Supporting information

Earth-Abundant and Environment-Benign Ni-Zn Iron Oxide Intercalated in the Polyaniline based Nanohybrid as Ultrafast Photodetector

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Experimental section

Characterization tools

Rigaku Smart lab Diffractometer used for X-ray diffraction (XRD) analysis with Cukα (λ=1.54Å) radiation (20–70°) was used for structural investigation. The average crystallite size was determined by using Debye Scherrer's equation. The morphological features and chemical composition of these samples were characterized by using a scanning electron microscope (SEM), associated with energy-dispersive X-ray spectroscopy (EDAX) (SEM; JEOL JSM-6490 LV). High-resolution transmission electron microscopy (HRTEM; Tecnai G2 20 S-TWIN [FEI], 200 KV) imaging was obtained at different scales and X-ray photoelectron spectroscopy (XPS; Thermofisher Scientific- Nexsa base) was used for the quantitative surface and chemical composition of the prepared samples. Fourier transform infrared (FTIR) spectra were recorded by using the instrument (FTIR; Thermo-Scientific Nicole 6700) spectrometer over a range of 400–4000 cm^{-1} and absorbance properties were recorded by UV/Vis

spectrometer (UNIKAM 5625) carried out in the range of 195-1100 nm. RAMAN spectroscopy and Photoluminescence (PL). Keithley electrometer/source meter (6517 B) and Newport optical meter were used to record transient photoresponse and optical power intensity of the light source respectively.

Fabrication of photodetector device

1mg NZF-PANI ultrasonicated for 30 minutes in the 5ml NMP and 1×1 cm^2 Whatman filter paper dipped in the solution. Later the process was repeated for 10 cycles and dried at room temperature. Copper wire electrodes were deposited onto the nanohybrids coated filter paper substrate using conductive silver paste. The prepared metal-semiconductor-metal i.e., metal-nanohybrids-metal photodetector device on the paper substrate was further used for the photoresponse studies.

Structural analysis of pure NZF nanomaterial

Reitveld refinement by using Full-proof software was carried out as shown in Fig. S1and the XRD pattern of the pure NZF matched with the reported data.[1] The crystallite size (D) for the NZF has been calculated using Debye-Scherrer's formula;

$$\mathbf{D} = \frac{K\lambda}{\beta cos\theta}$$

where β is the full-width half maxima of (311) peak, λ(= 1.54 Å) is the wavelength of Cu K_α X-ray source, θ (radian) is the angular position of (311) peak.

The lattice parameter, 'a' has been estimated using the formula for (311) plane [5];

$$\mathbf{a = d\ (h^2 + k^2 + l^2)^{1/2}} \text{ or } \mathbf{d} = \sqrt{11}d$$

Inter-planar spacing's between the lattice plane'd' calculated by using Bragg's law as taken n=1;

$$\mathbf{d} = \frac{n\lambda}{2\,sin\theta}$$

Since each primitive unit cell of the spinel structure contains 8 molecules; the value of X-ray density, 'd' calculated by using the following relation as given;

$$\mathbf{d_x} = \frac{8M}{Na^3}$$

Where 'N' is the Avogadro number, 'M' is the molecular weight of the sample and 'a' is the lattice parameter [5].

Stress and strains have been also estimated for the prepared nanoparticles using the formulae [6];

$$\textbf{Stress, S} = \frac{\lambda}{\Delta sin\theta} - \frac{\beta}{tan\theta} \text{ and}$$

$$\textbf{Strain, } \varepsilon = \frac{\beta cos\theta}{4}$$

The observed values of the crystallite size, lattice parameter, inter-planar spacing, X-ray density, and stress & strain are presented in Table S1 from the XRD pattern of NZF.

Table S1 Parameters calculated from XRD pattern of NZF

Sample	**Crystallite size 'Δ' (nm)**	**Lattice parameter 'a' (Å)**	**Inter-planar spacing 'd' (Å)**	**X-Ray density 'd_x' (g/m^3)**	**Stress 'S'**	**Strain 'ε'**
NZF	20.31	8.517	2.568	5.22g/m^3	2.562×10^{-3}	1.706×10^{-3}

