Localized Electronic Desalting Around Field-Effect Sensors For Molecular Detection In Droplets With Enhanced Sensitivity

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***Abstract*— Direct molecular sensing in nano-biosensors facilitates a label-free route for point-of-care applications. However, screening by background salt ions interferes with sensing from physiological media by decreasing the apparent charge at the sensor and reducing the overall sensitivity. We demonstrate localized electronic desalting of a FET biosensor in sub-nanoliter droplets using on-chip polarizable electrodes to locally deplete ions around the target analytes. By overcoming ionic shielding, charge transduction to the FET and, consequently, the sensitivity can be maximized. The on-chip electrodes also gate-bias the FET for simultaneous sensing during desalting. This method can pave the way for multiplexed electronic detection with high sensitivity from physiological media.**

I. Background

Nanowire-based FET devices [1] have enabled label-free electronic detection of small biomolecules, such as nucleic acids, proteins, and viruses. Despite being highly scalable, the inability to commercialize these sensors is largely because we cannot sense directly from blood or serum due to shielding of molecular charge by the excess of ions [2], [3]. To date, most sensing occurs in low salt [4], with additional fluidic exchange or dilution, and it is strongly limited by sub-optimal binding specificity and kinetics of biological processes in weak buffer.

II. Localized Desalting and Sensing

Towards overcoming fundamental shielding issues, we propose (Fig. 1(a,b)) localized desalting by absorbing excess ions in the electrochemical double layer (EDL) of polarizable electrodes. If a 100mM droplet is depleted to 1% of ions, the Debye length increases from 1 nm to 10 nm so that analytes' charge can effectively transduce the FET. Limited electrode area available for absorption necessitates that desalting be localized in droplets to prevent replenishment of ions from bulk. Using a model for EDL charging from high salt [5], we calculate the largest droplet size that can be depleted to 1% of its initial strength (Fig. 1(c)). For desalting from 100mM to 1mM at 1 V bias, the droplet must be much smaller than 1 nL. The on-chip electrode pair also supply gate bias for the FET so that sensing occurs during desalting itself (Fig. 2(a)).

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This coupled biasing allows sufficient time for sensing, without having to worry about back-diffusion of ions. Ionic current (inset of Fig. 2(a)) determines the extent of desalting. We improve the capacity with nanotextured electrodes, made of electrodeposited Pt-black, to get an order of magnitude increase. Further, through novel surface treatment by cyclic voltammetry (CV) in 1X PBS, we get ~100-fold increase in the effective absorption area over flat electrodes (Fig. 2(b)) as measured by electrochemical impedance spectroscopy (EIS).

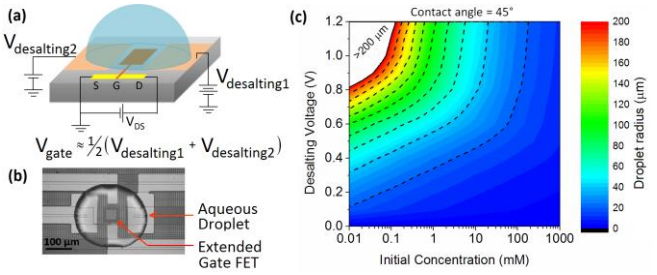

Figure 1. Schematic of (a) FET biosensor with on-chip desalting, (b) image of an extended gate FET with patterned on-chip Pt electrodes and (c) plot of the largest droplet radius (µm) that can be depleted using 10^4 µm^2 electrodes

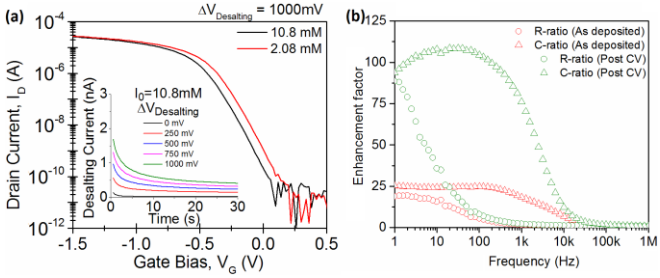

Figure 2. (a) I_D-V_G sweeps with on-chip gate bias while depleting 500 pL droplet at 1 V desalting bias. Inset shows desalting current in a 10.8mM droplet. (b) Net area increase with Pt-black electrode and CV-treatment through R/C-scaling from EIS shows 100X increase over smooth Pt at low-*f*.

References

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