Supporting Information

π-Conjugated Amine-ZnO Nanohybrids for Selective Detection of CO_2 Gas at Room Temperature

Biswajit Mandal[1], Ankan Biswas[2], Aaryashree[1,2], Daya Shankar Sharma[1], Ritesh Bhardwaj[1], Mangal Das[1], Md Ataur Rahman[3], Sruthi Kuriakose[3], Madhu Bhaskaran[3], Sharath Sriram[3], Myo Than Htay[4], Apurba K. Das[2], and Shaibal Mukherjee[1,*]

[1]Hybrid Nanodevice Research Group (HNRG), Electrical Engineering, Indian Institute of Technology Indore, Indore 453552, India

[2]Department of Chemistry, Indian Institute of Technology Indore, Indore 453552, India

[3]Functional Materials and Microsystems Research Group and the Micro Nano Research Facility, RMIT University, Melbourne, Victoria 3001, Australia

[4]Hashimoto-Myo Laboratory, Department of Electrical and Computer Engineering, Shinshu University, 4-17-1 Wakasato, Nagano City, Nagano Prefecture-380-8553, Japan

[*]Email: shaibal@iiti.ac.in

Table of contents

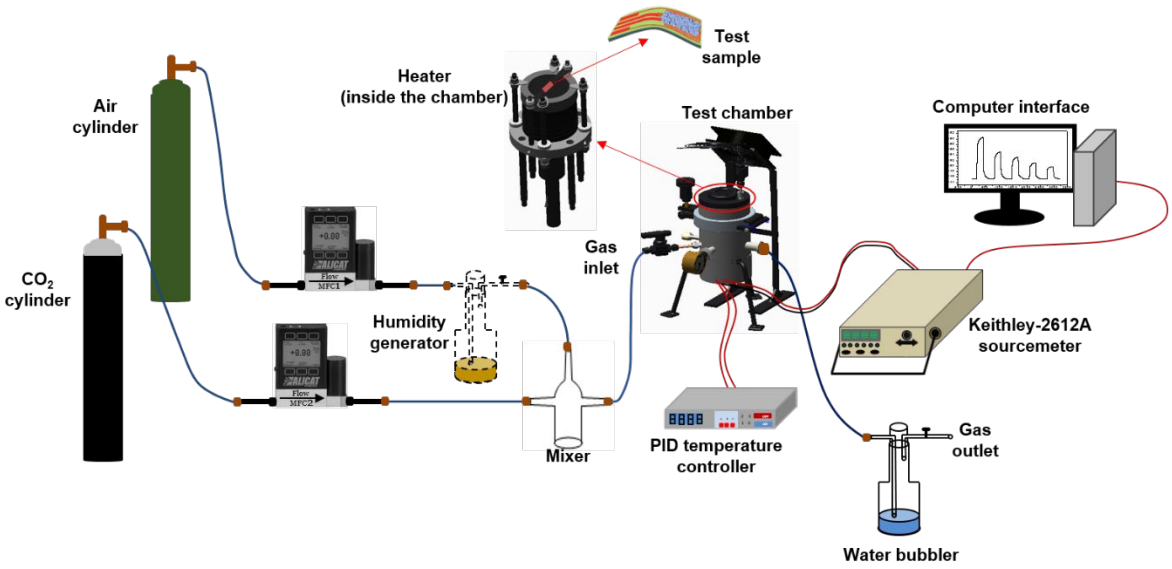


Figure S1: Typical gas sensing set up for conditioning and calibrating a carbon dioxide gas sensor.

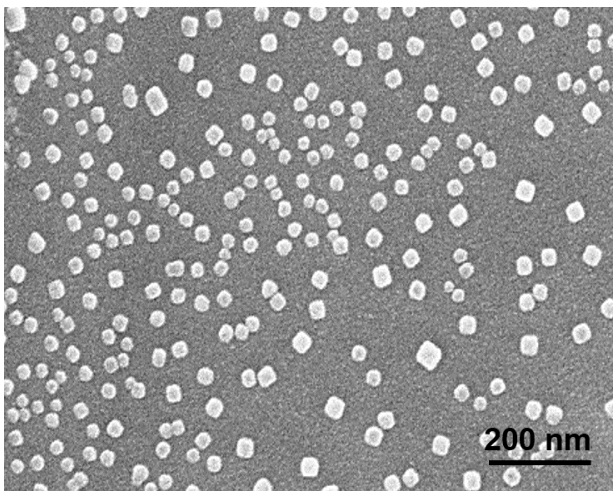


Figure S2: FESEM image of NBA nanoparticles.

