Supplementary Files

Nano-engineering and functionalization of hybrid Au-Me$_x$O$_y$-TiO$_2$ (Me=W, Ga) hetero-interfaces for optoelectronic receptors and nociceptors

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**Supplementary Figure S1.** Various developed optoelectronic devices based on (1) Au/WO$_3$:TiO$_2$/ITO, (2) Au/Ga$_2$O$_3$:TiO$_2$/ITO and (3) Au/Ga$_2$O$_3$ (N$_2$):TiO$_2$/ITO heterostructures.
Supplementary Figure S2. Sequential stage of deposition of WO$_3$:TiO$_2$ heterostructured film. (a) AFM (top) and FESEM image (down) of surface of bare Au film. The bare surface of Au substrate composed of granular Au structures (b) AFM image (top) and FESEM image (down) of WO$_3$ film deposited on Au substrate. Ultra-thin WO$_3$ film covered the surface of granular Au film. (c) AFM image (top) and FESEM image (down) of WO$_3$:TiO$_2$ heterostructured film. Both WO$_3$ and TiO$_2$ film have ultra-fine granular morphology.
Supplementary Figure S3. (a) Development of Pt protective coating on the top of the ALD deposited WO\textsubscript{3}/TiO\textsubscript{2} heterojunction and filed ion beam (FIB) cut for analysis of interface cross-section. (b) Magnified SEM image identified WO\textsubscript{3}/TiO\textsubscript{2} heterojunction. (c) High-magnification FIB-SEM measurement of the WO\textsubscript{3}/TiO\textsubscript{2} heterojunction interface. (d) High-resolution TEM observation of the WO\textsubscript{3}/TiO\textsubscript{2} heterojunction interface depicts the development of atomic-level ultra-sharp hetero-interfaces between WO\textsubscript{3} and TiO\textsubscript{2} films.
Supplementary Figure S4. (a) The FE-SEM top-view image of surface of as-deposited Ga$_2$O$_3$, (b) annealed Ga$_2$O$_3$ in N$_2$ atmosphere, (c) Ga$_2$O$_3$-TiO$_2$, and (d) Ga$_2$O$_3$ (N$_2$)-TiO$_2$ heterostructured films. The as-deposited Ga$_2$O$_3$ film has ultra-fine structure (Supplementary Figure 4a). After annealing in N$_2$ atmosphere, the grain size of Ga$_2$O$_3$ film is slightly increased (supplementary Figure 4b). The SEM observations showed development of uniform TiO$_2$ films over Ga$_2$O$_3$ and Ga$_2$O$_3$ (N$_2$) films.
Supplementary Figure S5. The spectrum in ultra-low binding energy region. The characteristics of Ga-N bonding is characterized in Ga$_2$O$_3$ films annealed in N$_2$ atmosphere.

Supplementary Figure S6. The characteristic peaks of Ga-3d in (a) Ga$_2$O$_3$, (b) Ga$_2$O$_3$ (N$_2$-450°C) and (c) Ga$_2$O$_3$ (N$_2$-600°C). The intensity of XPS characteristic peak of Ga-O bonding is constantly decreasing after RTA in N$_2$ atmosphere. It should be mentioned that the tangible decrease of Ga 3d peak of Ga-O bonds happened at the sample annealed at 600°C, an indication of replacement of Ga-N bonding instead of Ga-O bonding.
Supplementary Figure S7. Variation of photo-conductance values of Au/Ga$_2$O$_3$:TiO$_2$/ITO devices under illumination of visible LED lights with different wavelengths and intensities.
Supplementary Figure S8. Variation of photo-conductance of Au/Ga$_2$O$_3$ (N$_2$):TiO$_2$/ITO devices under illumination of visible LED lights with different wavelengths and intensities.
Supplementary note 1-Calculation of Schottky barrier height

Barrier height of a metal–semiconductor contact can be experimentally measured and determined by using I-V curves. Considering that the current is due to thermionic emission, the relation between the applied forward bias and current can be expressed by eq. (1):

\[ J = J_0 \exp \left( \frac{qV}{nkt} \right) \]

