Supporting Information

Efficient capture and isolation of tumor-related circulating cell-free DNA from cancer patients using electroactive conducting polymer nanowire platforms

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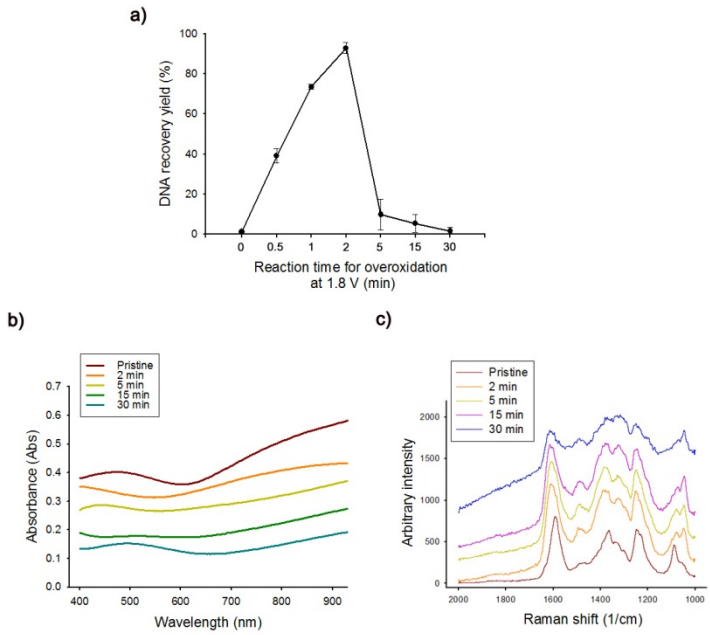
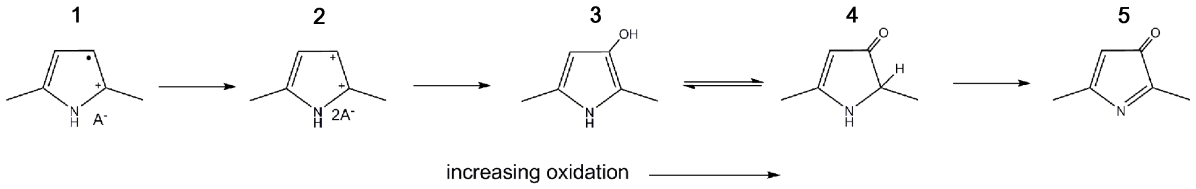


Figure S1. (a) cfDNA recovery yield of Ppy/Au NWs overoxidized at 1.8 V for various reaction times. (b) UV-Vis absorption spectra and (c) Raman spectra of Ppy overoxidized at 1.8 V for various times.

Spectroscopic changes were clearly observed depending on the overoxidation conditions of Ppy (Supplementary Figure 1b-c). Several spectroscopic studies have previously demonstrated the unique features of overoxidized Ppy. Specifically, Beck et al suggested that the underlying mechanism of overoxidation in Ppy involved the following steps (Scheme 1).[1] The electropolymerization of Ppy results in a doped state ("oxidized") through the destruction of the π-bonding of the conjugated polymer backbone, ultimately leading to a possession of positive charges (polarons, Step 1). However, the single electron tends to combine with an adjacent electron in the conjugated system, which causes dication (bipolaron, Step 2) with increasing oxidation.



Scheme 1. Overoxidation mechanism in Ppy films[1]

Typically, Ppy tends to irreversibly lose the positively charged state derived from the presence of the oxygen-containing groups in the Ppy backbone when it is further overoxidized at high positive potentials (Steps 3–5, Scheme 1). In our study, we electrodeposited Ppy on Au NWs by applying 0.8 V and consecutively performed overoxidation at 1.8 V for 2 min to increase the positive charge density of the Ppy backbone. The UV spectra of the oxidized Ppy collected at 1.8 V exhibited several features that indicated the progressive doping status (Supplementary Figure 1b). Specifically, Ppy overoxidized at 1.8 V for 2 min showed a peak at 800 nm that is associated with the bipolaron band, corresponding to "the highest oxidation state" or "a fully doped state"[1-4]. However, Ppy overoxidized for ≥5 min showed a substantial reduction in the bipolar absorbance at 800 nm and a peak at 500~550 nm, corresponding to neutral forms. Moreover, Raman spectra of the overoxidized Ppy

