

## Electronic Supplementary Information

### Electrochemical synthesis on single cells as template

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#### Procedure for the synthesis of graphene oxide

Graphene oxide was synthesized via the modified Hummer's method. Graphite flakes (~ 325 mesh size, Alfa Aesar) were oxidized using a combination of powerful reagents i.e., sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), potassium per sulphate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>). 3g of graphite flakes were dissolved in 10 ml of H<sub>2</sub>SO<sub>4</sub>. Oxidizing agents K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and P<sub>2</sub>O<sub>5</sub> were added to the graphite in sulphuric acid and stirred at 90 °C till the flakes were dissolved. The stirring continued for 4 more hours at 80 °C and the solution was then diluted with 500 ml of Milli-Q Millipore™ water (Ultrapure water > 16MΩ). After the dilution, the solution was stirred overnight, filtered, washed with de-ionised water and then dried to get the powdered form of graphene oxide.

Pre-oxidized GO powder was then subjected to further oxidation with 125 mL of H<sub>2</sub>SO<sub>4</sub> and 15g of Potassium permanganate (KMnO<sub>4</sub>) in an ice bath where the solution was stirred for 2 more hours. 130 mL of Milli-Q Millipore™ water was added to the mixture and this caused the temperature to rise to 95 °C. After 15 minutes, 15 mL of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) was added to reduce the manganese in the solution to manganese sulphate (Mn → MnSO<sub>4</sub>). Finally, the solution was diluted with 400 mL of Milli-Q Millipore™ water and resultant yellow suspension was stirred overnight. GO was filtered and washed till the rinsed water pH was found to be approximately 7.[1, 2]

#### Surface functionalization

For this purpose, Silicon chips patterned with gold electrodes were washed with 2-propanol and Milli-Q Millipore™ water and subsequently sonicated in 50:50 by volume solution of 2-propanol and Milli-Q Millipore™ water to remove any residual particles on the surface. Their surface was then hydroxylated by placing them in "piranha" solution (7:3 concentrated H<sub>2</sub>SO<sub>4</sub>: 30% H<sub>2</sub>O<sub>2</sub>) (CAUTION: piranha solution reacts violently with organic compounds!). The chips were then washed thoroughly with Millipore™ water. The chips were then placed in a solution of (3-Aminopropyl)triethoxysilane ( 1mL in 100 mL of Millipore™ water ) for 10 minutes. The chips were then annealed on a hot plate at 120 °C for 30 minutes. Once cooled, the chips were used for the deposition.[2]

#### Calcium-Gold solution (Ca-Au)

Calcium-Gold solution was found to be a favorable binding agent and it was prepared by mixing calcium chloride solution with the gold colloid in the ratio 1:11 respectively. Calcium chloride solution was prepared by dissolving anhydrous calcium chloride in Millipore™ water (1mg/1mL solution). Thus prepared calcium chloride solution was mixed with gold colloid (10nm, BBI International) and stirred for 24 hours. The change in color from wine red to blue indicated the formation of gold nanoparticle chain. [4]

#### Graphene oxide-Calcium-Gold solution (GO-Ca-Au)

Graphene oxide is attached to the Calcium-Gold nanoparticles by mixing the solutions of GO and Calcium-Gold (Ca-Au). GO ( 0.5mg/1mL) solution is centrifuged at 500 rpm for 3 min to remove micron sized particulates and then added to preformed Calcium-Gold solution in the ratio 1:20 is stirred for 8 hours to get homogeneous solution of GO-Ca-Au.

#### Harvesting of *Saccharomyces Cerevisiae* (Yeast cell)

*S. cerevisiae* strain BY4741 (MATa his3Δ leu2Δ met15Δ ura3Δ) is used in the experiments. 2g of yeast-peptone-dextrose broth (YPD) broth powder was dissolved into 40mL of Millipore™ water and autoclaved to get the broth solution. Yeast cells were grown in YPD broth at 30 °C for 8 hours, shaking at 200 rpm. After 8 hours, the cells reach a logarithmic growth phase and they are centrifuged and subsequently washed with Millipore™ water to remove any YPD residue. Washed cells were re-suspended in water for further deposition with graphene.

#### *Saccharomyces Cerevisiae* (Yeast cell) on GO-Ca-Au

Yeast cells harvested after 8 hours of growth in the YPD broth were centrifuged and washed. 100μL of such cell suspension is added to 1mL of GO-Ca-Au solution and allowed to mix for an hour.