(1)

Where \( n \) is ideally factor, \( T \) is the temperature in Kelvin, \( q \) is the electron charge, \( k \) is the Boltzmann constant and \( I_0 \) is the reverse saturation current which can be extracted by extrapolation the straight line of \( \ln I \) to intercept the axis at zero voltage. The Schottky barrier height (SBH) can be calculated by extrapolation of semi-logarithmic \( J-V \) curves to \( V=0 \). The SBH can be calculated from (3):

\[ \Phi_B = \frac{kT \ln \frac{T^2 A^*}{J_0}}{q} \]

(2)

\[ A^* = \frac{4\pi m^* k^2}{h^3} \]

(3)

Where \( m^* \) is the effective electron mass, and \( h \) is the Planck’s constant. The \( A^* \) is the effective Richardson constant\(^{1-4} \) which is equal to 54.05 Acm\(^{-2}\)K\(^{-2}\) for WO\(_3\), 41.1 Acm\(^{-2}\)K\(^{-2}\) for Ga\(_2\)O\(_3\) and 26.4 Acm\(^{-2}\)K\(^{-2}\) for N\(_2\) doped Ga\(_2\)O\(_3\). The experimental \( J-V \) characteristics and the logarithmic scale of the same graphs are shown in Figure S4-S20. We used low forward bias of \( J-V \) curves to measure the SBH at Pt/TiO\(_2\) junctions. Taking the logarithmic version of eq. 2, we can extract the \( n \) and \( I_0 \) from the slope and Y axis of \( \ln J-V \) plot. After performing least square fitting on the \( \ln J-V \) plot in the linear region, the values of \( n \) and \( J_0 \) from the slope and the Y-axis can be determined.
Supplementary Figure S9. The variation of Schottky barrier height at Au/WO$_2$ at different light wavelengths.

Supplementary Figure S10. The $J$-$V_{ds}$ characteristics of Au/WO$_3$ device and Ln$J$-$V$ plot of the Au/WO$_3$ junction (Schottky diode) at the 273K and under dark condition.
**Supplementary Figure S11.** The $J-V_{ds}$ characteristics of Au/WO$_3$ device and Ln$J$-$V$ plot of the Au/WO$_3$ junction (Schottky diode) at the 273K under and $\lambda$= 470 nm illumination.

**Supplementary Figure S12.** The $J-V_{ds}$ characteristics of Au/WO$_3$ device and Ln$J$-$V$ plot of the Au/WO$_3$ junction (Schottky diode) at the 273K and under $\lambda$= 535 nm illumination.
Supplementary Figure S13. The $J-V_{ds}$ characteristics of Au/WO$_3$ device and Ln$J$-$V$ plot of the Au/WO$_3$ junction (Schottky diode) at the 273K and under $\lambda= 590$ nm illumination.

Supplementary Figure S14. The $J-V_{ds}$ characteristics of Au/WO$_3$ device and Ln$J$-$V$ plot of the Au/WO$_3$ junction (Schottky diode) at the 273K and under $\lambda= 655$ nm illumination.
**Supplementary Figure S15.** The variation of Schottky barrier height at Au/Ga$_2$O$_3$ at different light wavelengths.

**Supplementary Figure S16.** The $J$-$V_{ds}$ characteristics of Au/Ga$_2$O$_3$ device and Ln$J$-$V$ plot of the Au/WO$_3$ junction (Schottky diode) at the 273K and under dark condition.
Supplementary Figure S17. The $J$-$V_{ds}$ characteristics of Au/Ga$_2$O$_3$ device and LnJ-V plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda$= 470 nm illumination.

Supplementary Figure S18. The $J$-$V_{ds}$ characteristics of Au/Ga$_2$O$_3$ device and LnJ-V plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda$= 535 nm illumination.
Supplementary Figure S19. The J-V$_{ds}$ characteristics of Au/Ga$_2$O$_3$ device and (b) LnJ-V plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda$ = 590 nm illumination.

