ASSOCIATED CONTENT

Supporting Information. Electronic Supplementary Information (ESI) available: [Additional Details on preparation, model for device sensitivity and characterization]. See DOI: 10.1039/b000000x/

1. Semi-quantitative model for device sensitivity

We first use n-type depletion region as an example for analyzing potential barrier height change. When the positively charged hemoglobin molecules are absorbed on the surface of the NW, the electrons will be induced and the balance in the space charge region will be broken. Therefore, a new balance needs to be established. The appearance of the induced electrons caused the drop of the energy bank level in both n and p region. But the extent of the change is different, which caused the change of the p-n junction potential barrier height.

The calculation follows that: $n_{n0}\cdot n_{p0}$ are the balance electrons concentrations in n-type and p-type zone, respectively. p_{p0} is the balance hole concentrations in p-type zone. Φ is the p-n junction potential barrier height. Q is the induced charges.

$n_{n0}\cdot p_{p0} = ni^2$

$\Phi = q\cdot V_D = E_{Fn}-E_{Fp}$

$V_D = (E_{Fn}-E_{Fp})/q = [k_0\cdot T\cdot \ln(n_{n0}/n_{p0})]/q = [k_0 T\cdot \ln(n_{n0}\cdot p_{p0}/ni^2)]/q$

After adsorbing charges on the surface:

$V_D' = k_0 T\cdot \ln[(n_{n0} + Q)\cdot(p_{p0} - Q)/ni^2]/q$

The change of the potential barrier height is defined by:

$\Delta\Phi = q\cdot\Delta V_D = q\cdot(V_D'-V_D)$

$= k_0 T\cdot\{\ln[(n_{n0} + Q)\cdot(p_{p0} - Q)/ni^2] - \ln(n_{n0}\cdot p_{p0}/ni^2)\}$

$= k_0 T\cdot\ln[(n_{n0} + Q)\cdot(p_{p0} - Q)/(n_{n0}\cdot p_{p0})]$

When $Q > 0$ and $n_{n0} > p_{p0}$, $\Delta\Phi < 0$, that is the potential barrier height decreased.

When Q increases, the Φ will further decrease.

Under the reverse basis, the conductance is mainly dependent on the minority carrier. $n_{p0} = n_{n0}\exp(-qV_D/k_0T)$

$p_{n0} = p_{p0}\exp(-qV_D/k_0T)$

$Js = qD_n n_{p0}/L_n + qD_p p_{n0}/L_p$

$= [(qD_n/L_n)\, n_{n0} + (qD_p/L_p)\, p_{p0}]\exp(-qV_D/k_0T)$

$= [(qD_n/L_n)\, n_{n0} + (qD_p/L_p)\, p_{p0}]\exp(-\Phi/k_0T)$

When $\Delta\Phi < 0$, $\Delta Js > 0$, the reverse current $J=-Js$ increases.

2. Design of the nanoprobe

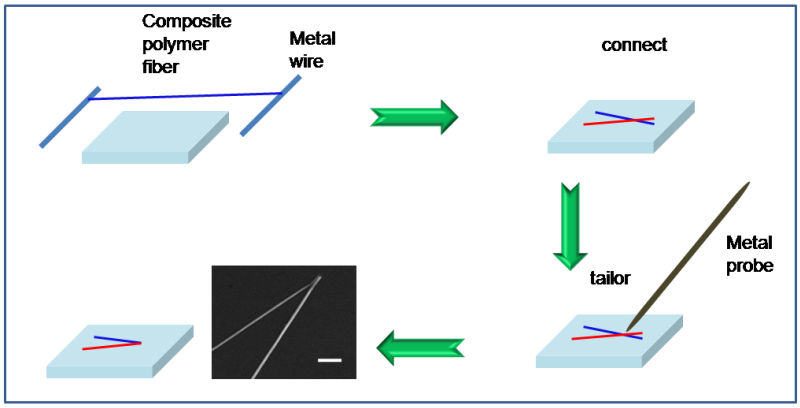

Figure S1. Schematic illustration of the fabricating procedure of single kinked NW heterojunction probe. A single composite polymer fiber containing Zn^{2+} with the diameter about 1μm was first deposited on a pair of parallel metal wires with vertical angle, and then placed on the substrate. The other single composite polymer fiber containing Ni^{2+} was assembled with the first fiber with a proper angle (controlled by prior marker) under the microscopy on the micro-manipulation platform. Then, the connected fibers were tailored by a metal probe on the micro-manipulation platform to form a tip. Finally, the sample was calcinated in air. More than 10 kinked NWs can be fabricated in 1 hour, and then for several hours calcinations. The change of kinked angle and arm length of the heterojunction will cause the variation in the electrical performance. Actually, the little variation can be got by precisely controlling the both aspects. Inset: Representative SEM image of a kinked ZnO-NiO NW with a 30° overall geometry. Scale bar, 10 μm.

