\textsubscript{3}HHTP\textsubscript{2} materials. It has affected the bandgap of materials. The bandgap of pristine NRs-Ni\textsubscript{3}HHTP\textsubscript{2} was 3.54eV, after C\textsuperscript{+12} ion irradiation band gap decreases. It was 3.41eV and 3.44eV for fluence rate of 1x10\textsuperscript{11} ion/cm\textsuperscript{2} and 1x10\textsuperscript{12} ion/cm\textsuperscript{2} respectively shown in figure 3 (b-1, b-2 and b-3). This was due to the creation of pronounced coalescence phenomena in higher fluence (1x10\textsuperscript{12} ion/cm\textsuperscript{2}) irradiated material[32]. It shows complementary results with structural and morphological characteristics. Due to high energy, a little bit more damage was created in the material.
Figure 3: a) UV-Vis absorbance spectra with Tauc's plots (b-1, b-2 and b-3) of pristine (black) and C\textsuperscript{12+} irradiation with fluence rate 1x10\textsuperscript{11} (red) and 1x10\textsuperscript{12} ion/cm\textsuperscript{2} (blue) on NRs-Ni\textsubscript{3}HHTP\textsubscript{2} MOF.

The bandgap was calculated by using Tauc's equation (II).

\[ \alpha h\nu = B (h\nu - E_g)^{1/2} \quad \text{(III)} \]

where \( E_g \) is an energy bandgap of the material, \( \alpha \) is the coefficient of absorbance calculated from equation (III), \( A \) is absorbance and \( d \) is the thickness of deposited material.

**Field Effect Transistor (FET) measurements**

The FET measurements were carried out by measuring the output and transfer characteristics of pristine and irradiated MOFs. Output characteristics were performed by modulating drain to source voltage (\( V_{ds} \)) in the window 0 to 10 V at gate voltage (\( V_{gs} \)) 1 to 4V for NRs-Ni\textsubscript{3}HHTP\textsubscript{2} MOF shown in figure 4-a whereas for C\textsuperscript{12+} ion irradiated MOF materials output characteristics were performed by keeping same \( V_{ds} \) window at constant gate voltage (\( V_{gs} \)) 1V as shown in figure 4-b. Moreover, transfer characteristics (as shown in figure 4-c) were measured by modulating gate to source voltage in window -30 to 30 \( V_{gs} \) at \( V_{ds} = 0.5 \text{V} \). Excellent
ON/OFF behavior of FET was observed. The significant changes in output and transfer characteristics in pristine and SHI irradiated device were observed. Significant enhancement in drain current ($I_{ds}$) was observed in SHI irradiated MOF materials. This is due to SHI induced defects and the creation of free radicals and ions in irradiated MOF. The SHI enhances charge transportation in irradiated MOF materials.

![Graphs showing FET measurements](image)

**Figure 4:** FET measurements i.e. Output characteristics for a) NRs-Ni$_3$HHTP$_2$ MOF and b) after C$^{+12}$ ion irradiation on MOF material whereas c) transfer characteristics, d) ChemFET sensing for SO$_2$ analytes.

**ChemFET sensing**

The NRs-Ni$_3$HHTP$_2$ and C$^{+12}$ ion irradiated with fluence $1 \times 10^{11}$ ion/cm$^2$ and $1 \times 10^{12}$ ion/cm$^2$ devices were tested in ChemFET modality for detection of SO$_2$ gas analytes from 1000 ppb to 625 ppb levels by keeping $V_{gs} = 1$V and $V_{ds} = 0.5$V constant as shown in figure 4-d. Reversible ChemFET sensing was observed for SO$_2$ gas analytes. It was showing remarkable dynamic sensing response against SO$_2$ analytes. The significant improvement in the sensing performance was observed in case of SHI irradiated MOF. The enhancement in sensing
performance may be attributed to the increased active sites for SO\textsubscript{2} adsorption on MOF after SHI irradiation. The statistical approach for calculating sensitivity for SO\textsubscript{2} analytes was adopted by using linear regression equations and normalized current responses are plotted against gas concentrations for pristine and SHI irradiated MOF as shown in figure 5-a. For NRs-Ni\textsubscript{3}HHTP\textsubscript{2} MOF linear regression equation was \( y = 0.0018x -1.009 \) with sensitivity 0.785. Moreover, for SHI irradiated MOF (C\textsuperscript{+12} ion irradiated MOF with fluence 1x10\textsuperscript{11} ion/cm\textsuperscript{2} and 1x10\textsuperscript{12} ion/cm\textsuperscript{2} ) linear regression equation were \( y = 0.0018x - 0.675 \) with sensitivity 0.931 and \( y = 0.0014x - 0.588 \) with sensitivity 0.9142 respectively. The C\textsuperscript{+12} ion irradiated MOF with fluence 1x10\textsuperscript{11} ion/cm\textsuperscript{2} shows excellent (0.931) sensitivity. On that line, repeatability was tested for 1000ppb using C\textsuperscript{+12} ion irradiated MOF with fluence 1x10\textsuperscript{11} ion/cm\textsuperscript{2} as shown in figure 5-b and it shows excellent repeatability.

