Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

ZnO(N)-Spiro-MeOTAD hybrid photodiode: An efficient self-powered fast-response UV (visible) photosensor

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Supporting Information-1:

Response time measurements of self powered hybrid ZnO-SPD under nanosecond Pulsed UV laser.

Recently, some reports [1,2,3] have used a nanosecond pulsed UV laser as an alternative to a mechanically chopped UV source for measurement of τ_{rise} and τ_{fall}. It is important to point out that in the case of nanosecond pulsed laser as an excitation source; the τ_{rise} is limited by the short pulse width of laser which does not give enough time for photocurrent saturation. Therefore, such measurements can give inappropriate rise time which might be lower by three orders of magnitude (10^3) than the true rise time. In order to support this argument we also carried out response time measurements under pulsed UV (KrF Excimer 248 nm) laser with a pulse width of 20 ns. **Fig. SI-1** shows the output voltage transient obtained across 1 MΩ resistance. In this case the τ_{rise} is observed to be 160 ns which is three orders of magnitude smaller than the rise time value (200 μs) obtained by mechanical chopping of a continuous UV source. The τ_{fall} can be estimated to be 10 ms and 40 ms on fitting a second order exponential decay which can be assigned to the relaxation processes within the photodiode structure. The slightly higher value of decay time in pulsed laser measurement can be attributed the lower wavelength (248 nm) of laser which causes the photo-excitation 2 eV higher than the band gap thereby inducing additional relaxation processes as compared to only band to band excitation. Therefore, an appropriate method to get the response time of a photodiode is to analyze the photoresponse Vs time graphs under light pulses chopped mechanically at a frequency which leads to saturation in the photocurrent.

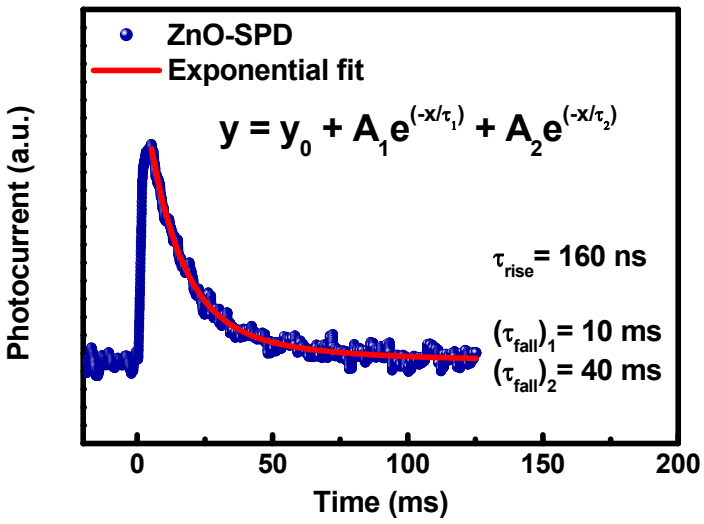

Figure SI-1: Transient photoresponse of ZnO-SPD obtained under a pulsed nanosecond laser

1. S. M. Hatch , J. Briscoe , S. Dunn, *Adv. Mater.* **2013**, *25*, 867.
2. P.N. Ni, C.X. Shan, S.P. Wang, X.Y. Liu, D.Z. Shen, *J. Mater. Chem*. C **2013**, 1, 4445.
3. S. Hatch, J. Briscoe, A. Sapelkin, W. Gillin, J. B. Gilchrist, M. P. Ryan, S. Heutz, S. Dunn, *J. Appl. Phys.* **2013**, 113, 204501.

Supporting Information-2: Raman analysis of N:ZnO and ZnO

The optical phonon modes shown by Wurtzite ZnO (C^4_{6v} space group) are $A_1+E_1+2E_2$ (Raman active), $2B_1$ (Raman silent), and A_1+E_1 (infrared active), where A_1 and E_1 modes split into LO and TO components. The Raman spectrum of ZnO sample in **Figure SI-2** shows E_2^{high} mode at 439 cm^{-1} with multiple phonon scattering signal at 334 cm^{-1}[38]. The Raman for ZnO shows absence of ($E_{1\ LO}+A_{1\ LO}$) Raman mode at 582 cm^{-1} which is usually assigned to disorder within the lattice.