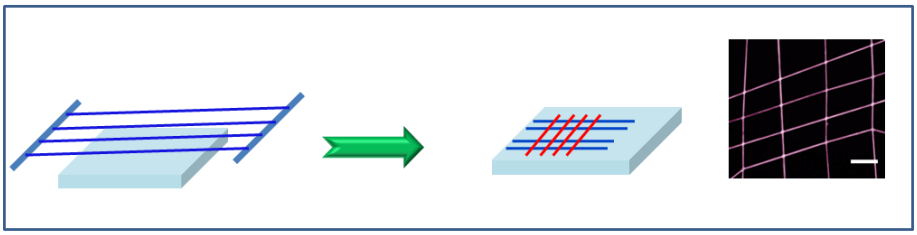

Figure S2. The preparation of the integrated network of heterojunction NWs. The approximately parallel-oriented fibers containing Zn^{2+} or Ni^{2+} were first deposited on the parallel metal wire then assembling and calcinating as discussed above. The key structural feature required to realize the multi-shaped building block is the preparation of parallel-oriented fibers as reported elsewhere.[1-2] Inset: Representative SEM image of the integrated ZnO-NiO NWs heterojunction network. Scale bar, 10 μm.

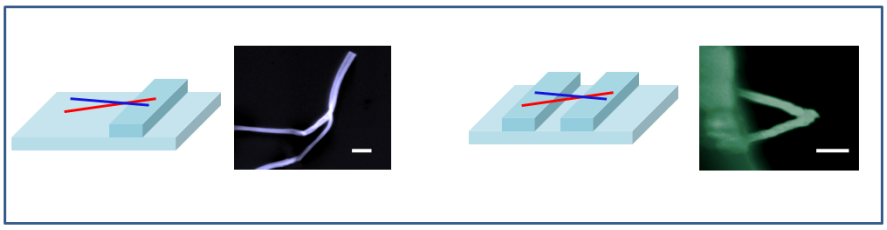

Figure S3. Two methods for fabricating single kinked NW based 3D nanoprobe. The left: Single fiber was controlled assembled on a substrate immobilized with a thin block to form a angle with respect to the substrate. Then the thin block was removed after calcinations. The right: Single fiber was controlled assembled on a substrate immobilized with two thin blocks, and the right thin block was removed after calcinations. Inset: Representative SEM images of the prepared 3D nanprobes using two different methods. Scale bar, 2 μm.

3. Characteristic of the prepared ZnO and NiO NWs

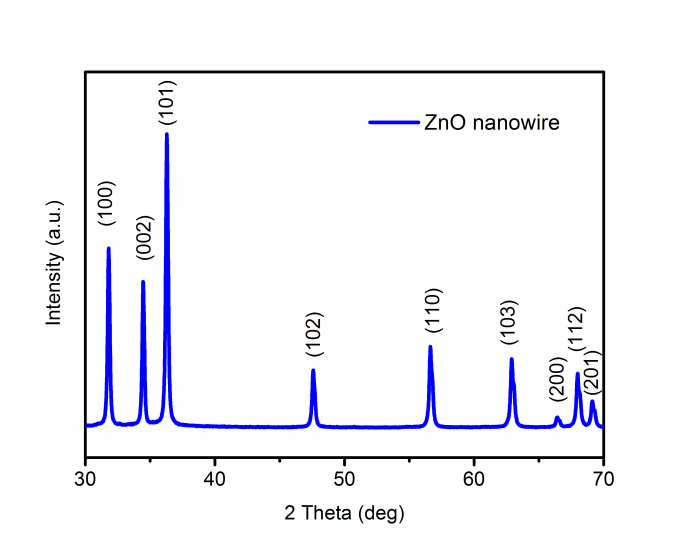

Figure S4. XRD patterns of the prepared ZnO NWs, all the diffraction peaks can be indexed as hexagonal ZnO crystal structure, and no impurity phase appears.

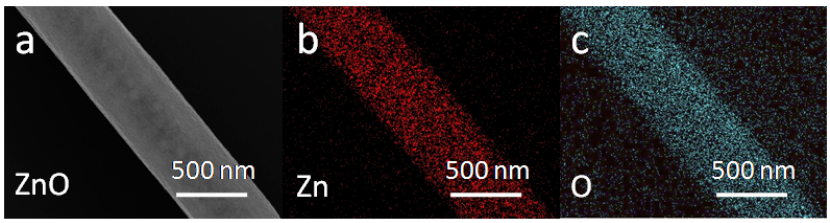

Figure S5. The EDX elemental mapping images of Zn and O in single prepared ZnO NW.

