Size-based Molecule Discrimination and Detection via Single-Walled Carbon Nanotube@Metal Organic Framework Composite Field-Effect Transistor

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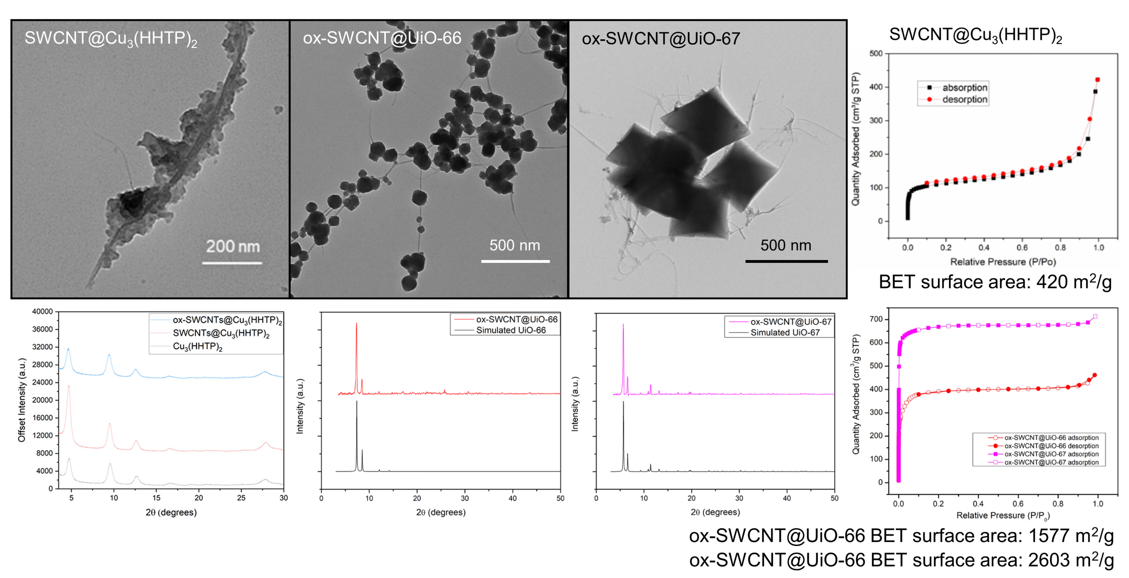
Introduction

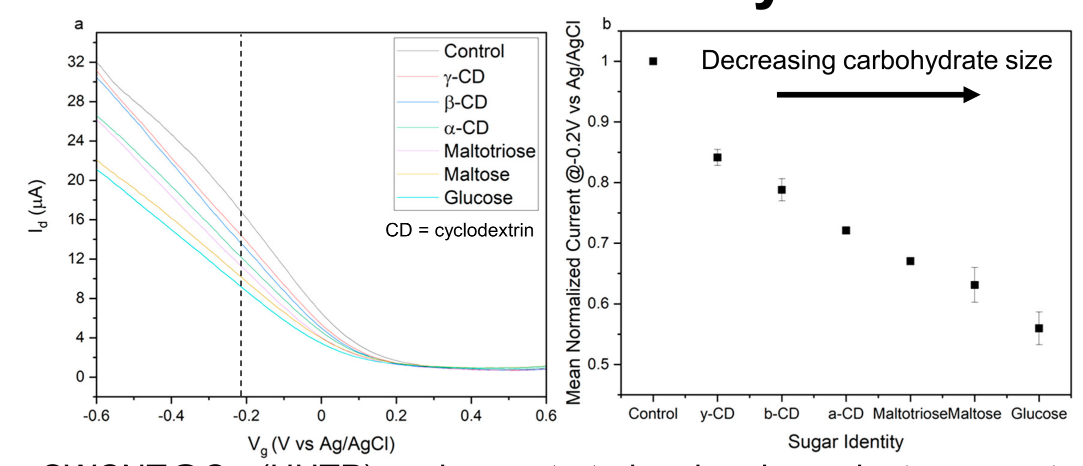
Single-walled carbon nanotube (SWCNT) is a compelling chemical sensing material due to its excellent chemical and physical properties. Sensors fabricated with SWCNTs usually demonstrate superior sensitivity. However, SWCNTs do not provide intrinsic chemical specificity and selectivity. Therefore, they are typically functionalized with another selective chemical layer to facilitate specificity. Using metal-organic framework as the layer is underexplored and innovative. Due to the intrinsic pore size of MOF structure, SWCNT@MOF composite field-effect transistor (FET) can demonstrate size-based sensing signal via analyte molecule obstructing the gate-voltage-driven ion diffusion inside the channels of MOF structure.