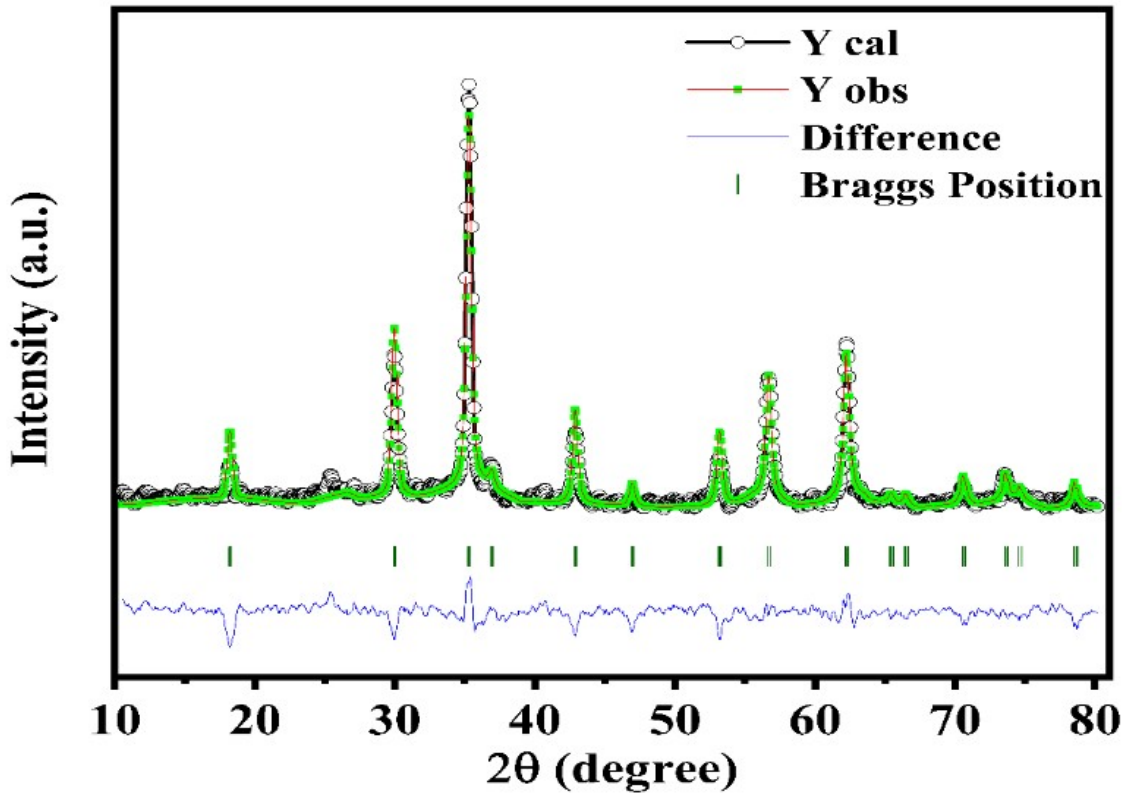

Fig. S1 Reitveld refinement of pure nickel zinc iron oxide (NZF) nanomaterial.

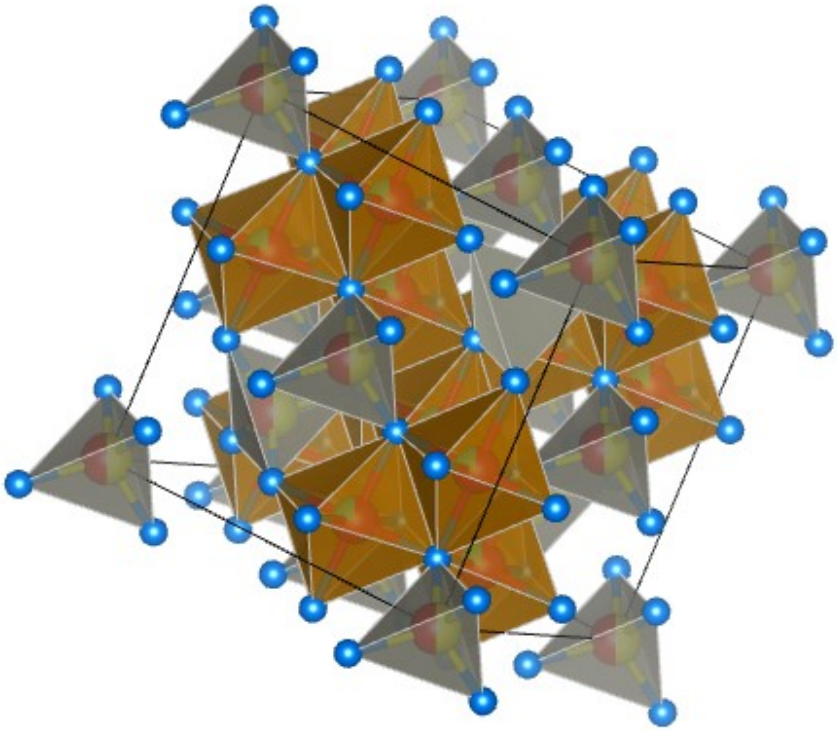

Fig. S2 Crystal structure of the nickel zinc iron oxide from the reitveld refinement.