Supplementary Figure S20. The J-V$_{ds}$ characteristics of Au/Ga$_2$O$_3$ device and LnJ-V plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda$ = 655 nm illumination.
Supplementary Figure S21. The variation of Schottky barrier height at Au/Ga$_2$O$_3$ (N$_2$) at different light wavelengths.

Supplementary Figure S22. The $J$-$V_{ds}$ characteristics of Au/Ga$_2$O$_3$ (N$_2$) device and Ln$J$-$V$ plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K under and dark condition.
Supplementary Figure S23. The $J-V_{ds}$ characteristics of Au/Ga$_2$O$_3$ ($N_2$) device and Ln $J$-V plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda = 470$ nm illumination.

Supplementary Figure S24. The $J-V_{ds}$ characteristics of Au/Ga$_2$O$_3$ ($N_2$) device and Ln $J$-V plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda = 535$ nm illumination.
**Supplementary Figure S25.** The $J$-$V_{ds}$ characteristics of Au/Ga$_2$O$_3$ (N$_2$) device and Ln $J$-$V$ plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda$ = 590 nm illumination.

**Supplementary Figure S26.** The $J$-$V_{ds}$ characteristics of Au/Ga$_2$O$_3$ (N$_2$) device and Ln $J$-$V$ plot of the Au/Ga$_2$O$_3$ junction (Schottky diode) at the 273K and under $\lambda$ = 635 nm illumination.
Supplementary note 2: Band alignment calculation at WO₃-TiO₂ and Ga₂O₃-TiO₂ heterostructure

Based on Kraut’s method, the valence band offset (VBO) can be extracted by following formula:\(^5, 6:\)

\[
\Delta E_V = (E_{W_4F}^{WO_3} - E_{VBM}^{WO_3}) - (E_{T_i2p}^{TiO_2} - E_{VBM}^{TiO_2}) - (E_{W_4F}^{WO_3} - E_{T_i2p}^{TiO_2})
\]

(4)

\[
\Delta E_V = (E_{Ga2p}^{Ga_2O_3} - E_{VBM}^{Ga_2O_3}) - (E_{T_i2p}^{TiO_2} - E_{VBM}^{TiO_2}) - (E_{Ga2p}^{Ga_2O_3} - E_{T_i2p}^{TiO_2})
\]

(5)

\[
\Delta E_V = (E_{Ga2p}^{Ga_2O_3(N2)} - E_{VBM}^{Ga_2O_3(N2)}) - (E_{T_i2p}^{TiO_2} - E_{VBM}^{TiO_2}) - (E_{Ga2p}^{Ga_2O_3(N2)} - E_{T_i2p}^{TiO_2})
\]

(6)

In which, \(E_{W_4F}^{WO_3}\) is core level (CL) spectra of W 4F, \(E_{VBM}^{WO_3}\) is the valence band maximum (VBM) of WO₃, \(E_{Ga2p}^{Ga_2O_3}\) is core level (CL) spectra of Ga 2p, \(E_{VBM}^{Ga_2O_3}\) is the valence band maximum (VBM) of Ga₂O₃, \(E_{T_i2p}^{TiO_2}\) is the CL of Ti 2P spectra, \(E_{VBM}^{TiO_2}\) is the VBM of TiO₂. To calculate the VBM of WO₃, Ga₂O₃, Ga₂O₃ (N₂) and TiO₂, the XPS spectra of WO₃-TiO₂, Ga₂O₃-TiO₂, Ga₂O₃ (N₂)-TiO₂ were used (Supplementary Figure S27-S29). To describe the integrated band offsets of WO₃-TiO₂, Ga₂O₃-TiO₂, Ga₂O₃ (N₂)-TiO₂ heterojunctions, the corresponding energy difference between conduction bands can be calculated from Formula (7, 8 and 9):

\[
\Delta E_C = E_{Bandgap}^{WO_3} - E_{Bandgap}^{TiO_2} - \Delta E_V
\]

