Supporting Information

Synergistic Effect of Au Interband Transition on Graphene Oxide/ZnO Heterostructure: Experimental Analysis with FDTD Simulation

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1. Raman Spectroscopy

The crystallite size of GO is calculated using the intensity ratio $I_D/I_G$ from Raman spectra as depicted by L. G. Cancado et.al\textsuperscript{1}.

$$L_a(\text{nm}) = 2.4 \times 10^{-10} \lambda_I^4 \left(\frac{I_D}{I_G}\right)^{-1}$$

(1)

Where $L_a$ is crystallite size, $\lambda_I$ is the wavelength of the excitation laser, which is 514 nm (or 2.41 eV) and area intensity ratio ($I_D/I_G$) of D and G peak of Raman spectra which is calculated to be 1.76. Now, the constant C ($\lambda$) is equal to $(2.4\times10^{-10})\lambda^4$, which is dependent on the excitation wavelength of the laser used in Raman spectra. After substituting the values in equation 1, the crystallite size of GO is calculated to be 9.5 nm.

2. UV-Vis Spectroscopy

(a) Transmittance measurement of graphene oxide
Figure S1: Transmittance spectrum of Graphene Oxide.

The transmittance of the GO shows that it is highly transparent in the NIR and visible region. The dip in transparency is seen in UV at ~305 nm wavelength of the electromagnetic spectrum, which is essentially the absorbance region of GO. The GO assists in the device's overall photoresponse due to absorbance in the UV region.

(b) Bandgap energy calculation of ZnO by Tauc plot

The optical bandgap of the synthesized ZnO is calculated using Tauc plot through UV-Vis spectra using the following equation:

\[(\alpha h\nu)^{1/n} = A^* (h\nu - E_g)\]  \hspace{1cm} (2)

Where \(h\) is Planck's constant, \(\nu\) is a photon frequency, \(\alpha\) is an absorption coefficient, \(E_g\) is the bandgap energy, \(A^*\) is a slope of the Tauc plot. And \(n\) is \(1/2\) for the direct allowed transitions. After calculation using equation 2, we found that the bandgap energy of ZnO is 3.25 eV.

Figure S2: Graph for bandgap energy calculation of ZnO by Tauc plot.
3. XRD Analysis

Debye-Scherrer formula is used to calculate the crystallite size of ZnO:

\[
d = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

(3)

Where \(d\) is the crystallite size, \(\lambda\) is the X-ray wavelength of Cu K-\(\alpha\) (i.e. 1.54 Å), \(\beta\) is FWHM of the peak in radian, \(\theta\) is Braggs' diffraction angle of the peak, i.e. 34° for (002) plane of ZnO. The FWHM for the (002) plane of Hexagonal crystal after subtracting the instrument broadening, i.e. 0.145°, is calculated to be 0.445° (0.59°-0.145°). After substituting all the values in equation 3 we calculated the value of crystallite size to be ~18 nm.

![XRD pattern](image)

**Figure S3:** XRD pattern for crystallite size calculation of ZnO by Sherrer equation.

4. Particle Size distribution Analysis from SEM Image.

![Particle size distribution](image)

**Figure S4:** Particle size distribution of ZnO.
The particle size of ZnO is measured from FESEM image using ImageJ software and plotted with Gauss Amp fitting using Origin 8.5 Software.

5. Photoelectrical Analysis

(a) On-Off switching of the device-1 (i.e. GO/ZnO/Au_film) with the light of 365 nm at different bias voltages

**Figure S5:** (a-i) On-Off switching of the device-1 (i.e. GO/ZnO/Au_film) with the light of 365 nm (2 mW at 0.1 Hz) from bias voltage -2 V to +2V.
(b) On-Off switching of the device-2 (i.e. GO/Au_np/ZnO/Au_film) with the light of 365 nm at different bias voltages

Figure S6: (a-i) On–Off switching of the device-2 (i.e. GO/Au_np/ZnO/Au_film) with light of 365 nm (2 mW at 0.1 Hz) from bias voltage -2 V to +2 V.

