Supporting Information

Label-free dual sensing of DNA molecules using GaN nanowires

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Figure S-1, corresponding author's name: Li-Chyong Chen

Figure S-1. Verification of *MPTS*-modification by X-ray photoelectron spectroscopic (XPS) technique: (a) S2p and (b) Au4f spectra of *MPTS*-modified *GaNNWs*, treated with Au NPs.

Figure S-1a, narrow scan of Au4f spectra, illustrated two intense peaks, corresponding to binding energies of Au4f_{5/2} and Au 4f_{7/2}, characteristics of Au⁰ species (pure Au metal signal). However, a clear indication of shoulders at higher binding energy along with the main signals reveals an oxidative state of Au species. By fitting with four Gaussian functions with the same FWHM of 1.05 eV, two additional peaks are found at the binding energies of 89.02 and 84.93 eV, adjacent to Au⁰ 4f_{5/2} (87.73 eV) and Au⁰ 4f_{7/2} (84.06 eV) respectively. The intense high binding energy peaks at ~85 eV (adjacent to Au⁰ 4f_{7/2} peak) is mostly due to Au⁺ sulfide species¹.

Figure S-1b represents the S2p XPS spectrum with presence of two doublets. The best fit to the data was obtained with four Gaussian functions with the same full width at half maximum (FWHM) of 1.5 eV, the standard spin–orbit splitting of 1.2 eV and an area ratio of 1:2 (S2p_{1/2}: S2p_{3/2}). The first doublet, D(1), corresponding to binding energies of S2p_{3/2} and S2p_{1/2} at 161.761 and 162.898 eV, respectively, are characteristic of thiolate species and evidence the chemisorptions of organosulfur molecules on Au NPs². The second doublet, D(2), with S2p_{3/2} at 163.343 and S2p_{1/2} at 164.59 eV, has been assigned to unbound thiol or disulfide species

within or on top of the thiolate layer. Same signal has been observed on poorly rinsed alkanethiol SAM^{3,5} and has been assigned to unbound thiol. Another possibility can arise from progressive S-Au bond breaking and creation of new sulfur species, under prolonged X-ray radiation⁵. Both can be possible in our case, since in order to improve the poor S2p signal, a long accumulation time has been used.

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- (2) Ishida, T.; Choi, N.; Mizutani, W.; Tokumoto, H.; Kojima, I.; Azebara, H.; Hokari, H.; Akiba, U.; Fujihira, M. *Langmuir* **1999**, 15, 6799.
- (3) Castner, D. G.; Hinds, K.; Grainger, D. W. *Langmuir* **1996**, 12, 5083.

Figure S-2, corresponding author's name: Li-Chyong Chen

Figure S-2. Verification of *MPTS*-modification. a, A typical bright-field and dark-field (inset) TEM images exhibiting the distribution of Au NPs on the *MPTS*-modified *GaNNWs*. b, The corresponding HR-TEM image and SAD pattern (inset) confirming the identity of Au NPs on the NW.

The possibility of physisorption of Au NPs on NW-surface can be ruled out, since the sample was subjected to multiple cleaning and rinsing. For controlled experiment, pristine NWs (without any surface-modification) were treated with same Au NPs in a similar fashion. The bright field TEM image (Figure S-2c) and the corresponding HR-TEM image (Figure S-2d) revealed absence of Au NPs on the NWs surface. The comparative study clearly showed that only NWs with *MPTS*-modification will have Au NPs attachment.

Figure S-3, corresponding author's name: Li-Chyong Chen

Figure S-3. Visualization of DNA-immobilization & hybridization.

Verification of probe DNA-immobilization: Figure S-3a shows a fluorescent image of *MPTS*-modified *GaNNWs* treated with FAM-labeled *pLF*, along with its corresponding transmitted (Figure S-3b) and the resultant overlapped images (Figure S-3c). The fluorescence from FAM produces a clear evidence of the immobilization of *pLF* on the *MPTS*-modified NWs.