Material characterization

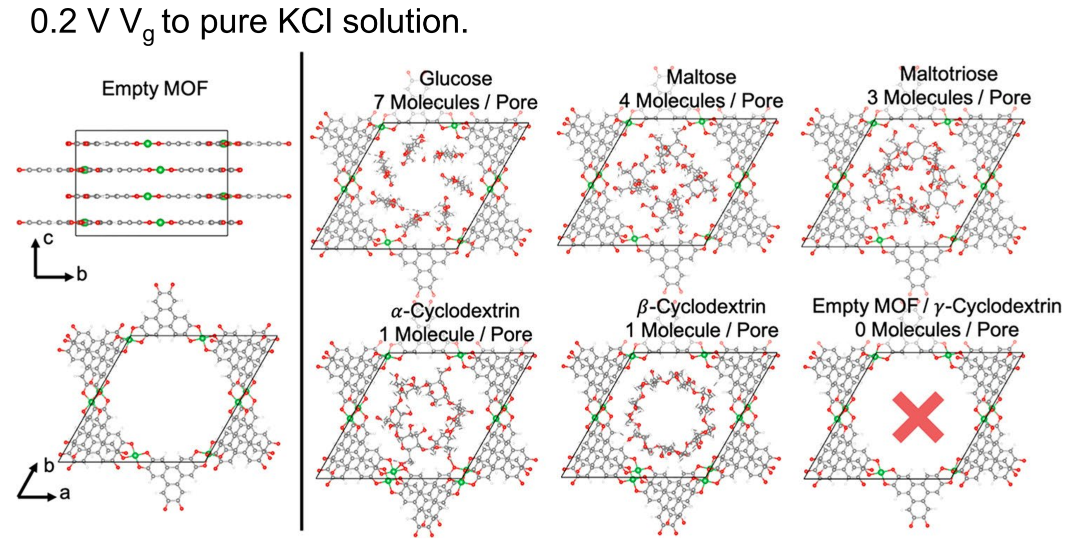


SWCNT@MOF composites combined the porosity of MOF and the electric conductivity of SWCNT. Templated MOF growth was facilitated via π-π stacking between the sp^2 carbon of CNT and the MOF ligand and/or the covalent interaction between the carboxylic functionality on oxidized SWCNT (ox-SWCNT) and the MOF metal precursor. MOF chemistry was preserved after hybridization with SWCNT as depicted by the X-ray diffraction (XRD) and N_2 adsorption/desorption isotherm.