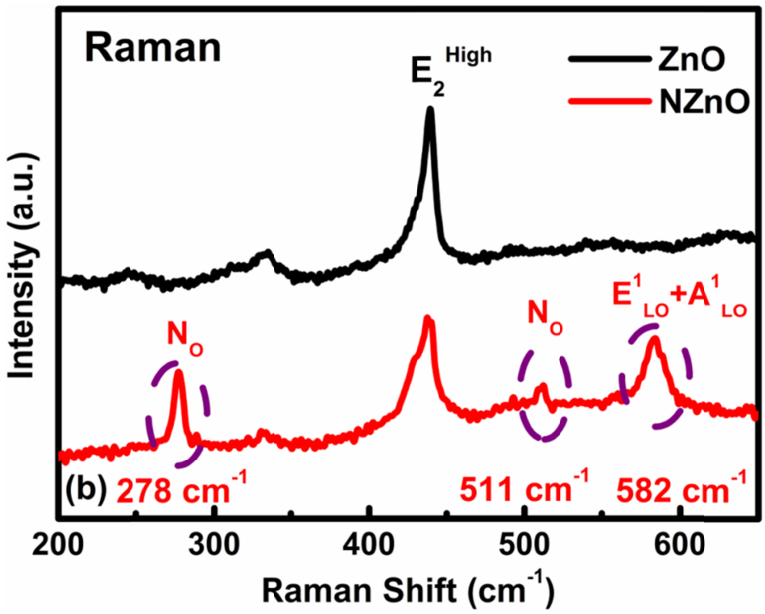

Figure SI-2: Raman comparison of ZnO and N:ZnO nanorad arrays

In the Raman spectrum of N:ZnO ($E_{1\ LO}+A_{1\ LO}$) the Raman mode at 582 cm^{-1} appears pointing towards lattice disorder caused by incorporation of nitrogen. The Raman spectrum of N:ZnO also shows characteristic features related to nitrogen doping at 278 cm^{-1} and 511 cm^{-1}. Friedrich et al. have shown using *ab initio* Density Functional Theory (DFT) that the Raman mode at 278 cm^{-1} can be assigned to the complex between interstitial zinc (Zn_i) and nitrogen substituting oxygen (N_o) whereas the Raman mode at 511 cm^{-1} is assigned to the complex between oxygen interstitial (O_i) and zinc interstitial (Zn_i) due to nitrogen doping. Thus, the Raman modes at 279 cm^{-1} and 511 cm^{-1} point towards successful incorporation of nitrogen within the ZnO lattice which results in broadband absorption of ZnO.

Reference: F. Friedrich, M. A. Gluba and N. H. Nickel, *Applied Physics Letters*, 2009, **95**.

Supporting Information-3: Cytotoxicity study on Spiro-MeOTAD

HepG2 cells (human hepatoma cell line) were grown in Eagle's Minimum essential Medium (MEM Gibco, Carlsbad, CA, USA) supplemented with 10% Fetal Bovine serum and penicillin/ streptomycin, under 5% CO2 atmosphere at 37º C.

The cytotoxicity of Spiro-MeOTAD and (Mercaptopropionic acid capped CdTe) CdTe-MPA on HepG2 cells were assessed by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay. For MTT assay, cells were seeded at the density of 105 cells/ well in 96 well plates and incubated for 12-16 hrs at 37º C before starting the treatment. Cells were treated with increasing concentration of Spiro-MeOTAD and CdTe-MPA respectively (in the range of 2µg/ ml to 10µg/ ml) and incubated for 24 hrs. At the end of incubation period, MTT solution was added to a final concentration of 0.05 mg/ ml to each well and incubated in dark at 37º C for 4 hrs. Formazan crystals were dissolved by adding 100 µl DMSO to each well and the optical absorbance was measured at 540 nm on a plate reader. The readings in untreated cells were considered to be 100 % viable. Cytotoxicity of CdTe-MPA was also performed in order to show the comparative analysis.

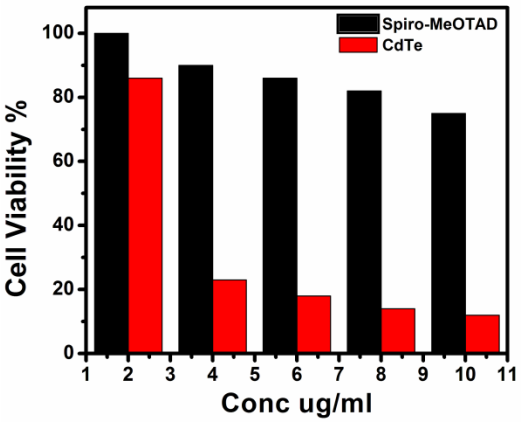

Fig. SI-3 The cyto-toxicity data of Spiro-MeOTAD and cadmium based visible semiconductor (CdTe)

It can be clearly seen from **Fig. SI-3** that Spiro-MeOTAD is far less toxic as compared to CdTe.

Supporting Information-4: Electrochemical Mott-Schottky Plots of ZnO and N:ZnO

In order to verify the type of conductivity of ZnO and N:ZnO we carried out the electrochemical Mott-Schottky Measurements on ZnO and N:ZnO samples in 0.5M Na2SO4 with three electrode assembly (ZnO/N:ZnO as working electrode, Pt as counter electrode and Ag/AgCl as reference electrode). The 1/C2 vs Potential against Ag/AgCl are plotted in the following diagram. Positive slops of ZnO and N:ZnO Mott-Schottky plots confirm that both posses n type conductivity.