Morphological and elemental analysis of NZF-PANI hybrid material

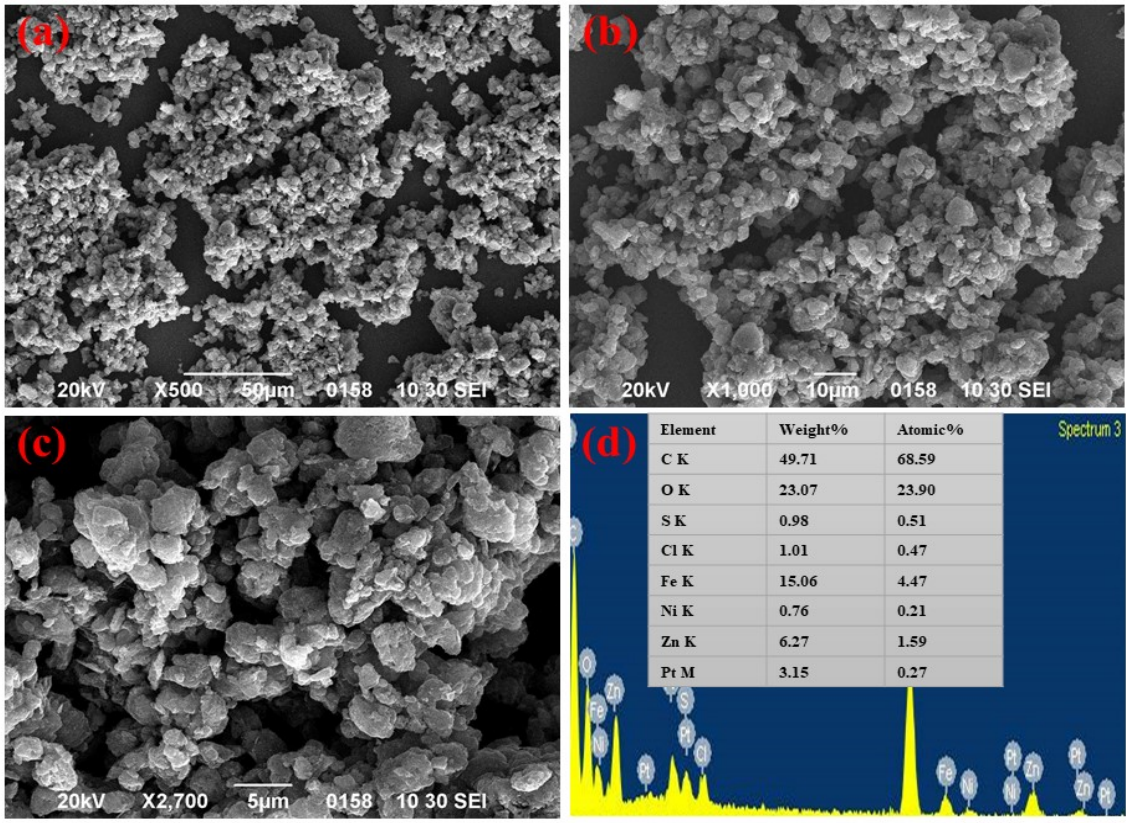

Fig. S3 SEM micrographs at different magnifications (a), (b) and (c); (d) EDS spectrum of the NZF/PANI hybrid material and their elemental composition.

The SEM micrographs of the NZF-PANI hybrids represent irregular spherical particles are shown at 50 µm and 10 µm in Fig. S2 (a.b). In Fig. S2 (c), NZF material is highly interlinked with the polyaniline (PANI) chain; it must be the surface of the NZF polymerized and incorporated within the polymer. The elemental analysis was investigated by energy-dispersive X-ray spectroscopy (EDS) which confirms the presence of nickel, zinc, iron, oxygen and carbon in the hybrid material as shown in Fig. S2(d). The elemental composition found to be carbon (C) 49.71%, oxygen (O) 23.07%, iron (Fe) 15.06%, nickel (Ni) 0.76%, and zinc (Zn) 6.27%. A small amount of chlorine (Cl) and sulfur (S) was found due to some impurities in the

sample which does not remove on washing and drying the sample. Platinum is used as a coating for sample characterization.