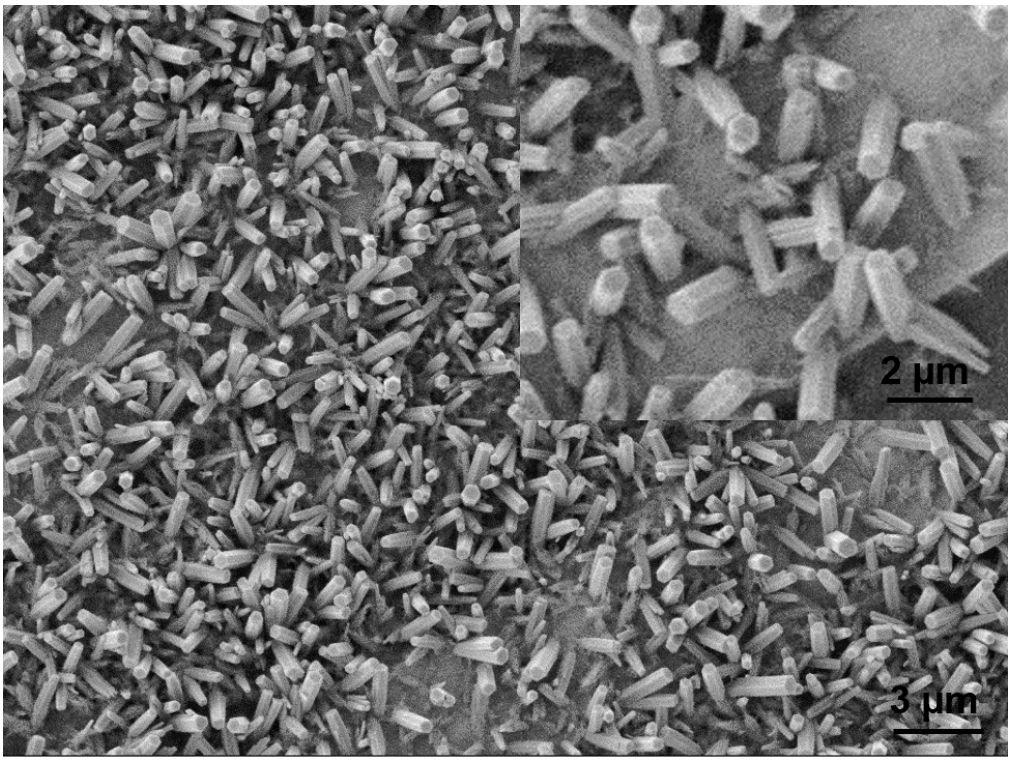


Figure S3: FESEM image of ZnO nanorods grown on IDEs patterned seed layer coated flexible substrate (reaction time 3 h). Inset shows ZnO nanorods at higher magnification.

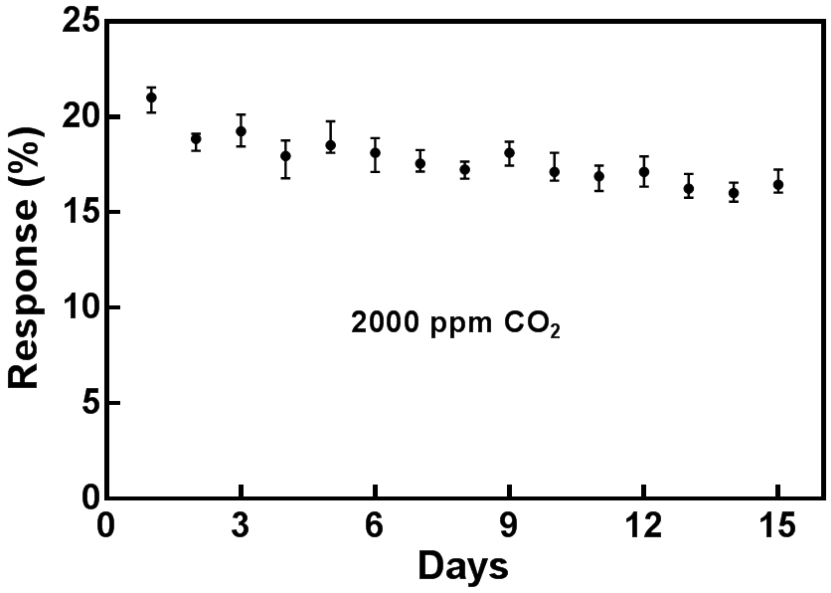


Figure S4: Stability study of the NBA-ZnO nanohybrid sensor for 15 days

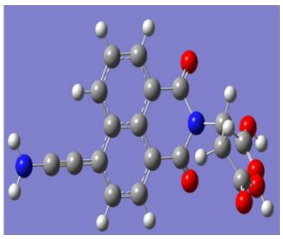
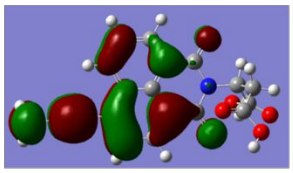
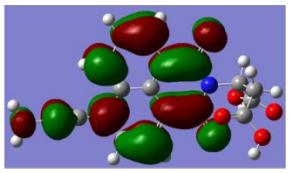
NBA	HOMO	LUMO	Calculated Energy band Gap (eV)
	 -5.74 eV	 -2.49 eV	-3.25 eV

Figure S5: DFT calculation of NBA compound for HOMO and LUMO energy level.