In order to rule out the possibility of physisorption of probe DNA molecules, the pristine NWs (without *MPTS*-modification) were directly treated with FAM-labeled *pLF* in a similar fashion. No fluorescence from FAM, hence no indication of DNA (Figures S-3d-f) can be observed. Thus, the immobilization of probe-DNA molecule on the NW-surface is indeed established through a binding with *MPTS*, rather than mere physisorption.

Verification of DNA-hybridization: (Figure S-3g-i) described in text (please check Figure 2c-e).

Figure S-4, corresponding author's name: Li-Chyong Chen

Figure S-4. The *in situ* electrochemical impedance study on immobilization of *pLF* (3.3 μM). The *in situ* impedance study on *pLF*-immobilization on *GaNNWs* was performed at every hour, using 1 ml of 10 μM *pLF* in 5 ml PB Buffer solution (pH=7.42). The final concentration was 3.3 μM of *pLF*. a, shows Nyquist plots at different time (immobilization-time). The corresponding Bode plots represent the variation of phase angle with frequency in b. The original peak, in Bode plot (Figure S-4b), corresponding to *MPTS*-modified *GaNNWs* (similar to the spectra at time = 0 hrs), was found to be shifted to higher frequency with the immobilization-time. At longer immobilization-time (about > 10 hrs), an indication of additional peak formation, at higher frequency, can be observed. Nyquist Plot (Figure S-4a) also exhibits an appearance of hump (an indication of an additional semicircle region) at the higher Z' -range. The phenomenon is not as prominent as for *pLF*-modified NWs (the concentration of *pLF* is 10 μM) used in the *in situ* DNA-hybridization study (Figures 3a-b), because of low concentration value of *pLF* (3.3 μM) used in the present study. Nevertheless, it is quite clear that, due to *pLF*-immobilization, an additional capacitive element was created, as discussed in the text.

Figure S-5, corresponding author's name: Li-Chyong Chen

Figure S-5. The EIS study on surface-modification of *GaNNWs*. a, Nyquist plots of unmodified, hydroxylated and *MPTS*-modified *GaNNWs*. b, The corresponding Bode Plot representing variation of phase angle with frequency.

Figure S-5 revealed that neither the “hydroxylated” nor the *MPTS*-modified *GaNNWs* showed any individual electrochemical characteristics. Both the plots suggested an increase in interfacial electron-transfer resistance (R_{et}) between *GaNNWs* and electrolyte, which is a usual phenomena since the insulating nature of oxide/*MPTS* layer could hinder the electron-transfer from electrolyte to NWs.

Figure S-6, corresponding author's name: Li-Chyong Chen

Figure S-6. The *in situ* EIS study on DNA-hybridization detection: Ultrahigh Sensitivity. a, Nyquist plots of unmodified, *pLF*-modified and *dsDNA*-modified *GaNNWs* (at different concentrations of *LF* targets, *in situ* DNA-hybridization results). b, The corresponding Bode Plot representing variation of phase angle with frequency.

Figure S-6, an extension the experiment presented in **Figure 3**, revealed that the DNA-*GaNNWs* system can respond at very high sensitivity to DNA-hybridization phenomena, even at **sub-pM** concentration level, without any appreciable optimization for sensitivity or detection-condition.

Figure S-7, corresponding author's name: Li-Chyong Chen

Figure S-7. Photoluminescence analysis on the *MPTS*-modification of *GaNNWs*. The PL spectra of unmodified and *MPTS*-modified *GaNNWs* were depicted. It is quite clear that the blue shift of band-edge emission from 365 nm (for as-grown sample) to 358 nm, after *MPTS*-modification, along with the appearance of a prominent shoulder at 330 nm, similar to that observed after *pLF*-immobilization (Figure 5a). Moreover, the blue emission of GaN around 425 nm was also suppressed, along with the pronounced enhancement of PL intensity. Though there is no example, to our knowledge, on the surface passivation effect of *MPTS* on GaN, the changes in luminescence behavior of *GaNNWs*, after *MPTS*-modification, definitely indicates the passivation of surface states due to the *MPTS*-binding on the NW-surface. Further detail study on the effect of *MPTS*-modification on *GaNNWs* will be carried out in future.