(7)

\[
\Delta E_C = E_{Bandgap}^{Ga_2O_3} - E_{Bandgap}^{TiO_2} - \Delta E_V
\]

(8)

\[
\Delta E_C = E_{Bandgap}^{Ga_2O_3(N2)} - E_{Bandgap}^{TiO_2} - \Delta E_V
\]

(9)
Supplementary Figure S27. Parameters for calculation of energy band alignment at WO₃-TiO₂ heterostructures.
Supplementary Figure S28. Parameters for calculation of energy band alignment at Ga$_2$O$_3$-TiO$_2$ heterostructures.
Supplementary Figure S29. Parameters for calculation of energy band alignment at Ga$_2$O$_3$ ($N_2$)-TiO$_2$ heterostructures.
Supplementary Figure S30. Photocurrent variation of WO\textsubscript{3} and WO\textsubscript{3}-TiO\textsubscript{2} heterostructured device at different light wavelengths, various light intensities and different TiO\textsubscript{2} thicknesses (7 nm and 19 nm).
Supplementary Figure S31. Photocurrent variation of Ga$_2$O$_3$-TiO$_2$ (7 nm) heterostructured device at different light wavelengths, and various light intensities.
Supplementary Figure S32. Photocurrent variation of Ga$_2$O$_3$-TiO$_2$ (19 nm) heterostructured device at different light wavelengths, and various light intensities.
Supplementary Figure S33. Photocurrent variation of Ga$_2$O$_3$(N$_2$)-TiO$_2$ (7 nm) heterostructured device at different light wavelengths.
Supplementary Figure S34. Photocurrent variation of Ga$_2$O$_3$ (N$_2$)-TiO$_2$ (19 nm) heterostructured device at different light wavelengths, and various light intensities.
Supplementary Figure S35. Variation of dark current of Ga$_2$O$_3$-TiO$_2$ (19 nm) and Ga$_2$O$_3$ (N$_2$)-TiO$_2$ based devices which were employed as nociceptive devices.

Table S1: The characteristics of receptors of presented study for $\lambda$= 655 nm light with the power density of 25 $\mu$W/cm$^2$.

<table>
<thead>
<tr>
<th>Device</th>
<th>Photoresponsivity</th>
<th>EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$-TiO$_2$</td>
<td>0.4 mA/W</td>
<td>6.28%</td>
</tr>
<tr>
<td>Ga$_2$O$_3$-TiO$_2$</td>
<td>1.8 mA/W</td>
<td>28.2%</td>
</tr>
<tr>
<td>Ga$_2$O$_3$(N$_2$)-TiO$_2$</td>
<td>3.6 mA/W</td>
<td>56.5%</td>
</tr>
</tbody>
</table>
**Supplementary Figure S36.** The nociceptive performance of another similar Ga$_2$O$_3$ (N$_2$)-TiO$_2$ device presented for comparison. (a) The relaxation characteristics of device. (b) The behaviour of device in normal and abnormal state. (c) The hyperalgesia and allodynia characteristics of device.

**Table S2:** The signal to noise ration of Ga$_2$O$_3$ (N$_2$)-TiO$_2$ normal nociceptor devices for $\lambda= 655$ nm light at on-state and saturation condition for different light intensities.

<table>
<thead>
<tr>
<th>Light power intensity ($\mu$W/cm$^2$)</th>
<th>Signal to noise ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>$11\times10^6$</td>
</tr>
<tr>
<td>10</td>
<td>$25\times10^6$</td>
</tr>
<tr>
<td>15</td>
<td>$78\times10^6$</td>
</tr>
<tr>
<td>20</td>
<td>$91\times10^6$</td>
</tr>
</tbody>
</table>
References:

1. V. S. Fomenko, G. V. Samsonov, Handbook of thermodynamic properties, electronic work functions and Richardson constants of elements and compounds, Plenum Press data Division, NewYork • 1966