indicated that the chemical changes that occur during the overoxidation process are highly similar in pattern to those detected using UV-Vis analysis. As shown in Fig. S1b, Ppy overoxidized for 2 min showed peaks of C-H stretch (1082 cm^{-1}) and C=C stretch (1581 cm^{-1}). However, Ppy overoxidized for 30 min showed an increase in the intensity of N-H deformation at 1055 cm^{-1} and C=O stretching at about 1610 cm^{-1}, but a decrease in the intensity of C-H stretch at 1082 cm^{-1}; this indicates the disappearance of the charged state of the polymer (i.e., of polarons and bipolarons) and the formation of oxygen-bearing compounds (i.e., of compounds containing carbonyl groups).

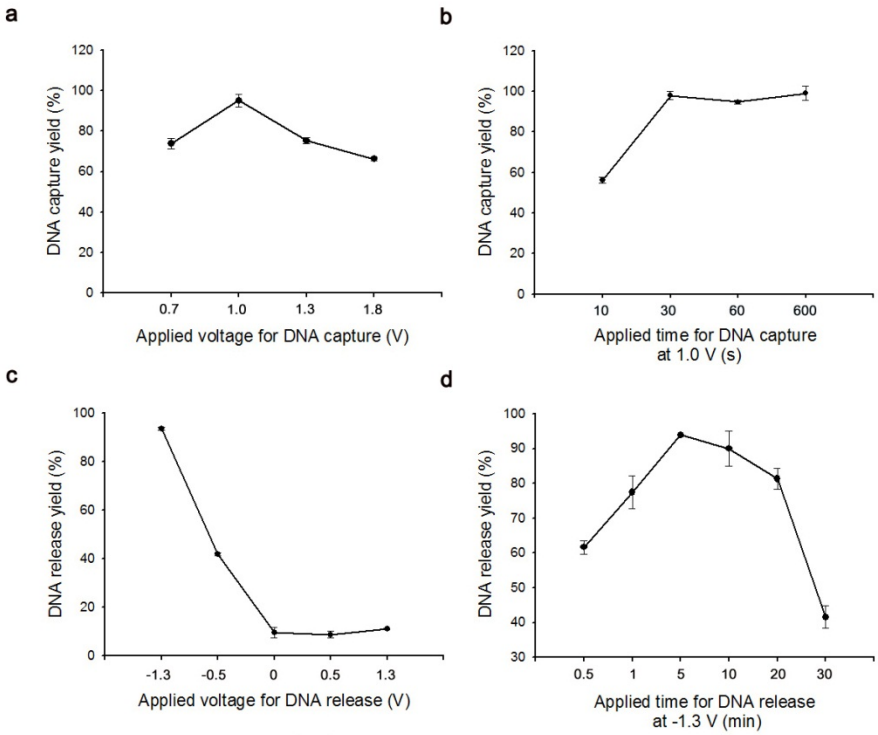


Figure S2. (a), (b) DNA-capture efficiencies of Ppy/Au NWs as a function of applied voltages and reaction times. (c), (d) DNA-release efficiencies of Ppy/Au NWs as a function of applied voltages and reaction times.