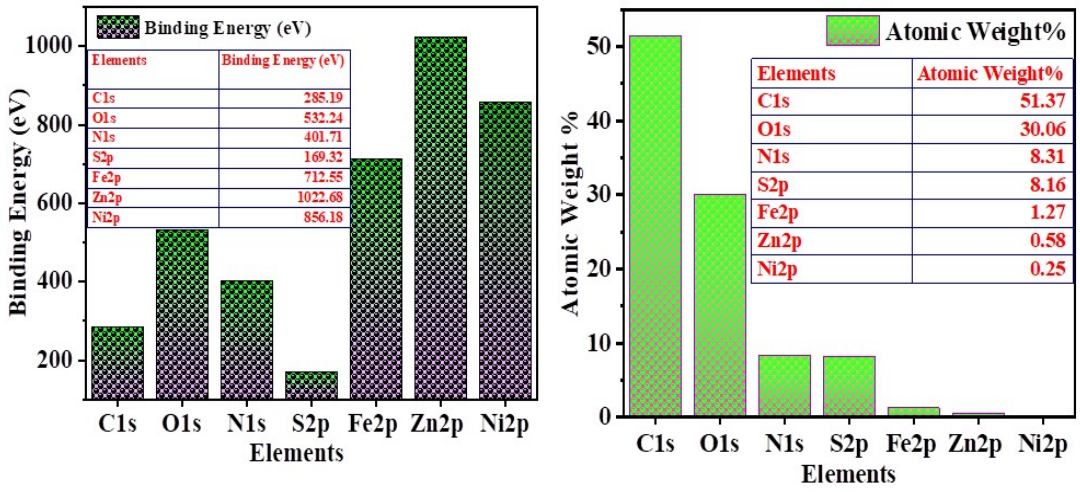

Fig. S4 Binding energy and atomic weight of all the elements present in the NZF-PANI nanohybrids.[2]

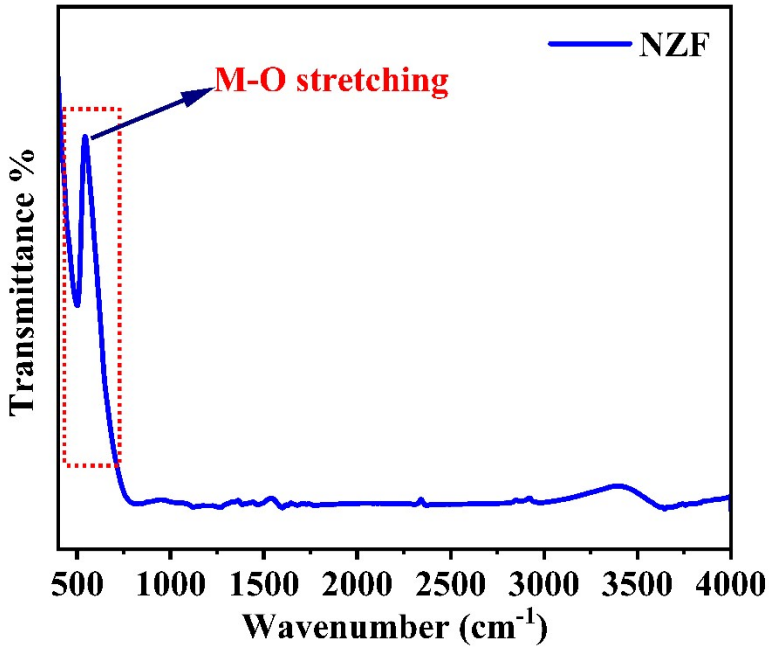

Fig. S5 FTIR of the pure NZF material.[1]