#### DEP

In order to deposit a graphene oxide layer to serve as the nucleation sites in the ZnO synthesis, a dielectrophoretic process was used. The gold array chips were secured in a fluidic well. This well was filled with 0.0005% graphene oxide solution. The gold arrays were fixed at a 5MHz, 2Vpp AC bias relative to the ground. DEP deposition was conducted for 2hours before the chip

was removed and washed briefly with millipore water. No temperature increase in the solution was observed during the course of DEP deposition of the GO sheets.

## Apparatus

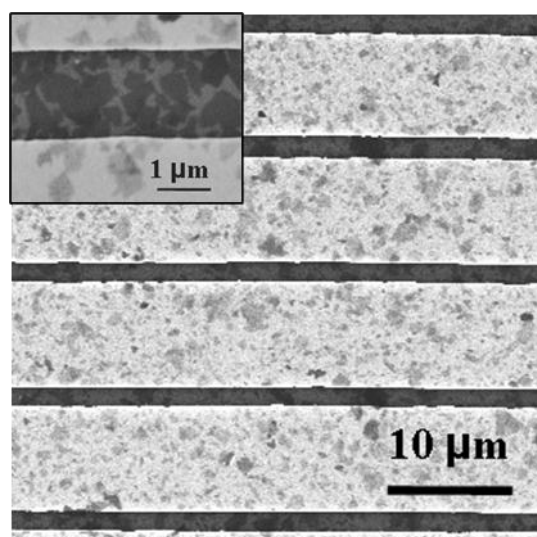
Field Emission Scanning electron microscopy (FESEM) was done with a LEO 1530 Gemini field emission gun attached with EDX/OIM. Electrical characterization was done using a custom-built IV setup consisting of Agilent 6614C DC power supply and Hewlett Packard 3458A multimeter. A Newport solar simulator was used as the light source. This source with a AM 1.5G filter provides approximately 1.3 sun output. Electrochemical synthesis was performed using a Princeton Applied Research Potentiostat/Galvanostat Model 273A, the software used was Powersuite 2.58. Glancing angle ( $0.6^\circ$ ) X-Ray diffraction was done a PANalytical machine using  $\text{CuK}\alpha$  line as the X-ray source.

## ZnO Growth

A 0.01M KCL and 0.125mM  $\text{ZnCl}_2$  solution was prepared as the synthesis solution. A Gold Array electrode chip, previously treated with DEP deposition of Graphene was secured in the fluidic well such that the gold array area was isolated from the electrical contact area. The fluidic well was composed of a thermally conducting plastic such that uniform temperatures would be maintained for the duration of the experiment. The set point was determined such that the interior of the fluidic well would be maintained at  $\sim 75$  degrees Centigrade. Subsequently a Ag/AgCl reference electrode was used and a bias of  $-0.955\text{V}$  was maintained across the gold electrode array. Synthesis was conducted in the prepared solution for 10mins at a temperature of 80 degrees.

## DEP deposition results

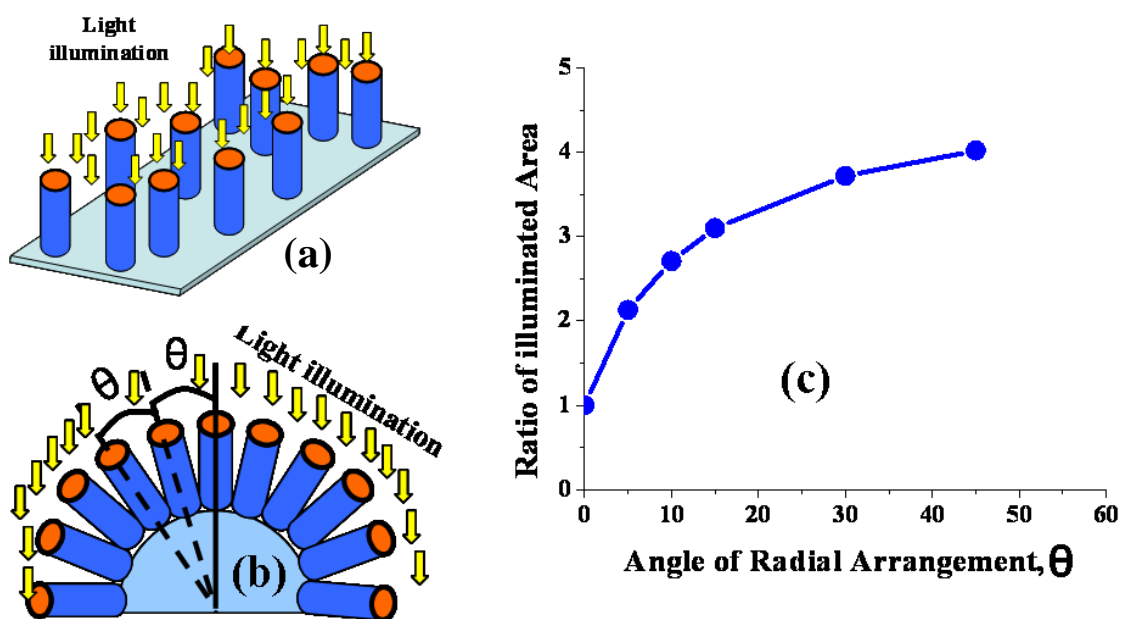
Following DEP deposition, FESEM images (fig. S-1) clearly show the sheets forming conducting bridges across the Au finger electrodes.