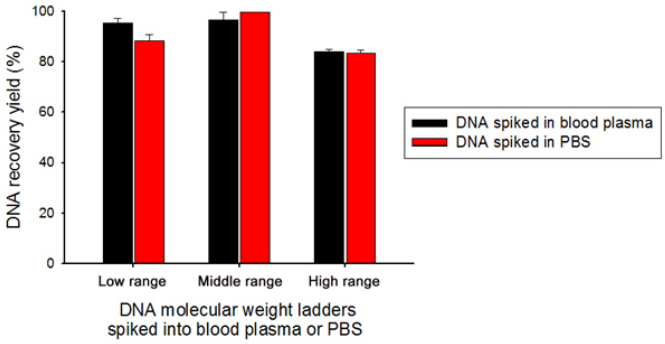


Figure S3. Comparison of DNA extraction yields by using DNA ladders of varying lengths spiked in human plasma or phosphate-buffered saline (PBS). To investigate the effect of the components of blood plasma (e.g., proteins, lipids) on DNA extraction, known amounts of DNA ladders of 3 sizes, 10 bp (low range), 100 bp (middle range), and 3.5 kb (high range), were dissolved into 200 μL of either human plasma or PBS and then applied to fully oxidized Ppy/Au NWs. After capturing DNA by applying dual potentials of 1.8/1.0 V on the surface of Ppy/Au NWs, a negative potential of -1.3 V was immediately applied to detach the captured DNA. The data shown represent the means ± SD of 5 independent experiments.

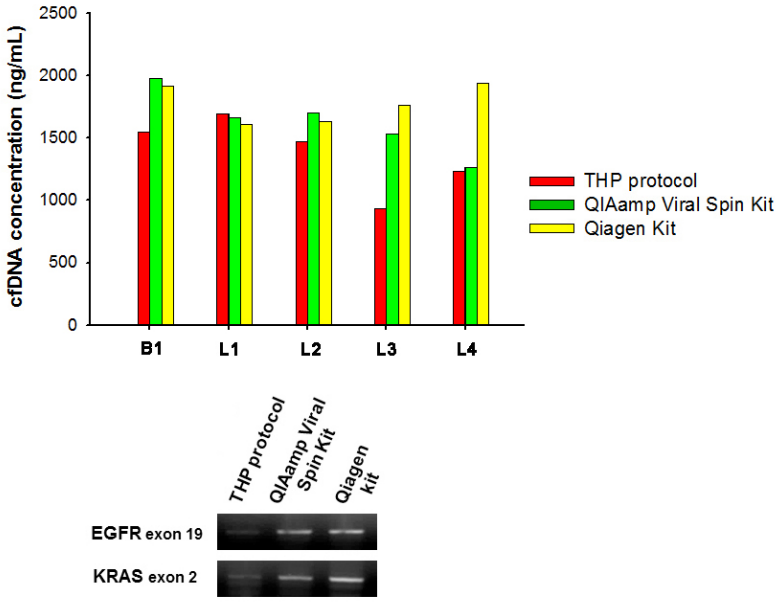


Figure S4. Assessment of cfDNA extracted using various methods. (Top) Concentration of the eluted cfDNA from 1 mL of blood plasma from patients with breast cancer (B1) and lung cancer (L1–L4) using the four techniques. (Bottom) Electrophoresis results for the amplified fragments of the E*GFR* and *KRAS* genes. In cfDNAs extracted from the plasma of breast (B1) and lung (L1–L4) cancer patients by means of the four techniques, PCR products of the EGFR and KRAS genes were amplified and appeared as electrophoretic bands of 207 and 192 bp, respectively.