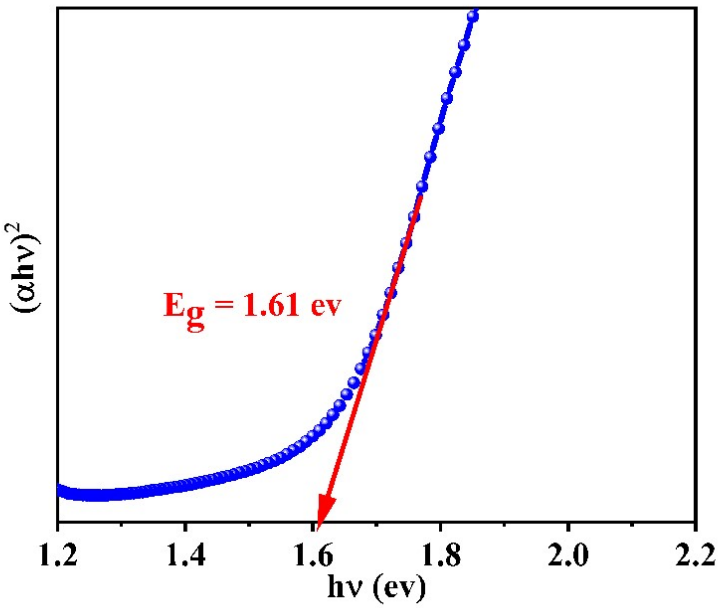

Fig. S6 Tauc plot for the optical bandgap of the NZF-PANI nanohybrids

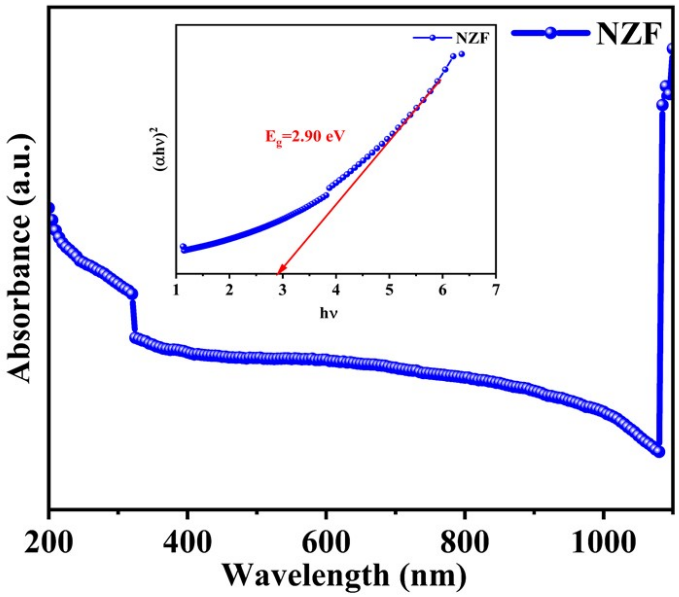

Fig. S7 UV-visible spectroscopy of the pure nickel zinc iron oxide and tauc plot in the inset image.

I-V characteristics of the pure NZF material

For the current-voltage characteristics it can be seen that the device structure is Ohmic type. In the NZF sample the responsivity was observed only to 1.827 mA/W with the EQE of 0.619%. The main reason behind the low responsivity and EQE is that in the NZF device a very low photocurrent in the order of nano-ampere is observed. One of the best observations from the Ni-Zn iron oxide is that a huge on-off ratio of 121.759 with the excellent LDR of 41.710 dB is observed. A detectivity of 1.179×10^{11} Jones was also observed, this is because of the very low dark current in the NZF material.

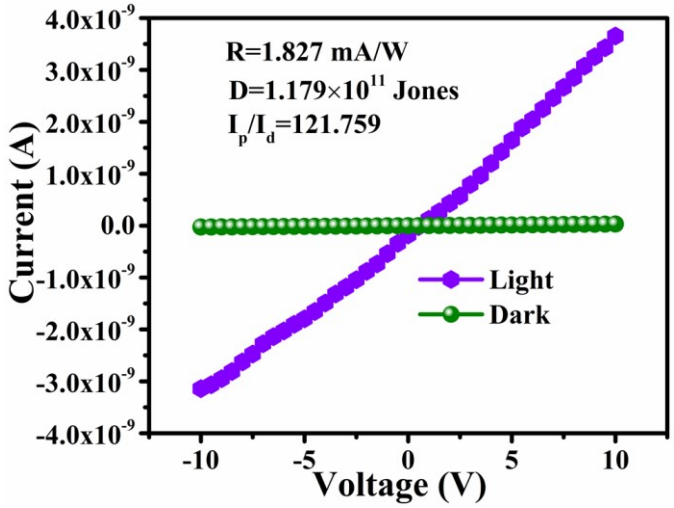

Fig. S8 I-V characteristics of the NZF under dark and light conditions.

References

1. S. Singh, A. Bhaduri, R. K. Tripathi, K. B. Thapa, R. Kumar and B. C. Yadav, *Solar Energy*, 2019, **188**, 278-290.
2. A. G. Mustafin, L. R. Latypova, A. N. Andriianova, I. N. Mullagaliev, S. M. Salikhov, R. B. Salikhov and G. S. Usmanova, *RSC Advances*, 2021, **11**, 21006-21016.