**Figure S-1.** FESEM image shows the deposition of the GO sheets between the Au finger electrodes due to dielectrophoretic forces. Inset shows a higher magnification image where the sheets are clearly visible as forming a bridge between the electrodes

## Difference in illumination area

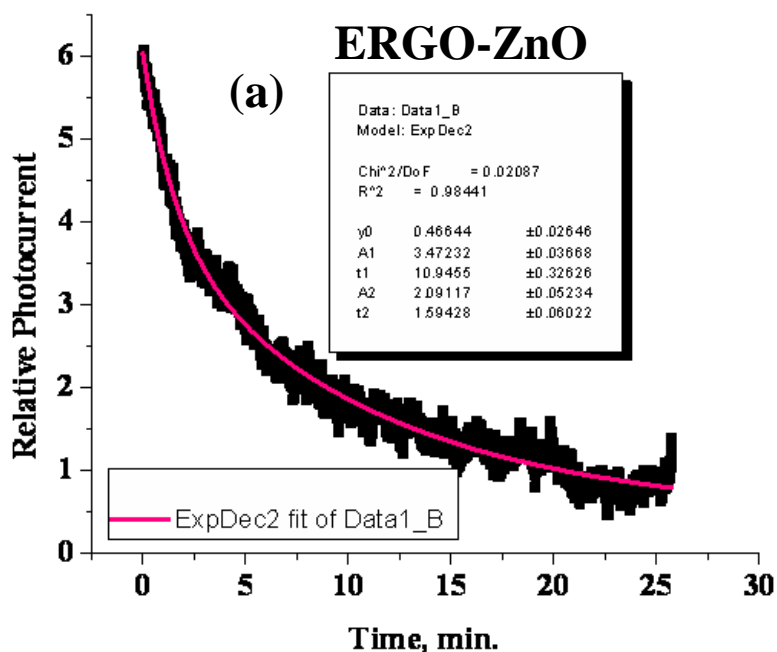
The comparison of the illuminated area is performed by considering vertical nano rods on a planar surface (Figure S-2a) and to simulate the ZnO-ERGO-Cell, angular rods on a hemisphere, (Figure S-2b). Both the assemblies are then considered to be illuminated by a collimated normal light source. Each assembly is taken to have an identical number of rods, with 200 nm diameter and 500 nm lengths. The ratio of the illuminated area is calculated for a varying angle of radial arrangement. The angle is governed by the no. of rods taken in the system. For e.g. with three rods the angle of radial arrangement will be  $90^\circ$ . For a  $45^\circ$  arrangement the no. of nano rods will be five. The increase in illuminated area for the radial arrangement is shown in Figure S-2c. We observed an increase of 200-400 % for radial angular arrangements of  $10^\circ$ - $45^\circ$ .