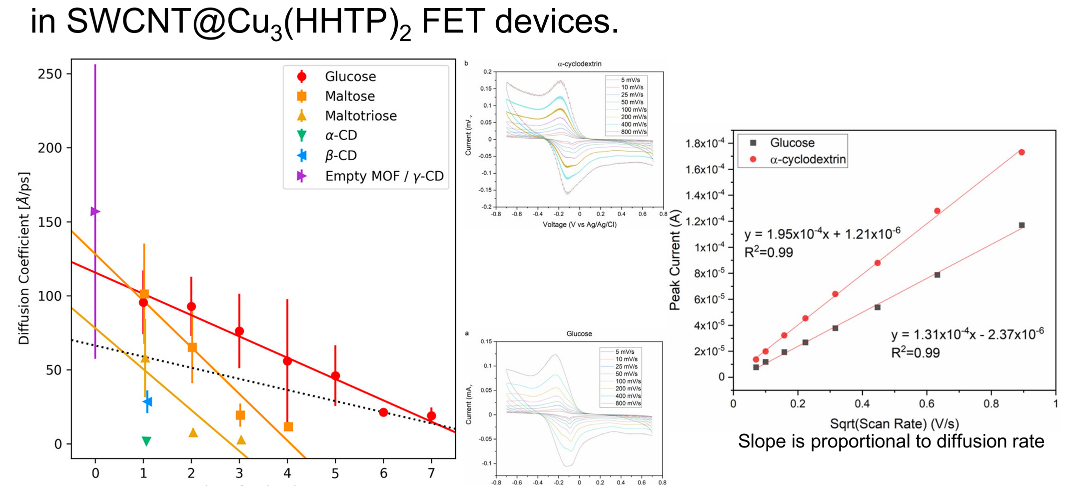
Discrimination of carbohydrates



SWCNT@Cu$_3$(HHTP)$_2$ demonstrated size-dependent current decrease when FET transfer characteristics (I-V_g) were measured in 50 mM KCl solution with 500 μM carbohydrate dissolved. Signals were determined by normalizing the current decrease @ –0.2 V V_g to pure KCl solution.

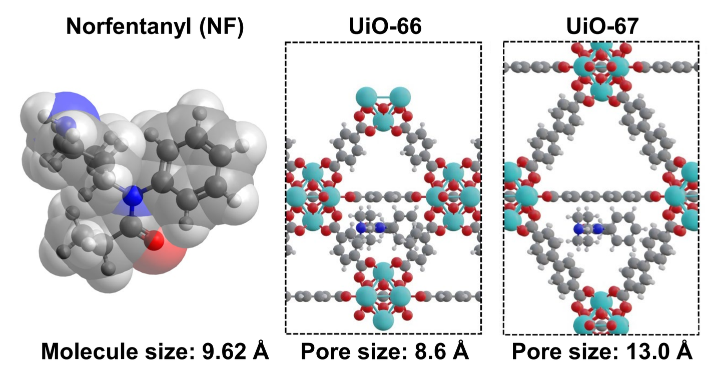


Optimized model for Cu$_3$(HHTP)$_2$ unit cell and each of the maximally packed configurations. Small-sized glucose molecules pack the channel most tightly, causing the most prominent obstruction. Consequently, largest current decrease was observed in SWCNT@Cu$_3$(HHTP)$_2$ FET devices.

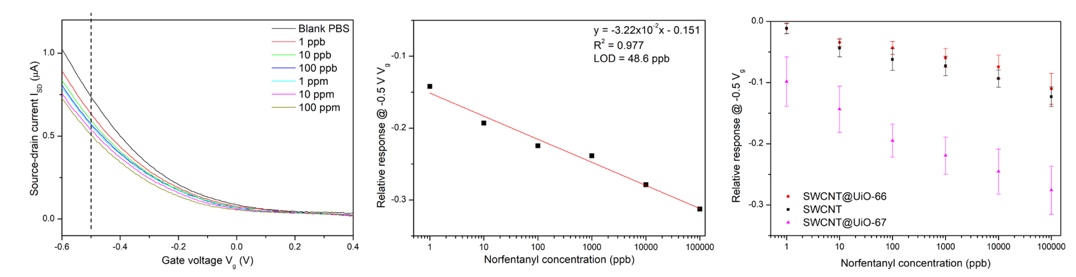


Ion diffusion obstruction was validated theoretically and experimentally. Diffusion coefficients were calculated using molecular dynamic simulations. Cyclic voltammetry (CV) was performed using a glassy carbon electrode decorated with SWCNT@Cu$_3$(HHTP)$_2$. CV tests were conducted with $Ru(NH_3)_6Cl_3$ in 0.1 M KCl with 1 mM carbohydrate dissolved.

