Supplemental material for '' **Plasmonic Metal-to-Semiconductor Switching in Au nanorod-ZnO nanocomposite films''**

Fei Wu•, Limei Tian•, Ravindra Kanjolia*, Srikanth Singamaneni•, Parag Banerjee•

•Department of Mechanical Engineering and Materials Science, One Brookings Drive, Washington University in St. Louis, St. Louis, MO – 63130.

*SAFC Hitech, 1429 Hilldale Ave, Haverhill, MA – 01832.

Section S1. The detail processes of synthesizing AuNRs.

Synthesis of gold nanorods: Gold nanorods were synthesized using a seed-mediated approach.[1] Seed solution was prepared by adding 0.6 mL of an ice-cold solution of 10 mM sodium borohydride into 10mL of magnetically stirred 0.1 M CTAB and 2.5×10^{-4} M $HAuCl_4$ aqueous solution at room temperature. The color of the seed solution changed from yellow to brown. Growth solution was prepared by mixing 95 mL of 0.1 M CTAB, 1.0 mL of 10 mM silver nitrate, 4.5 mL of 10mM $HAuCl_4$, and 0.55 mL of 0.1 M ascorbic acid in the same order. The solution was homogenized by gentle stirring. To the resulting colorless solution, 0.12 mL of freshly prepared seed solution was added and set aside in dark for 14 h. Prior to use, the AuNR solution was centrifuged at 13,000 rpm for10 minto remove excess CTAB and redispersed in DI water (18.2MΩ-cm). The centrifugation procedure was repeated twice.

Adsorption of AuNR on glass surface: Glass substrates were cut into approximately 1×2 cm rectangular slides and cleaned in piranha solution (3:1 (v/v) mixture of H_2SO_4 and 30% H_2O_2) followed by extensive rinsing with DI water. AuNR was adsorbed onto glass substrates following the modification of the surface with (3-mercaptopropyl)-triethoxy-silane (MPTES) by exposing the glass surface to 1% MPTES in ethanol for 15 min followed by ultrasonication in ethanol for 15 min and rinsing with nano-pure water. Subsequently, the glass surface was exposed to AuNR solution for 2 h and 48 h to obtain different density of AuNR on substrates respectively, followed by rinsing with water to remove the loosely bound nanoparticles.

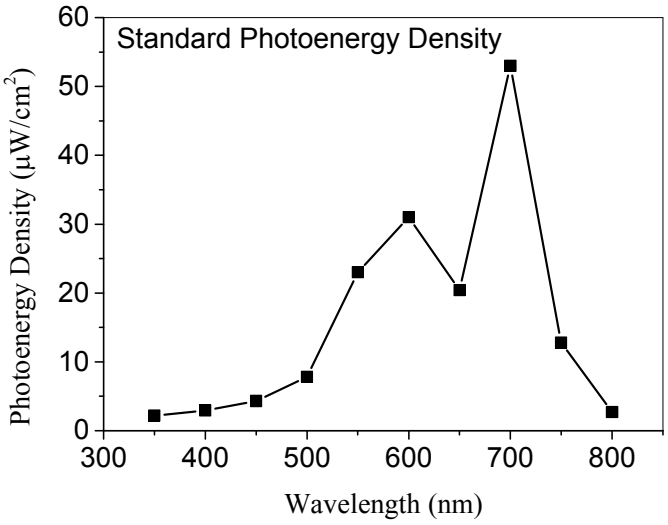

Figure S2. A light meter (PM100D Thor Labs) was used to measure the light intensity of the Edwards MI150 high intensity lamp at specific wavelengths from 300 nm to 800 nm with 50 nm intervals. The Si photodetector was placed inside the JANIS ST-500 probe station at the same position/orientation from the lamp as that used for testing the AuNR-ZnO samples. As can be seen in the graph above, there is very weak UV light intensity, indicating that the photoresponse observed in our experiment comes from visible light. The integrated white light power density is 5.7 mW/cm^2.