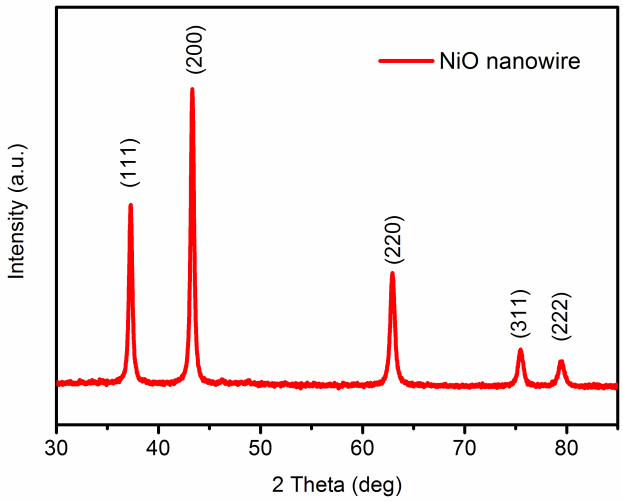

Figure S6. XRD patterns of the prepared NiO NWs, all the diffraction peaks reveal pure cubic crystalline NiO phase, and no impurity phase appears.

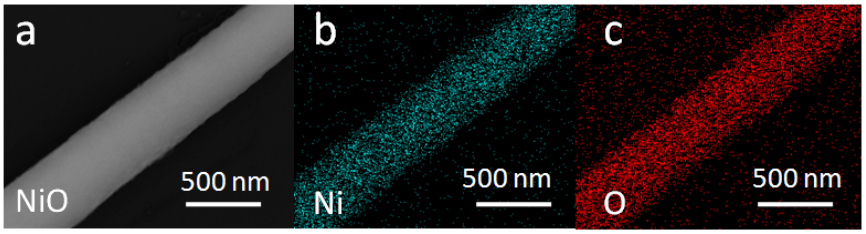

Figure S7. The EDX elemental mapping images of Ni and O in single prepared NiO NW.

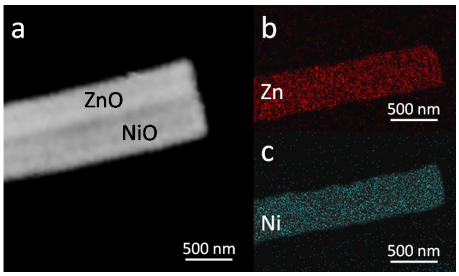

Figure S8. The EDX elemental mapping images of Ni and Zn at the tip of a kinked NW heterojunction.

4. **The specific performance and mechanism of the increased sensitivity as the increased embedded nanospheres (NS).**

The sensitivity (S) is defined as $S = \Delta I / I_0$, I_0 is the initial current, ΔI is the change of the current. In our experiment, the sensitivity increased as the increased embedded NiO NSs, the more NiO NSs in the ZnO NW arm, the more dramatic response. However, the increase of the sensitivity is not proportional to the number of embedded NiO NS. It is a qualitative performance, and hard to achieve quantification. As the ZnO NW and NiO NS have opposite conductivity types, the p-type NiO NS will block the electrons transport in the n-type ZnO NW channel. When introducing more p-type NiO NSs into n-type ZnO NW, the resistance will increase, as a result, the initial current will decrease. According to the definition ($S = \Delta I / I_0$), the sensitivity will increase. However, the NiO NS is usually not in the axis of the ZnO NW and there is always some part of the NiO NS is wrapped by ZnO NW during the synthesis process. In our experiment, the change of initial current is not proportional to the number of embedded NiO NS. So it is a qualitative performance.

5. Response to hemoglobin with various concentrations

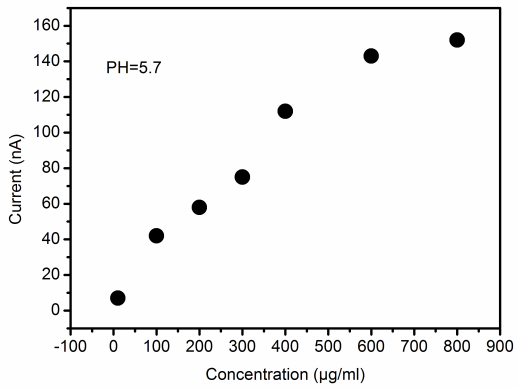

Figure S9. The response to various concentrations of hemoglobin, the increased concentrations result in the increased current.

6. Cell experiment

HL-1 cells are a cardiac muscle cell line derived from AT-1 mouse atrial cardiomyocyte tumor lineage. HL-1 cells were cultured using published protocols.[3] Nanoscale probe recording and cell manipulation were carried out in Tyrode solution (pH ~ 7.3). We monitored the calibrated potential change of nanoprobe while an isolated HL-1 cell was moved into contact and then away from the nanoprobe using a glass micropipette under microscopy visualization. While the nanoprobe tip is within the cell, the recorded potential changes and then maintains a relatively constant value and finally returns to baseline when the cell is detached from the nanowire probe end.

References

[1] T. D. Brown, P. D. Dalton, D. W. Hutmacher, Adv. Mater. 2011, 23, 5651–5657.

[2] D. Li, Y. Xia, Adv. Mater. 2004, 16, 1151–1170.

[3] W. C. Claycomb, N. A. Lanson, B. S. Stallworth, D. B. Egeland, J. B. Delcarpio, A. Bahinski, N. J. Izzo, Proc. Natl. Acad. Sci. USA 1998, 95, 2979-2984.