Figure 5: a) plot of concentration versus normalized current with R-squared value b) repeatability for SO\textsubscript{2} analytes c) standard error bar and d) selectivity performance of C\textsuperscript{+12} ion irradiation with fluence 1x10\textsuperscript{11} ion/cm\textsuperscript{2} sensor towards various gases.

The standard error bar is one of the crucial points in sensor properties. The calibration plot is shown in figure 5-c. It exhibited lower deviation at higher concentration of SO\textsubscript{2} analytes whereas higher deviations at lower concentrations. The cross selectivity performance of SHI irradiated MOF for various gas analytes i.e. SO\textsubscript{2}, NO\textsubscript{2}, NH\textsubscript{3}, CO and CH\textsubscript{4} were also investigated.
It shows good selectivity towards SO\(_2\) analytes as shown in figure 5-d. The SHI irradiated MOF (C\(^{12}\) ion irradiated with fluence 1x10\(^{11}\) ion/cm\(^2\) sensor) exhibits improved selectivity due to increased stacking coefficient for SO\(_2\) adsorption in sensing material. The long-term stability was also investigated continuously for 60 days on pristine as well as irradiated sensors as shown in supporting information (SI) figure S1-1. The SHI irradiated MOF exhibited degradation after 25 days. It might be because of creation of more number of defects due to SHI irradiation. The low energy SHI irradiated MOF showed better results than higher energy SHI irradiated MOF in terms of long term stability. The most important parameters in the sensor are response and recovery time, lower detection limit and operating temperature. Table 2 shows comparison of above mentioned sensing parameters of earlier reported work and present work. It can concluded that present work shows better results as compared to earlier reported work. It shows excellent response and recovery time i.e. 20 and 23 sec for 1 ppm SO\(_2\) concentration at room temp (RT) with a lower detection limit of 625 ppb.

| Material                  | Response/recovery time (sec) | Lower detection limit | Operating temp. | Ref. |
|---------------------------|-----------------------------|-----------------------|-----------------|-----|
| S-doped SnO\(_2\)        | 30 /50 for 100 ppm           | 10 ppm                | 180°C           | [33]|
| NiO ZnO nanodisks         | 52 / 41 for 20 ppm           | 3 ppm                 | 240°C           | [11]|
| Ru/Al\(_2\)O\(_3\)/ZnO    | ~60 / ~360                   | 5 ppm                 | 350°C           | [34]|
| AuNPs-SnO\(_2\)           | 34 / 14 for 20 ppm           | 500 ppb               | 200°C           | [35]|
| NRs-Ni\(_3\)HHTP\(_2\) irradiation with C\(^{12}\) at fluence 1x10\(^{11}\) ion/cm\(^2\) | ~20 / ~23 for 1 ppm | 625 ppb | RT | Present work |

Table 2: Presented work sensing parameters compared with recent works of literature

Sensing mechanism

The sensing mechanism is the key factor to understand the sensing behavior of materials. To understand the sensing mechanism, we have calculated bandgap using Tauc's plot as shown in figure 3-b (1, 2 and 3). It shows decrease in banggap after SHI irradiation. After SHI irradiation, defects, free radicals and ions were created on sites of materials. These defects act as an electron trapper with adsorption of the oxygen species from gas analytes. Moreover, these defect were responsible for adsorbing oxygen species and creating oxygen ions thereby preventing electron-hole recombination rate[36]. This was responsible for decreasing drain current after exposing to gas analyte as shown in figure 6.

![Figure 6: schematic for material synthesis, ion irradiation and sensing mechanism](image-url)
4 Conclusions

The NRs-Ni$_3$HHTP$_2$ MOFs were successfully synthesized by the chemical method. The SHI irradiation C$^{12+}$ with fluence 1x10$^{11}$ and 1x10$^{12}$ ion/cm$^2$ have induced changes in structural, spectroscopic, morphological, optical and FET properties of NRs-Ni$_3$HHTP$_2$ MOFs. The NRs-Ni$_3$HHTP$_2$ MOF was amorphized after SHI irradiation which was confirmed by XRD. The XRD pattern exhibits the creation of defects in irradiated materials. The size of NRs-Ni$_3$HHTP$_2$ MOF decreases with decreasing the surface roughness and form a cluster in irradiated materials which was confirmed from surface morphology by SEM and AFM. The decrease in surface roughness was attributed to discontinuous tracks, which lead to amorphization. The drain current of NRs-Ni$_3$HHTP$_2$ MOFs based FET was enhanced due to the trapping of free mobile carriers after the SHI irradiations. The SHI induced surface defects in NRs-Ni$_3$HHTP$_2$ MOFs were responsible for enhancing sensing properties. Therefore, it can be concluded that SHI irradiated NRs-Ni$_3$HHTP$_2$ MOFs showed improved material properties which were responsible for enhancing sensing properties.

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