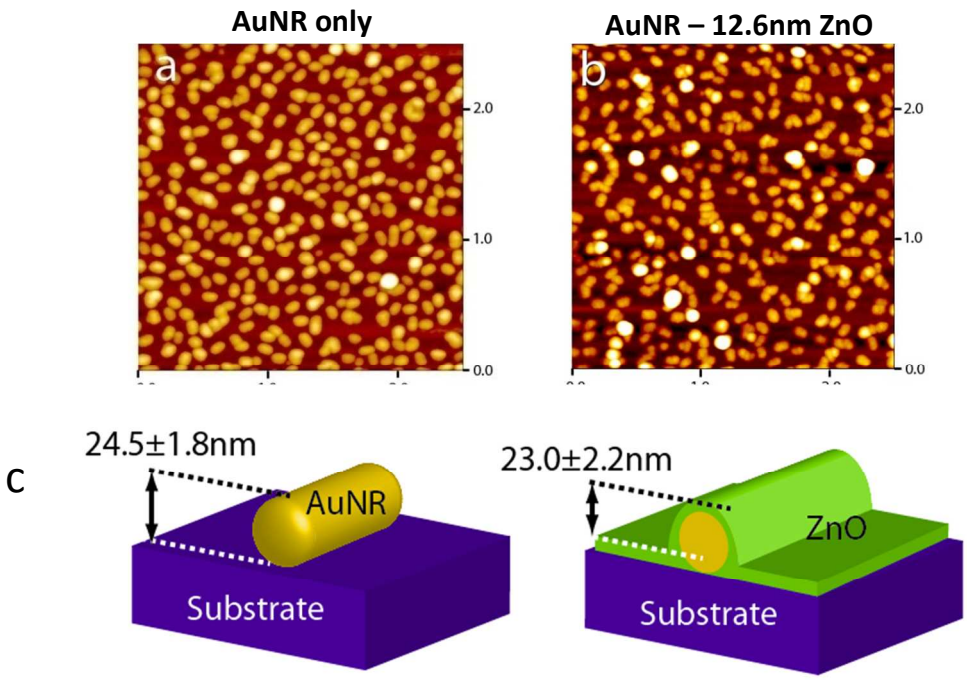

Figure S3. The AFM image of a) pristine low density AuNRs, b) low density AuNRs-12.6nm ZnO, (height scale in both images : 80 nm) c) schematic of AuNRs coated with ZnO; Analyses of height measurements across 50 AuNRs revealed that the diameter of AuNRs does not change significantly when depositing 12.6nm ZnO. The diameter of AuNRs before ZnO deposition (24.5±1.8nm) and after 12.3nm ZnO (23.0±2.2nm) remained virtually unchanged, suggesting conformal deposition of ZnO on these nanostructures.

Section S4. The calculation of the depletion width of AuNRs-ZnO.

$$W_d = \sqrt{4\varepsilon_0\varepsilon_{ZnO}\emptyset/qN_0}$$

where,[2] ε_{ZnO}, relative dielectric constant=8.5[2]; ϕ, due to band bending at the surface =1.15eV[3]; and N_0, free carrier concentration[4] =7×10^{18}/cm^3 for ALD ZnO films. From the equation and using the values above, W_d is calculated to be 17.6nm. This implies that for the12.6nm sample, the whole film is depleted whereas only part of the 20.3 and 35.6nm films are depleted. For the nanocomposite films comprising of AuNRs and the ZnO thin films, the situation is slightly different due to the presence of the AuNRs. Since the Au-ZnO contact is Schottky contact with a barrier height of 0.65eV[5], the band diagram of the AuNR-ZnO nanocomposite films resembles an asymmetric, back-to-back Schottky diode.

References

1 K. S. Lee and M. A. El-Sayed, J Phys Chem B **109** (43), 20331 (2005); C. J. Orendorff and C. J. Murphy, J Phys Chem B **110** (9), 3990 (2006).

2 R. Collins and D. Thomas, Physical Review **112** (2), 388 (1958); J. M. Bao, I. Shalish, Z. H. Su, R. Gurwitz, F. Capasso, X. W. Wang, and Z. F. Ren, Nanoscale Res Lett **6** (2011).

3 K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, and B. E. Gnade, J Appl Phys **79** (10), 7983 (1996).

4 E. Guziewicz, M. Godlewski, T. A. Krajewski, L. Wachnicki, G. Luka, W. Paszkowicz, J. Z. Domagala, E. Przezdziecka, E. Lusakowska, and B. S. Witkowski, Acta Phys Pol A **116** (5), 814 (2009); E. Przezdziecka, L. Wachnicki, W. Paszkowicz, E. Lusakowska, T. Krajewski, G. Luka, E. Guziewicz, and M. Godlewski, Semicond Sci Tech **24** (10) (2009).

5 Sanghyun Ju, Sunkook Kim, Saeed Mohammadi, David B. Janes, Young-Geun Ha, Antonio Facchetti, and Tobin J. Marks, Appl Phys Lett **92** (2), 022104 (2008).