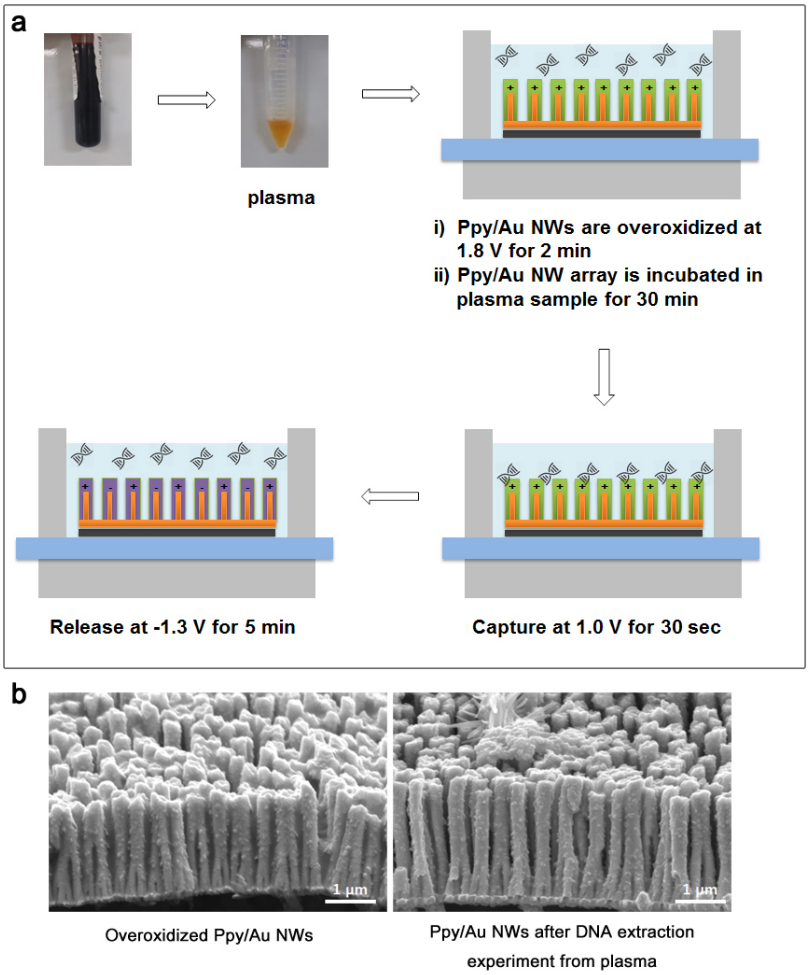
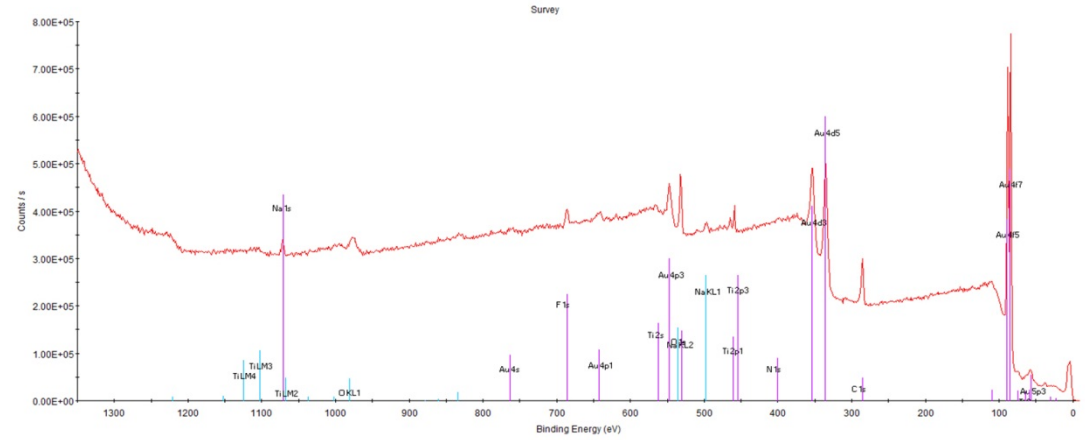


Figure S5. Schematic of the procedure used for preparing Ppy/Au NW arrays and the cfDNA capture/release performance of the arrays. a, Sample collection and preparation process used for isolating cfDNA from plasma. b, SEM images of Ppy/Au NWs before (left) and after (right) DNA-extraction experiments.