The figure S5 (a-i) shows the ON-OFF ratio of the device-1 (i.e. GO/ZnO/Au_film) at bias voltage from -2 V to +2 V, which shows that the device-1 works well in the photoconductive mode as well as in self-powered mode but with the increase in current ratio at the applied bias voltages (i.e. photoconductive mode) as compared to self-powered mode. Similarly, device-2 (i.e. GO/Au_np/ZnO/Au_film), shown in figure S6 (a-i), also shows an increase in current ratio at photoconductive mode compared to self-powered mode. Now, if we compare device-1 and device-2, we observe a many-fold increase in current ratio at all the bias voltages of device-2 compared to device-1, which is due to the contribution of the Au_np in the device-2.
6. Ultra-violet photoelectron Spectroscopy of GO work function Calculations

![Figure S7: UPS spectrum for the estimation of the work function of GO.](image)

The UPS spectrum of GO is taken using He-I excitation of energy 21.22 eV. The work function is calculated using equation 4\(^4\)^\(^6\):-

$$\Phi = h\nu - \Delta E$$  \(\text{(4)}\)

Where \(\Phi\) is a work function, \(h\nu\) is the energy of He-I, i.e. 21.22 eV and \(\Delta E\) is calculated considering the intersection point of the slope of the spectrum at a higher energy at y-axis (y = 0) and the Fermi level where the tail of the spectrum merges with the y-axis (y = 0). After calculation using equation 4, the work function of GO is estimated to be \(~5.84\) eV\(^7\).

7. FDTD Simulation

A commercial software "Ansys Lumerical" is used for the simulation to look into the optical cross-section and spatial electric field intensity distribution associated with Au, ZnO and Au/ZnO heterostructure\(^8\). The same software package has been used extensively by many researchers\(^9\)\(^-\)\(^11\). Spherical geometry is considered for simulating nine Au nano-spherical nanoparticles, and hexagonal geometry is considered for ZnO. The experimental data of Palik and Johnson, and Christy are extracted from the Lumerical database to calculate the real and imaginary part of the permittivity values of glass and Au, respectively\(^12\)\(^,\)\(^13\). However, ZnO thin film’s experimental refractive index data is taken from the recently available publication\(^14\).
Since the refractive index governs the intensity of scattered light\textsuperscript{15}, the relative refractive index of the surrounding medium is considered 1.0 for air. FDTD simulation space is defined in the beginning. Subsequently, symmetric, antisymmetric, including perfectly matched layers (PML) boundary conditions are applied (which absorbs radiation and can reflect evanescent fields) in the edges of this space\textsuperscript{16,17}. The dimensions of the FDTD model space is preferred to be sufficiently large to ensure that the simulated structure never interacts with the evanescent fields. The primary reason for choosing the bigger FDTD spaces is to ensure that the space of the FDTD simulation does not influence the absorption spectra. Figure S8(a) indicates the entire simulation setup under the FDTD region. The mesh size is automatically generated in the areas where the refractive index changes quickly as well as the geometries are small. The override meshing dimensions dx, dy and dz are set to 0.3 nm. Total Field Scatter Field (TFSF) is employed as a light source that makes use of plane waves within the shape of a box in which the nanoparticles are kept inside. One side of the box provides the incident light, propagation direction and polarization. S polarized radiation is considered and allowed to incident perpendicular direction to the plane containing Au\_np, shown in figure S8(b). We also performed the simulation process using P polarized radiation and found similar results. Furthermore, power monitors are positioned in such a way that they may form small boxes, one of these kept inside the TFSF source and another one positioned outside of the source.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(a) Schematic for the simulation setup under the FDTD region using Total Field Scatter Field (TFSF) and (b) Schematic setup for the incident light and the propagation direction of S polarized radiation perpendicular to the plane of Au\_np.}
\end{figure}

All the parameters for simulation of the spatial distribution of electric field intensity (|E|\textsuperscript{2}) of Au\_np and combined Au\_np/ZnO nanostructure are listed in Table S1 and Table S2.
**Table S1:** Crystallite size and thickness of ZnO layer

| Structure  | Radius (nm) | Thickness (nm) |
|------------|-------------|----------------|
| Hexagonal  | 12          | 80             |

**Table S2:** Parameters related to the simulated region

| Parameter                     | Dimension along x (nm) | Dimension along y (nm) | Dimension along z (nm) |
|-------------------------------|-------------------------|-------------------------|-------------------------|
| Mesh region                   | 40                      | 40                      | 160                     |
| Light source (TFSF)           | 360                     | 360                     | 140                     |
| Total field region            | 330                     | 330                     | 120                     |
| Scattered field region        | 400                     | 400                     | 160                     |

**Figure S9:** (a) FDTD simulated spatial distribution of electric field intensity of 4 nm size Au_np at ~526 nm, i.e. LSPR region, and (b) FDTD simulated spatial distribution of electric field intensity of Au_np/ZnO at 526 nm wavelength of the electromagnetic spectrum. (c) FDTD simulated UV-Vis absorption cross-section spectra with size variation of the Au_np.

The spatial electric field intensity ($|E|^2$) distribution of the Au_np and Au_np/ZnO at the plasmonic region is shown in figure S9 (a-b) above. And figure S9 (c) shows absorption cross-section spectra for the size variation of the Au nanoparticle.
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