---Electronic Supplementary Information---

Ultrasensitive Detection of Cancer Cell and Glycan Expression Profiling Based on Multivalent Recognition and Alkaline Phosphatase-Responsive Electrogenerated Chemiluminescence Biosensor

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Fig. S1 (A) UV–vis spectra of Au NPs (a) and ALP-Con A-Au NPs conjugates (b). Inset exhibits the TEM picture of the ALP-Con A-Au NPs nanoprobes. (B) UV spectral of ALP-Con A-Au NPs probe activity analysis in 50 mM Tris-HCl solution (containing 5 mM PNPP, 2 mM MgCl₂, 1 mM ZnCl₂, pH 9.0). The inset shows the picture of the ALP substrate PNPP (a), Au NPs and PNPP (b), ALP and PNPP (c) and ALP-Con A-Au NPs with PNPP (d). (C) The TEM pattern of the PAMAM conjugated chemically reduced graphene oxide.



Fig. S2 Cyclic voltammograms (A) and electrochemical impedance spectra (B) spectra of (a) bare GCE, (b) rGO-DEN/GCE, (c) aptamer/rGO-DEN/GCE, (d) CCRF-CEM cell/aptamer/rGO-DEN/GCE, and (e) ALP-Con A-Au NPs/CCRF-CEM cell/aptamer/rGO-DEN/GCE in 0.5 M KCl solution with 5 mM $[Fe(CN)_6]^{4/3-}$, respectively. Scan rate is 100 mV/s.

| Lectins | Origin | Binding Specificity |
|---------|-------------------------|---|
| Con A | Canavalia ensiformis | Terminal α Man, Man α 3[Man α 6] Man |
| WGA | Triticum unlgari | (Neu5Ac) (Gal β4GlcNAc)1-3,4(GlcNAc β4GlcNAc)1-3,4 |
| PNA | Arachis hypogaea | Gal $\beta(1,3)$ GalNAc, Terminal β Gal |
| Neu5Ac: | N-acetylneuraminic acid | d. Gal: galactose. GlcNAc: N-acetylglucosamine. |

Man: mannose. GalNAc:N-acetylgalactosamine.

 Table S1 Glycan-Binding Specificities of the Lectins used for for cell determination.