Experimental section:

Synthesis of 2-(6-bromo-1,3-dioxo-1H,3H-benzo[de]isoquinolin-2-yl)-succinic acid dimethyl ester (compound 2):

To a 250 mL round bottom flask (1.118 g, 4.035 mmol) of 4-bromo-1,8-naphthalic anhydride was added and dissolved with 30 mL of ethanol. After that, (0.780 g, 4.845 mmol) of dimethyl ester of L-aspartic acid was added into the reaction mixture and stirred with a magnetic stirrer. The flask was fitted with a condenser and refluxed at 80 ºC for overnight. The reaction was monitored by TLC. After completion of reaction; the reaction mixture was extracted by ethyl acetate and washed with 1 M HCl (30 mL x 3). The organic layer was collected; dried over dry Na_2SO_4 and collected as white solid. Yield = 1.45 g, (3.46 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, 1H, *J* = 7.28 Hz), 8.62 (d, 1H, *J* = 8.52 Hz), 8.44 (d, 1H, *J* = 7.76 Hz), 8.07 (d, 1H, *J* = 7.80 Hz), 7.87 (t, 1H, *J* = 7.60 Hz), 6.24 (t, 1H, *J* = 6.76 Hz), 3.73 (s, 3H), 3.67 (s, 3H), 3.56-3.50 (m, 1H), 2.99-2.95 (m, 1H) ppm. ESI-MS m/z calculated for $C_{18}H_{14}BrNO_6$: 441.9902 $(M+Na)^+$; Found: 441.9870 $(M+Na)^+$.

Synthesis of 2-[6-(4-amino-phenylethynyl)-1,3-dioxo-1H,3H-benzo[de]isoquinolin-2-yl]-succinic acid dimethyl ester (compound 5):

251.4 mg (0.60 mmol) of compound **2** was dissolved in 5 mL THF and 5 mL of Et_3N in a 100 mL, round bottom flask. The flask was capped by septum and argon gas was purged into the

solution for 10 min by syringe. After that, CuI (5 mol% of compound **4**) and $Pd(PPh_3)_2Cl_2$ (5 mol% of compound **4**) were added followed by addition of 77.25 mg (0.66 mmol) of compound **4**. The reaction mixture was refluxed for overnight under argon atmosphere at 70 ºC. The reaction was monitored by TLC and after completion; reaction mixture was extracted with ethyl acetate and washed with brine, dried over dry Na_2SO_4. Ethyl acetate was evaporated to get solid crude, which was purified by column chromatography (100 mesh silica gel, 30% ethyl acetate in hexane as eluent) to yield compound **5**. Yield = 213.5 mg (0.46 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, 1H, *J* = 8.28 Hz), 8.64 (d, 1H, *J* = 7.28 Hz), 8.55 (d, 1H, *J* = 7.52 Hz), 7.90 (d, 1H, *J* = 8.0 Hz), 7.83 (t, 1H), 7.48 (d, 2H, *J* = 7.28 Hz) 6.70 (d, 2H, *J* = 7.28), 6.27 (t, 1H, *J* = 6.52) 4.01 (s, 2H), 3.74 (s, 3H), 3.68 (s, 3H) 3.56 (dd, 1H, *J* = 6.56 Hz, 6.76 Hz), 2.96 (dd, 1H, *J* = 6.52 Hz, 6.56 Hz) . HRMS (ESI) m/z calculated for $C_{26}H_{20}N_2O_6$: 479.1214 $(M+Na)^+$, Found: 479.1215 $(M+Na)^+$.

Synthesis of 2-[6-(4-amino-phenylethynyl)-1,3-dioxo-1H,3H-benzo[de]isoquinolin-2-yl]-succinic acid (compound 1):

200 mg (0.44 mmol) of compound **5** was dissolved in 1:1 methanol-THF. After that, 2 mL of 1 (N) aqueous NaOH solution was added into the reaction mixture. The reaction mixture was stirred for overnight. After completion of reaction, reaction mixture was dissolved in 50 mL water and washed with ether (1 x 50 mL). Aqueous part was collected and neutralized by 1 (N) HCl. After getting slightly acidic pH, the desired product was extracted by ethyl acetate (3 x 50 mL) from red turbid aqueous part. Ethyl acetate was dried over dry Na_2SO_4 and evaporated to get desired product as red solid. Yield = 179.3 mg (0.42 mmol, 95%). ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ = 8.80 (d, 1H, *J* = 9.92 Hz), 8.58 (d, 1H, *J* = 7.04 Hz), 8.45 (d, 1H, *J* = 7.04 Hz) 8.00-7.95 (m, 2H), 7.47 (d, 2H, *J* = 7.52 Hz), 6.64 (d, 2H, *J* = 7.56 Hz), 5.96 (m, 1H), 5.88 (s, 2H), 2.77-2.71 (m, 1H), 1.22-1.15 (m, 1H) ppm. HRMS (ESI) m/z calculated for $C_{24}H_{16}N_2O_6$: 451.0901 $(M+Na)^+$, Found: 451.0902 $(M+Na)^+$.

Scheme S1: Reaction scheme for the synthesis of NBA (compound **1**)