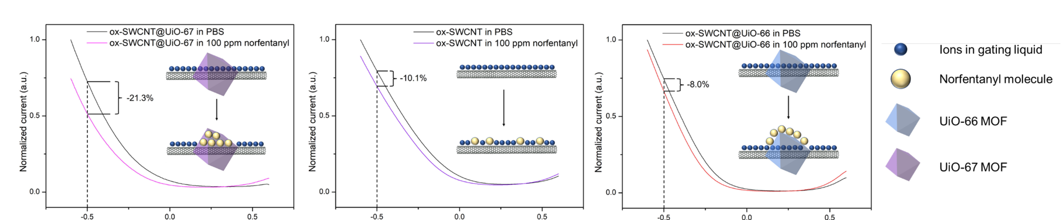
Detection of norfentanyl



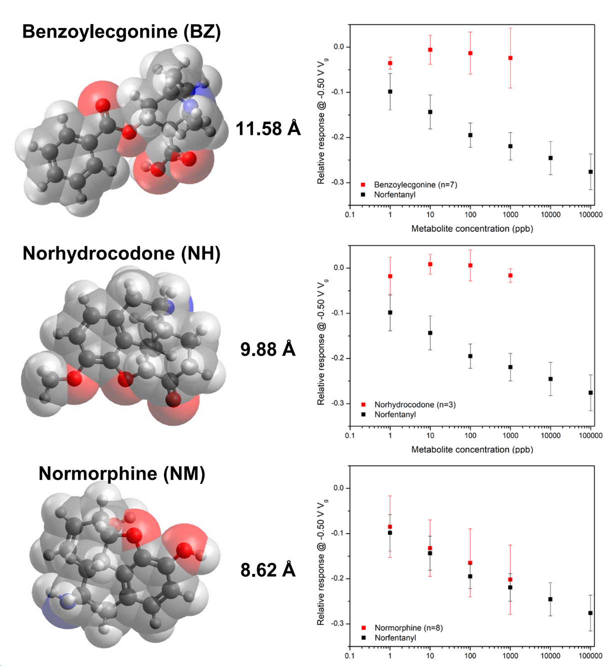
Size comparison between NF molecule and pores of UiO-66 and UiO-67. The pore size of UiO-66 is too small for NF to enter while UiO-67 pores provide enough space for NF molecule to reside inside.



NF sensing result from a typical ox-SWCNT@UiO-67 device and its linear fitting calibration. Comparison between ox-SWCNT@UiO-66, bare ox-SWCNT and ox-SWCNT@UiO-67 FET devices showed that UiO-67 can enhance the sensing signal while UiO-66 decrease the sensing signal compared to bare ox-SWCNT.



UiO-67 enhanced sensing signal due to the obstruction of ion diffusion inside its channel by the NF molecules. UiO-66 reduced the signal due to the prevention of the interaction between ox-SWCNT and NF. ox-SWCNTs responded to NF because of non-preferential adsorption.



BZ, NH, and NM are the metabolites of hydrocodone, cocaine and morphine, respectively. UiO-67 can successfully screen out the interference from molecules with larger sizes. However, for molecule with smaller sizes, UiO-67 can still enhance the signal, which is an evidence for the size-based sensing mechanism. Sensor array constructed with various MOF pore sizes are needed to improve specificity.

Conclusion

SWCNT@MOF composite material introduces an innovative sensing method for SWCNT-based FET sensor. Unlike conventional SWCNT-based FET sensors that rely on the electrostatic effect of the analyte to alter CNT conductance, SWCNT@MOF FET sensing operates via the inhibition of ion transportation to SWCNT surfaces, accomplished by the analyte molecules obstructing MOF channels. SWCNT@MOF FET sensors offer a versatile platform for detecting analytes that are challenging for conventional chemical sensing methods by shifting the focus to detecting their size.

Outlook

As SWCNT@MOF FET devices discern signals based on analyte size rather than strict chemical selectivity, they do not inherently provide chemical specificity. However, thanks to the development of modern computational algorithms and the rapid evolution of machine learning (ML) technologies, data processing techniques can now discern subtle sensing signal features that may not be detectable through human effort. ML-assisted sensing has led to improvements in sensitivity and selectivity, even for materials that were once considered non-specific. Given the advantages of contemporary MOF engineering and algorithm development, the SWCNT@MOF FET sensor platform holds substantial potential for driving innovation in chemical sensing methodologies.

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References

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