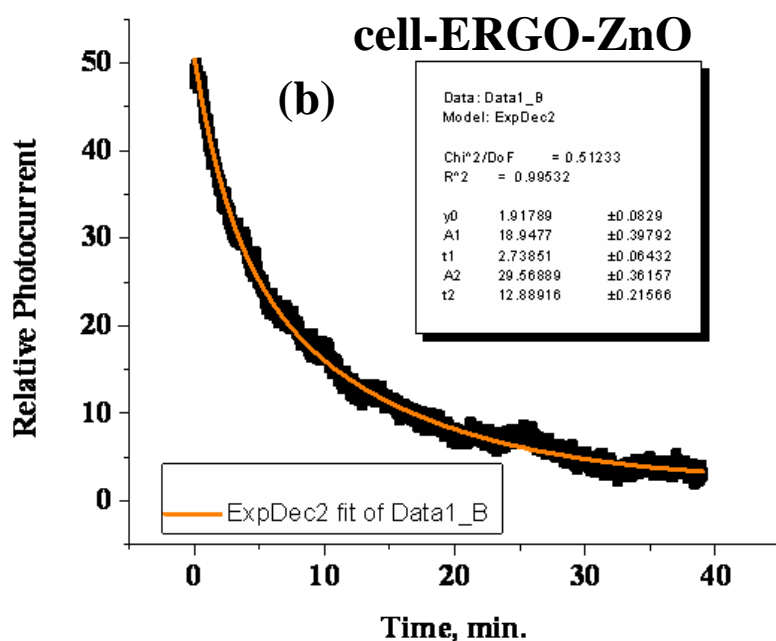


**Figure S-2:** (a) A typical vertical arrangement of the ZnO nanorods on being illuminated from a light source. Primarily only the cross sectional area of the rods will interact with the light photons. (b) An angular arrangement of the nano rods will lead to interaction of the light photons with the cross sectional area and also the cylindrical surface of the nanorods. The extend of cylindrical surface interacting with the photons will be governed by the angle of radial arrangement. (c) The ratio of the area illuminated in radial arrangement compared to vertical arrangement. Equal numbers of nano rods were taken in each arrangement. The total number of nano rods was governed by the angle of radial arrangement leading to a  $180^\circ$  profile in the set-up. The rods were taken to be 200 nm in diameter and 500 nm in length.

#### Decay of the photocurrent response:

The decay of the photocurrent in ZnO devices is typically fit to a double exponential decay indicative of the trapping of the holes by surface states and its possible relaxation mechanisms. For the ERGO-ZnO device the fits leads to decay times of  $\sim 11$  and 1.6 min. The cell-ERGO-ZnO device leads to decay time 13 and 2.7 min. The near identical range of the decay times is indicative that similar relaxation process underlies both the devices. This is expected since in both the devices the photo-excited electron-hole pairs are generated, with the electrons being injected into graphene while the holes are trapped by the surface states in ZnO.





**Figure S-3:** Double exponential decay fit to the relaxation of the photocurrent. (a) For the ERGO-ZnO device. (b) The fit to cell-ERGO-ZnO device.

#### Relative Effect of photo generated charge carriers between gold and ERGO:

Au typically has free carrier density of  $\sim 10^{23} / \text{cm}^3$ , in comparison graphene sheets (CVD prepared) have a reported carrier densities on the order of  $\sim 10^{11} / \text{cm}^2$ . The thickness of the sputtered gold layer on the IDGE is 50 nm, hence the carrier density is  $\sim 5 \times 10^{17} / \text{cm}^2$ . The observed photocurrent generated per device is  $\sim 40$  nano amps, this corresponds to  $\sim 2.5 \times 10^{11}$  photo generate charge carriers that are transferred to the Au-ERGO conducting pathway.. A single Au IDGE has an area of  $\sim 10^{-3} \text{ cm}^2$ . The total carrier concentration in the Au electrode is therefore orders of magnitude higher than the photo generate carriers. Hence the primary effect in photo current generation is due to the interaction between the ERGO and ZnO.

We have confirmed this by growing ZnO rods under similar conditions on a plane ITO coated substrate. ITO has a carrier density of  $\sim 10^{21} / \text{cm}^3$ .<sup>6</sup> The thickness of ITO was 150 nm (hence a carrier concentration of  $1.5 \times 10^{16} / \text{cm}^2$ ). Bias voltage was applied to this sample, on illumination with light (similar to the Cell-ERGO-ZnO sample) no increase in current was observed, due to the high carrier concentration in ITO which is hardly affected by the transfer of the photo-generated charge carriers from ZnO.

#### References

1. Hummers, W. S.; Offeman, R.E. *J. Am. Chem. Soc.* 1958, 80, 1339–1339.
2. Kovtyokhova, I.N.; Ollivier, J. P.; Martin, R. B.; Mallouk, E.T.; Chizhik, A. S.; Buzaneva, V.E.; Gorchinskiy, D.A. *Chem. Mater.* 1999, 11, 771- 778.
3. Zhu, C.; Guo, S.; Fang, Y.; Dong, S. *ACS Nano* 2010, 4, 2429-2437.
4. Maheshwari, V.; Kane J.; Saraf, R.F. *Adv. Mater* 2008, 20, 284-287.
5. He, S. J.; Song, B.; Li, D.; Zhu, C.F.; Qi, W.P.; Wen, Y.Q.; Wang, L.H.; Song, S.P.; Fang, H.P.; Fan, C.H. *Adv. Funct. Mater.* 2010, 20, 453–459.
6. Ishibashi, S.; Higuchi, Y.; Ota, Y.; Nakamura, K.; *J. Vac. Sci. Technol. A* 1990, 8, 1403.