Au NWs



Ppy-coated Au NWs (Ppy/Au NWs)

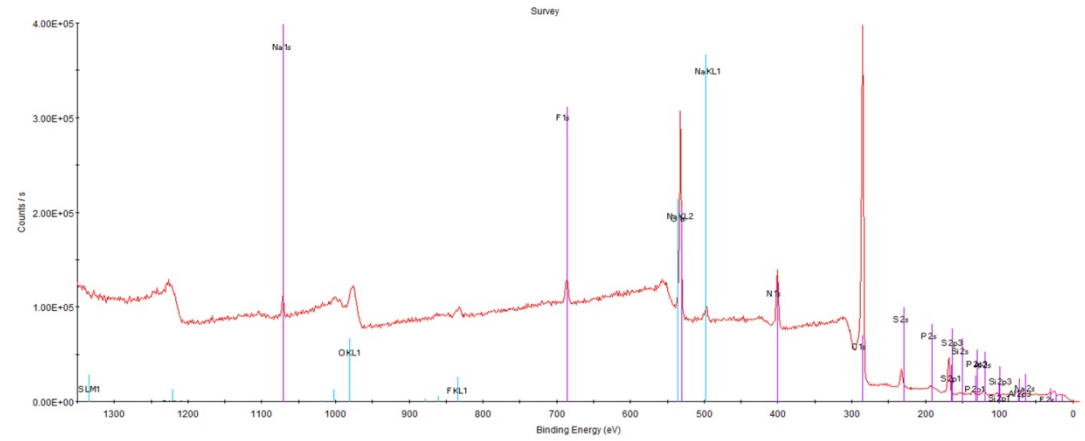
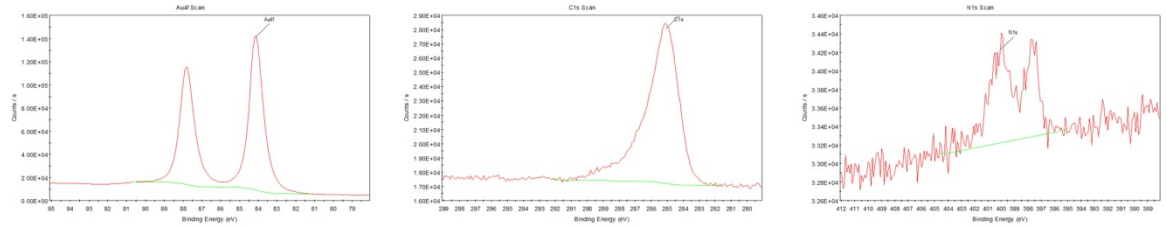


Figure S6. XPS survey spectra of Au NWs before (top) and after (bottom) the electrochemical deposition of polypyrrole (Ppy/Au NW arrays). In the spectrum recorded after Ppy coating, Au 4f peaks at 87.5 eV and at 84.0 eV were almost disappeared, indicating the presence of Ppy polymer on Au NWs.

Au NWs



Ppy-coated Au NWs (Ppy/Au NWs)

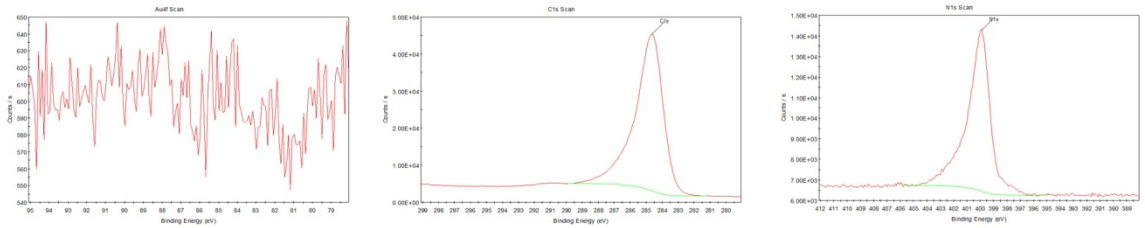


Figure S7. High resolution XPS spectra of Au 4f, C 1s, and N 1s recorded on the Au NWs (top) and Ppy/Au NWs (bottom), respectively. In Ppy/Au NWs, the disappearance of Au 4f peak and the increase in the intensity of C 1s and N 1s peaks confirm the successful electrodeposition of Ppy polymer on Au NWs.

Supplementary References

S1. F. Beck, O. Braun, M. Oberst, *Phys. Chem.* **1987**, *91*, 967-974.

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